J. Braz. Chem. Soc., Vol. 13, No. 4, 410-424, 2002.
Printed in Brazil - ©2002 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Review

Electrochemistry, Polymers and Opto-Electronic Devices: A Combination with a Future

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A eletroquímica surgiu quando Volta combinou um conjunto de materiais, montando um dispositivo chamado "pilha". Sob este ponto de vista, nada mais natural do que continuar observando a eletroquímica como uma poderosa ferramenta para montar dispositivos usando diversas combinações de materiais. Recentemente, os polímeros surgiram como uma alternativa para produzir dispositivos de baixo peso, substituindo os eletrodos metálicos. Assim, existem no mercado eletrodos transparentes baseados em vidro ou poli(tereftalato de etileno), recobertos com óxidos condutores. Também se desenvolveram eletrólitos baseados em polímeros, que funcionam na ausência de solventes. Os polímeros condutores, ou eletroativos, também surgiram como alternativa para se modificar a superfície destes eletrodos, produzindo respostas de forma controlada, com grandes vantagens sobre os óxidos de metais de transição. Neste cenário, pretende-se mostrar como a combinação de diversos materiais poliméricos pode levar à obtenção de dispositivos eletrocrômicos, células fotoeletroquímicas e células eletroquímicas emissoras de luz.

Electrochemistry came into life with the invention of the pile, by Volta in 1800. He combined different metal discs with a piece of tissue, swollen with an aqueous salt solution. The so-called *Pila di Volta* used a polymer for the first time in an electrochemical device and can be seen as a powerful idea to create new devices. Recently, polymers became an alternative to make thin and flexible devices. Thus, we find transparent plastic electrodes based on poly(ethylene terephtalate) coated with a transition metal oxide. There are also polymer electrolytes based on complexes of inorganic salts and poly(ethylene oxide) derivatives, with reasonable ionic conductivity in the absence of solvents. Finally, the electroactive polymers are efficient substitutes for the inorganic semiconductors because they can be synthetically tailored to produce the desired electronic answer. Combining these materials it is possible to assemble different types of electro-optical devices, like electrochromic, photoelectrochemical and light-emitting electrochemical cells.

Keywords: electrochemical devices, polymer electrolytes, conducting polymers

1. An Historical Survey

A considerable part of our history took place in the Italian Peninsula. From the Etrurian civilization, passing by the Roman Empire and its decadence, the Medieval Age and the great advances in the Renascence, the present Republic of Italy is the most amazing cultural and architectural patrimony of the occident. This effervescent history also proportioned remarkable contributions to the development of the Science, especially in Chemistry.

In this scenario, Electrochemistry was born as a Science at the end of the 18th Century. Based on Galvani's experiments (Luigi Galvani, Professor at University of Bologna) on the relationship between electricity and muscle contractions, Volta (Alessandro Volta, Professor at University of Pavia) announced to the scientific community in 1800 the invention of the electric pile, a "device" which would later revolutionize the concept of energy production.[1,2] This invention is considered the birth of the Electrochemistry.

It is noticeable that although Galvani's conclusions about his observations were wrong, his experiments directed Volta's attention to this area. Galvani-Volta controversy on Galvani's observations influenced Volta's experiments and, although Volta is now considered the "Father of the Electrochemistry", the importance of Luigi Galvani cannot be disregarded. He was the first to discover

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the current flow in a electrochemical system, although he did not realize it. It is also interesting that Volta invented the pile but this kind of electrochemical cell is now called galvanic cell.[1]

This historical approach serves to show us some interesting considerations about the title of this brief review. First of all, Electrochemistry was not born by theoretical studies or basic concepts, but with a device with large potential application. Besides, Volta's *pile* was constructed with a series of different metal discs piled with a piece of tissue between them, swollen with an aqueous salt solution. It is remarkable that, in the first device noticed, a polymer (the tissue) played an important role.

Nowadays, electrochemistry represents an important piece of the Chemistry and many technological advances come from the combination of different materials in electrochemical cells. Additionally, new electroactive polymeric materials are always in production, with different properties, such as electroluminescence, semiconductor behavior, electronic and ionic properties, electrochromism, etc. Two electrodes immersed in an electrolyte basically compose an electrochemical cell. The great variety of properties presented by polymeric materials suggests the combination of different polymers in several components of such cells, opening new opportunities of constructing high performance electrochemical devices for commercial purposes. For optical/electrochemical uses, polymers find application as active electrodes (electronically conducting polymers), solid electrolytes (ionic conducting polymer) and as transparent substrates (optically transparent plastic electrodes). Next sections show the perspectives and challenges of using polymers in electrochemical devices for optical applications, and some examples of these so-called "opto-electronic devices".

2. Active Materials

2.1 Electronically conducting polymers

Electronically conducting polymers possess different properties related to their electrochemical behavior. The importance and the potentiality of this class of materials was recently recognized by the world scientific community when Shirakawa, Heeger and MacDiarmid (prominent scientists in conducting polymer science) were laureated in 2000 with the Nobel Price in Chemistry by their research in this field. Although these materials are known as new materials, the first work describing the synthesis of a conducting polymer was published in the 19th century.[3] In that time, the "aniline black" was obtained as the product of the anodic oxidation of aniline and its electronic properties were not established. Despite this initial work, the discovery of conducting polymers as materials which present reasonable electrical conductivity is attributed to Shirakawa and co-workers, who exposed free-standing films of polyacetylene to vapors of chlorine, bromine, iodine, arsenic pentafluoride and sodium, obtaining an increase of twelve orders of magnitude in the conductivity.[4]

Conducting polymers are frequently called "synthetic metals" because they present electric, electronic, magnetic and optical properties inherent to metals or semiconductors, while retain the mechanical properties of conventional polymers. These properties are intrinsic to the doped material, being completely different from those originated from a physical mixture of a non-conductive polymer with a conducting material, such as metal or carbon powder. In intrinsic conducting polymers the conductivity is assigned to the delocalization of π-bonded electrons over the polymeric backbone, exhibiting unusual electronic properties, such as low energy optical transitions, low ionization potentials and high electron affinities.[5]

Electron delocalization is a consequence of the presence of conjugated double bonds in the polymer backbone. Figure 1 shows the structure of some conducting polymers and to make them electrically conductive, it is necessary to introduce mobile carriers into the double bonds, this is achieved by oxidation or reduction reactions (called "doping"). The concept of doping distinguishes conducting polymers from all other kinds of polymers. The controlled addition of known, small (< 10 %) non-stoichiometric amounts of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymer. This process can be assigned as *p*-doping or *n*-doping in relation to the positive or negative sign of the injected charge in the polymer chain by analogy to doping in inorganic semiconductors. These charges remain delocalized being neutralized by the incorporation of counter-ions (anions or cations) denominated dopants.

Most of the optical characteristics inherent to inorganic semiconductors, such as photoemission, photodetection and photocurrent, have also been observed in conducting polymers. Because these materials present ease of fabrication and potential low cost, their use to assemble "plastic" optical devices is becoming reality. Nowadays, efforts have led to devices with performances comparable to those based on inorganic semiconductors. Also, the possibility of controlling the electronic and optical properties of an organic device by tailoring the organic molecular structure permits their modification before fabrication.

The color change induced by the electrochemical doping-undoping enable the use of these materials in the

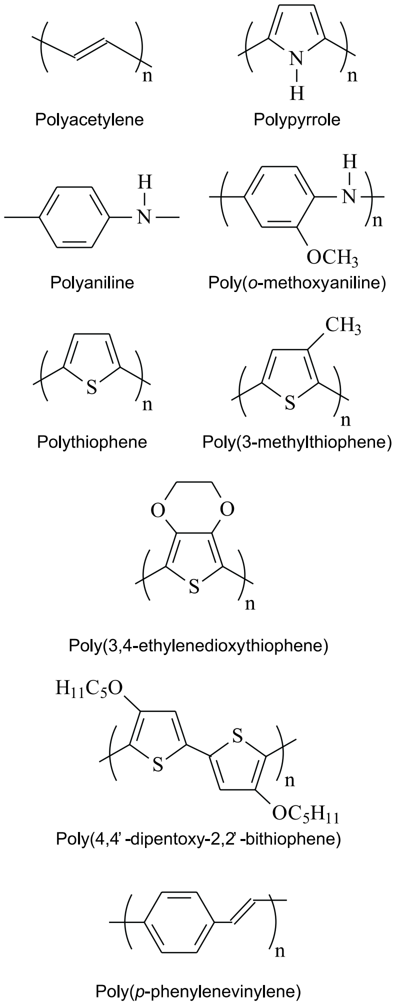

Figure 1. Structure of some conducting polymers mentioned in this article.

manufacture of multichromic displays or electrochromic windows.[6] Taking the hole-injecting properties of these polymers under an applied potential or current, flexible light emitting diodes (LED)[7,8] and light emitting photoelectrochemical cells (LEC) have also been developed.[9,10]

The photovoltaic effect observed in the conducting polymer | electrolyte interface by irradiating with energy higher than the polymer band gap, has been the focus of attention to produce low cost photoelectrochemical cells (PEC).[11-14] Although the efficiency of these devices is low, conducting polymers have been employed as donors in composites together with buckminsterfullerene (C_{60} and its derivatives) acting as acceptors, providing a molecular approach to high efficiency photovoltaic cells.[15,16]

Conducting polymers have been also investigated as active materials in other optical applications, such as photodetectors,[17] optocouplers,[18] full color image sensors[19] and lasers.[20] It is also important to point out the use of these materials in others areas of interest beyond optical devices. Other properties of the conducting polymers also enable their use as active components in batteries,[21-23] biosensors,[24,25] drug-releasing agents,[26] gas separation membranes,[27] electrochemical capacitors,[28] electromagnetic radiation shielding,[29,30] transistors,[31] polymer-polymer rectifying heterojunctions[32] and conductive textiles.[33]

The large spectrum of applications of conductive polymers using the variation of its optical properties upon "doping" or oxidation reduction reactions attracts the attention of many researchers and these materials have been extensively studied. The possibility of reversible doping/undoping, accompanied by the spectral changes, is the key for these studies.

Considering opto-electrochemical devices, works are now directed to find new materials with tailored optical properties. For example, attaching substituent groups to the 3- and/or 4-positions on the monomer has produced polythiophenes with low band gap. This procedure minimizes the occurrence of α,β coupling during the polymer synthesis, producing more regular structures with enhanced properties.[34] Fewer α,β linkage defects in the final structures lead to more effective conjugation, which is an essential feature to produce more conductive final products. As can be noted, there are many improvements to be done in order to make competitive commercial devices. On the other hand, polymers have unique properties that enable fabrication of flexible and low cost devices. Examples of opto-electrochemical devices using conducting polymers as active electrodes will be shown in the following sections.

2.2 Electrolytes: ionic motion in polymers

While electronic conductivity is the phenomenon related to the electrons-holes movement into solid conductors, ionic conductivity is described as the charge movement due to the ions motion. As the first applications regarding the electrical properties of polymers were directed to their insulating characteristics, ionic conduction in polymers was initially observed as an undesired property. However, this point of view changed in the 1970s when Wright and co-workers carried out the pioneering measurements of ionic conductivity in polymer-salt mixtures,[35] and Armand and co-workers proposed the use of such systems in secondary batteries.[36] Since that time, the research on solid polymeric electrolytes has grown intensely and reviews with historic surveys have been published.[37,38] The interest in these solid-state ionic conductors comes from the possibility of using them to substitute the liquid electrolytes in several electrochemical devices. The major challenge into replacing the liquid or gel electrolyte by a polymeric one is to keep the high operation efficiency, similar to the electrochemical devices based on liquid junctions. Besides improving the stability of the active interface, allowing a long-term durability, a polymer electrolyte eliminates problems concerning evaporation or leakage of the solvent.

The use of polymer in electrolytes can be divided in three categories, as follow: (a) a polymer swollen with a liquid electrolyte, which provides high values of conductivity, but does not eliminate the problems related to the liquid electrolytes; (b) a polymer containing cations or anions attached to the chain, which produces low conductivity values because of the low mobility of charge carriers; (c) a mixture of a salt in an ion-solvating polymer, that configures a dry and solid electrolyte system, can present conductivity values suitable for using in electrochemical devices and eliminates all difficulties relative to the use of liquid or gel electrolytes in commercial applications.

The thermodynamics involved in dissolution of a salt into a polymer matrix is the same observed in liquid solvents. In a simple analysis, the entropy favors the dissolution since the salt dissociation provides the increase in the number of particles in the system and, consequently, the increase of the system entropy. Differences observed by dissolving several salts in the same polymer are related to the lattice enthalpy of the salt, cohesive enthalpy of the solvent and solvation energy. Thus, the dissolution and dissociation of a salt into a polymer matrix will be more effective if the salt has low lattice energy, the solvent has a low cohesive enthalpy and high solvation energy.[39] Considering these statements, polar solvents are the ideal candidates for dissolving a salt. After dissociation, cations act as Lewis acids and interact with electron donors sites (Lewis bases) in the polymer chain. Otherwise, the anions have Lewis base character and interact with electron acceptor sites (Lewis acids) in the polymer.

Poly(ethylene oxide), PEO, is the reference polymer for ionic conduction, since it is the best matrix for alkali salts because of the high Lewis base character of the oxygen atoms present in this polyether. By this reason, great efforts have been devoted to make polymer electrolytes based in PEO, combining it with several salts.[40-42]

Several hypothesis have been proposed to explain the ionic motion in PEO chains. The first solid electrolyte systems were based in crystalline non-processable materials, such as Li_3N, AgI and β-alumina.[43] In analogy to these inorganic conductors, the ionic conductivity in PEO was initially associated to its crystalline phase. Conductivity measurements of PEO-salt complexes at several temperatures showed a large increase above the melting temperature of the polymer.[44] Besides, ionic conductivity is not significant below the glass transition temperature of its amorphous phase. Taking into account these observations, the ionic conductivity in semi-crystalline polymer-salt complexes was assigned to the segmental motion of the amorphous phase of the polymer chains.[45] Initially, this hypothesis was not fully accepted by scientists, but NMR studies indicated that it was right.[46] Thus, the conductivity pathway was attributed to the amorphous part of the polymeric matrix, assisted by the segmental motion of the polymeric backbone, and the additional possibility of simultaneous coordination of one metallic cation to several Lewis base sites because of the flexibility of the polymer chains.

This theory has been accepted from the 1970's and, until very recently, no studies were devoted to contradict it. However, a very recent work showed that, in contrast to the prevailing view, ionic motion in polymer systems could be higher in the crystalline phase than that observed in the amorphous phase.[47] In this interesting work, the results indicated that ionic conductivity occurs preferentially in the crystalline phase of the PEO-salt complex at temperatures ranging from the glass transition temperature of its amorphous phase to the melting temperature of its crystalline domain. However, ionic conductivity values in this temperature range are very low in comparison to those observed above the melting temperature. These interesting results open new perspectives to find new solid electrolyte systems, however, this recent model still does not explain the significant increase of the conductivity above the melting temperature, when the organized crystalline phase disappears.

Independent on the theories used to explain the ion motion; experimental results always show that PEO-based electrolytes show reasonable ionic conductivity for using in commercial electrochemical devices only above its melting temperature (*ca.* 65 ^{o}C), precluding its application at ambient temperature. Thus, several strategies have been used to decrease the crystallinity of PEO and improve the conductivity of its complexes at room temperature, such as: the addition of plasticizers, the use of PEO based blends[48-50] or the preparation of copolymers.[51] By adding low molar mass diluents, such as propylene carbonate, a plasticization effect is obtained and the conductivity at room temperature is improved. Increasing the plasticizer content in the mixture increases the ionic conductivity, but an inevitable deterioration of the mechanical properties is observed.[52] At high plasticizer content a gel electrolyte with $\sigma \sim 10^{-3}$ S cm^{-1} at room temperature is obtained.[53]

An alternative is the use of mixtures of PEO with different acrylic polymers.[48] The blends-salt complexes showed higher ionic conductivity in comparison to the pure PEO-salt complexes. This effect was not only assigned to the lowering of PEO crystallinity in the blends, but also to the presence of a highly flexible amorphous phase and the cooperative effect of polar groups on ionic transport. The elastomeric copolymers of ethylene oxide and epichlorohydrin present low crystallinity and reasonable ionic conductivity at room temperature.[54,55] Kohjiva and co-workers studied some complexes of these copolymers with $LiClO_4$, reporting a conductivity of 10^{-6} S cm^{-1} at 30 °C.[51] In another study a conductivity of 10^{-5} S cm^{-1} was measured after mixing $LiBF_4$ and poly(ethylene glycol) to this elastomer.[56] Recently, Ju and co-workers[57] reported the conductivity of a blend of nitrilic rubber with the copolymer of ethylene oxide and epichlorohydrin swollen by a solution of $LiClO_4$ in propylene carbonate. For the blend containing 40% (m/m) of $LiClO_4$ solution, $\sigma = 10^{-3}$ S cm^{-1} at room temperature.

Poly(ethylene oxide-*co*-epichlorohydrin) has been used as polymer matrix for solid electrolytes in several opto-electrochemical devices, including electrochromic displays[58] and photochemical cells.[59,60] A systematic study varying the proportion between the comonomers showed that metallic coordination occurs preferentially to the more basic oxygen atoms from ethylene oxide units, instead of those in the epichlorohydrin units.[61] This elastomer also shows to be versatile: the inclusion of a redox couple to this elastomer, like NaI and I_2, did not change significantly its conduction properties, permitting its use in photoelectrochemical cells. [62]

Polymer electrolytes must fulfill some requirements to be used in electrochemical applications. Initially, studies were directed to develop high performance lithium-polymer batteries and the solid electrolytes should present ionic conductivity higher than 10^{-5} S cm^{-1} at temperatures ranging from -20 to 60 °C, mechanical stability at this temperature range and an electrochemical window broader than 4 V.[63] Nowadays, new electrochemical devices are in development, making necessary the study of polymer electrolytes with special requirements.[64,65] For using it in an electrochromic device, for example, the polymer electrolyte film should also present high transparence to enhance the chromatic contrast of the entire device. Otherwise, mass transport takes place faster in electrochromic devices because the active electrodes are much thinner than those used in batteries. Thus, lower conductivity values are acceptable. Additionally, a photoelectrochemical cell needs an electrolyte containing a redox couple to transport to the counter electrode the photogenerated charge carriers.

As seen, the research on solid electrolytes is now directed to specific uses. Perspectives in this area are very optimist because, as mentioned above, the replacement of the liquid or gel electrolytes by a solid one in an electrochemical cell opens new possibilities of using such devices for commercial purposes.

3. Technology of Plastic Opto-Electronic Devices

3.1 Electrochromic displays and smart windows

Chromatic changes caused by electrochemical processes were described in the literature in 1876 for the product of the anodic deposition of aniline,[66] however, the *electrochromism* was defined as an electrochemically-induced phenomenon only in 1969, when Deb observed its occurrence in films of some transition metal oxides.[67] Electrochromism can be defined as the persistent change of optical properties of a material induced by reversible redox processes.

Electrochromism can be exploited in a series of optical devices with potential use in various applications, such as in information display and storage, in the automotive industry (as rear-view mirrors and visors), and in architecture (as smart windows to control luminosity and save energy thought the control of sunlight transmission).

Basically, an electrochromic device is a two-electrodes electrochemical cell in a sandwich configuration of thin layers. The arrangement of these layers depend on the operation mode, which can be reflective or transmissive.[68] The reflective mode is used to display or to decrease the reflected light, for example, in a car rear-view mirror. In these devices, one of the electrical contacts should be covered with a reflective layer, as a mirror. Transmissive mode operation is very similar, but all layers must become fully transparent when desired. For this reason, optically transparent electrodes must be used in the two electrical contacts. The schematic representations of the two operation modes are shown in Figure 2.

The requirements for high performance electrochromic devices are: a) high electrochromic efficiency, expressed in cm^2 C^{-1} and related to the injected charge in the material to change its color; b) short response time; c) good stability; d) optical memory, defined as the color stability under open circuit potential conditions; e) optical contrast, also called write-erase efficiency, and f) color uniformity.

Electronic conducting polymers are known as electrochromic materials since the initial systematic studies of their electronic properties. Electrochromism in

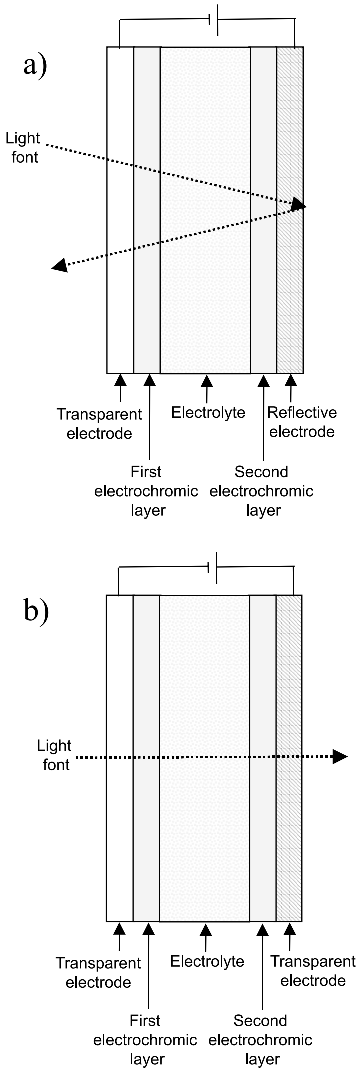

Figure 2. Schematic representation of an electrochromic device operating at (a) reflective mode and (b) transmissive mode.

polyaniline was first reported by Goppelsröder in 1876[66] and in polypyrrole by Diaz and co-workers in 1981.[69] In conducting polymers, the electrochromism, as well the electronic conductivity, is explained using the Band Model:[70,71] the doping process modifies their electronic structure, producing new electronic states in the band gap and causing the color changes. Electronic absorption shifts to higher wavelengths with doping, and the color contrast between doped and undoped forms is related to the polymer band gap energy, Eg.[72] Simultaneous to the doping-undoping processes, a mass transport takes place into the polymer bulk due to the counter-ions motion inside the films. This slower process controls the color variation kinetics in polymer films. Studies concerning the electrochromic properties of conducting polymers as single electrodes are discussed in vast literature[73-77] and a typical chromatic contrast between doped/oxidized and undoped/reduced states of a conducting polymer is shown in Figure 3.

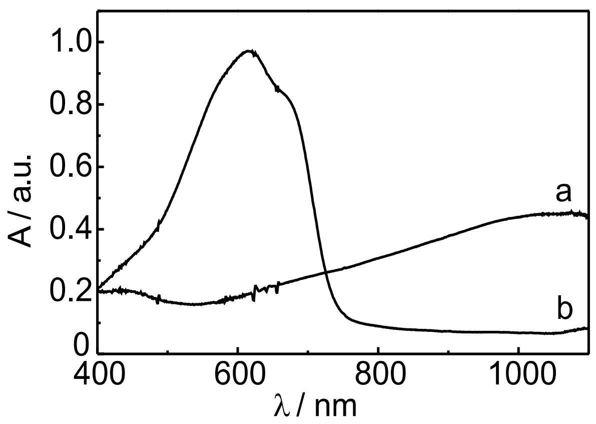

Figure 3. Absorption spectra of a poly(4,4'-dipentoxy-2,2'-bithiophene) film polarized at different potentials (*vs.* Ag|AgCl): a) –0.2 V, reduced state; b) 0.7 V, oxidized state.

As shown in Figure 2, electrochromic devices are constructed with several components: transparent electrodes, two electrochromic materials and an electrolyte. A special characteristic about the electrochromic materials is that, under device operation, one is deposited on the working electrode and the other on the auxiliary electrode. For this reason, to construct an electrochromic device, one active electrochromic material must possess anodic coloration (colored when oxidized) and the other must possess cathodic coloration (colored when reduced).

Electrochromic devices were originally assembled by using metal transition oxides, liquid or gel electrolytes and rigid transparent electrodes, typically ITO-glass (a glass plate recovered with an indium-doped tin oxide film). Nickel hydroxide was used in 1987 to assemble the first electrochromic device in Brazil.[78] However, the present technology permits the use of polymers in all components of an electrochromic device.

As mentioned in a previous section, the research on new solid polymer electrolytes for using in lithium-polymer batteries opened new possibility of assembling all-solid state electrochromic devices. Basically, the ionic conductivity and the electrochemical stability required for using a solid electrolyte in a battery are enough to use it in an electrochromic display. An additional requirement is that the solid electrolyte should present high transparence in the visible range. The use of solid polymer electrolytes in electrochromic devices solves several problems concerning the commercial applications of electrochromic devices, like solvent evaporation and leakage.

The interest on conducting polymers based electrochromic devices is due to the fact that these materials possesses several advantages such as, no dependence with angle of vision, good UV stability, large temperature range of operation and mainly, low production cost. Conducting polymers generally possess exclusively anodic coloration and, by this reason, its use for electrochromic applications was associated initially to inorganic cathodic coloration. For this reason, the first polymer based electrochromic devices usually associated a conducting polymer to an inorganic material, such as polypyrrole and WO_3,[79,80] polyaniline and Prussian blue,[81,82] or polyaniline and TiO_2-CeO_2.[83]

Since the 80's, several efforts have been made to obtain polymers with tailored electrochromic properties by the polymerization of specially designed monomers,[84-90] yielding polymers with $E_g < 2$ eV. Conducting polymers with such properties are quite transparent when fully oxidized and colored in the reduced state. The poly(4,4'-dipentoxy-2,2'-bithiophene), (absorption spectra shown in Figure 3) is an example of conducting polymer with cathodic coloration. This property not only allows the use of conducting polymers as cathodic coloration materials, but also permits the combination of two conducting polymers in the same electrochromic device, eliminating the cathodic colored inorganic material in such devices. Several works describe high performance devices using exclusively conducting polymers as active materials in electrochromic devices. Recently, we described several devices combining different conducting polymers, such as polypyrrole and poly(3,4-ethylenedoxythiophene),[91] or poly(N,N-dimethyl-pyrrole) and poly(4,4'-dipentoxy-2,2'-bithiophene).[58]

At this stage, only the transparent electrodes were not plastic materials and a new approach to make electrochromic devices was the production of flexible prototypes exclusively composed by polymeric materials. This idea opens new perspectives to use these systems for commercial purposes, and became reality when some companies, *e.g.* I.S.T. (Belgium), developed the technology of producing transparent conductive plastic electrodes by recovering a poly(ethylene terephtalate), PET, film with an indium-doped tin oxide layer. Using these electrodes, it was possible to assemble all-plastic and flexible electrochromic devices with good properties.[92,93]

The unique characteristics of these flexible electrochromic devices have opened new commercial opportunities. Major challenges in this area are now directed to construct large-area devices, to enable the real utilization of all-polymer electrochromic devices in smart window applications. In this direction, a device with an area of 20 cm^2 was constructed by combining poly(*o*-methoxyaniline), PoAnis, and poly(ethylenedioxythiophene), PEDOT.[94] In this work, homogeneous polymer films were deposited on ITO-PET electrodes by spin coating or spray coating and the complete device presented a chromatic contrast of 75 % at 640 nm. Figure 4 shows this flexible electrochromic device.

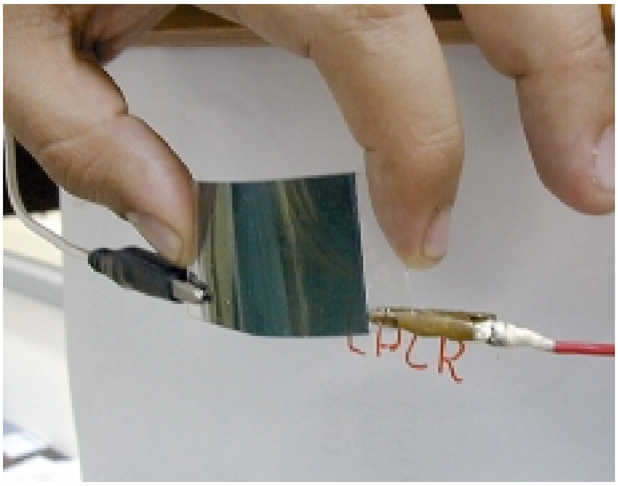

Figure 4. 20 cm^2 area all-plastic electrochromic device with the following configuration: ITO-PET || PoAnis| solid electrolyte | PEDOT || ITO-PET.

3.2 Photoelectrochemical cells

The growing demand for energy, associated to the limited resources of mineral fuels and environmental problems, has driven the research on solar energy conversion into electricity. Among the alternatives proposed to make use of solar energy, photovoltaic devices and photoelectrochemical cells are important tools to be considered. Commercial solar cells should comprise some properties, such as low cost, high conversion efficiency and reasonable lifetime. New developments in this area are now directed to find new low cost materials with semiconductor properties, and conducting polymers have been considered as active components in such devices. Progress in the field of organic solar cells are remarkable. In the decade of 1970 photon-electron conversion was around 10^{-5} %[95] and nowadays these cells present conversion efficiency of *ca.* 0.5%.[68]

Electronically conducting polymers present semiconductor behavior in the reduced state and this property can be exploited in several configurations to promote the conversion of light into electricity. Non-electrochemical photovoltaic devices are based in Schottky junctions or *p-n* junctions. Schottky junctions are formed by keeping in contact a reduced conducting polymer (which generally behaves as *p*-type semiconductor) and a metal with high work function, *e.g.* aluminum. Otherwise, light conversion can also be obtained by forming a heterojunction between *n*- and *p*-type conducting polymers.

Electrochemical processes can also be used to promote light conversion, because a Schottky junction is also formed when a semiconductor electrode is immersed in an electrolyte. Photoelectrochemistry is also the theme of several works because of the possibility of understanding the nature of electrode | electrolyte interface and several reviews cover the science and applications of photo-eletrochemical phenomena.[96,97] Nowadays photoelectrochemical cells presents an efficiency higher than 10 % for direct conversion of solar light into chemical energy.[98]

A photoelectrochemical cell is closely related to a battery, fuel cell, or other type of electrochemical system, in that it is composed of two electrodes and an electrolyte. Differently from batteries or fuel cells, in which the energy is initially stored in the reactants and is released through the electrical discharge circuit during chemical reactions, photoelectrochemical cells use the optical energy input to drive electrochemical reactions.

The basic processes that occur in such a system to achieve efficient solar energy conversion are well understood.[99] When a semiconductor modified-electrode is in contact with an electrolytic solution, a charge transfer occurs through the interface providing equilibrium between the Fermi level of the semiconductor and the redox potential of the solution.[100] Considering a *p*-type semiconductor immersed in an electrolyte with redox potential higher than the semiconductor Fermi level, it represents an electron transfer from the electrolyte to the electrode.

A common aspect in all electrode | electrolyte interfaces is the formation of electrically charged layers (ionic charge in the electrolyte and electronic in the electrode) with a capacitance related to these interfaces. For semiconductor electrodes a special situation occurs: these materials have lower density of charge carriers in comparison to metals. Thus, the electrically charged layer at the semiconductor (space charge region) is broader than that formed in the electrolyte. This situation induces the formation of an electric field in the space charge region, leveling the semiconductor Fermi level and the redox potential of the electrolytic solution, producing a band bending close to the electrolyte boundary, as shown in Figure 5 for a *p*-type semiconductor. This electric field is responsible for electron and holes transport at the interface, when they are in excess. At the surface, the semiconductor becomes depleted of majority carriers (for a *p*-type semiconductor, holes) and a depletion layer, W, is formed.

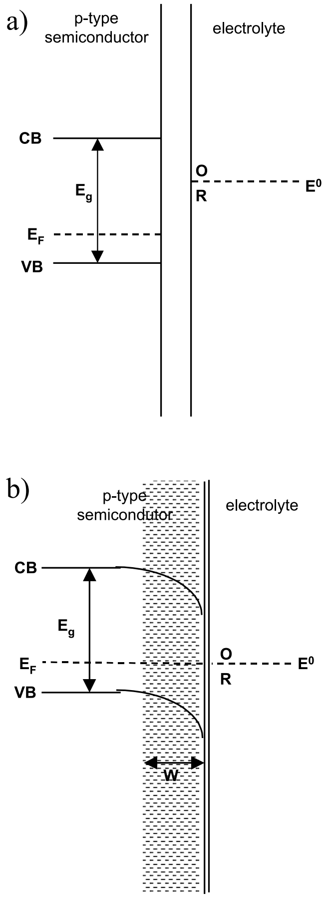

Figure 5. Representation of the formation of the Schottky junction between a *p*-type semiconductor and an electrolyte containing a redox couple O/R: a) before the contact, b) after contact, considering that the redox potential of the electrolyte is higher than the semiconductor Fermi level.

Irradiating the semiconductor with hν > Eg, valence band electrons are promoted to the conduction band, forming an electron-hole pair, also called exciton. In *p*-type semiconductors, it causes the migration of minority carriers (electrons) towards the interface, while majority carriers (holes) diffuse to the semiconductor bulk. At the boundary, the electrons, being regenerated at the counter electrode, producing the photocurrent in a short-circuited system, reduce oxidized species in the electrolytic solution. For *n*-type semiconductors the majority carriers are the electrons and an inverse behavior occurs. Additionally, the potential where no excess of charge exists is called “zero charge potential” and, under these conditions, the space charge region disappears and the bands do not bend. The potential where this situation occurs is known as “flat band potential”, E_{FB}. These processes are the basic operation mode of the so-called regenerative photoeletrochemical cells.

Inorganic semiconductors are the natural candidates for using in photoelectrochemical cells. The most promising candidates to replace the inorganic semiconductors in the assembly of solar cells are organic materials, due to their photosensitivity and photovoltaic effects. Among these, we have conjugated polymers,[11,101] organic molecules,[17] liquid crystals[102] and self-assembled organic semiconductors.[103] Conducting polymers are considered as an alternative for the following reasons: (i) semiconducting properties, as evidenced in a number of reports on solid state devices, such as Schottky barrier devices,[104] electroluminescent displays[105] and field effect transistors;[106,107] (ii) formation of oxidized polymer upon irradiation, due to electron injection into solution; (iii) easy production in the form of thin films with variable thickness; (iv) good environmental stability and (v) high hole mobility.[106]

Several studies report the photoelectrochemical properties of polymeric semiconductors, such as polypyrrole,[108] polyaniline,[109,110] poly(*o*-methoxyaniline),[74] poly(3-methylthiophene)[111] and PEDOT.[112] Special attention has been devoted to polythiophene and its derivatives because of the possibility of obtaining low band gap materials, which can convert visible light into electricity. Photoelectrochemical behavior of polythiophenes was investigated both in aqueous[113-115] and non-aqueous solutions.[116] In all cases, a cathodic photocurrent was observed on the polymer electrode at low doping levels. The photocurrent demonstrated a photovoltaic nature, originated from photostimulated charge separation at the Schottky barrier. The latter was evidenced by the occurrence of anodic photopotential, as well as by results of capacitance measurements. From this, it was inferred that the polymer is a *p*-type semiconductor and the Schottky barrier is localized at the polymer | electrolyte interface. Levi and co-workers arrived to similar conclusions, from the regularities of cathodic reactions occurring within that potential range.[117] By this reason, polythiophenes have been used in photoelectrochemical cells.[13,118]

The low conversion efficiency observed in conducting polymers can be related to the high density of traps in the films. These usually generate low mobility and high recombination rate, limiting the collection of the electron-hole pairs. However, these materials show high optical absorption in the entire solar spectrum. Several alternatives were proposed to enhance photoeffects in conjugated polymers. By combining different polymers it may be possible to adjust their band gap energy and obtain a more efficient light harvesting. Composites with different materials have also been produced, such as those where photoinduced electron transfer takes place in C_{60} (and its derivatives) and cyano-substituted poly(*p*-phenylene-vinylene) matrix, which acts as electron acceptor.[15,119] Composites where polymers are supported on microporous substrates exhibit enhanced photoresponse: Neves and De Paoli observed a significant increase of the photoresponse of polyaniline films by encapsulating the polymer in a cellulose acetate membrane.[109] Improved photoresponses were also obtained in a photoelectrochemical cell using poly(3-metylthiophene) supported in a TiO_2 film.[120] The sensitization of wide band gap semiconductors with conducing polymers has also been investigated, showing that some conducting polymers sensitize TiO_2, enabling conversion of visible light into electricity.[16,121]

A complete device should consist of a semiconductor electrode and an auxiliary electrode immersed in an electrolyte containing an adequate redox couple. The auxiliary electrode is responsible for the regeneration of the redox species and is generally covered with metals to catalyze this reaction (Pt, for example). For commercial applications, the use of liquid electrolytes, such as the I_3^-/I^- redox couple dissolved in acetonitrile, limits the application of photoelectrochemical cells, because it requires a perfect sealing of the cell to avoid leakage and evaporation. This restricts the shelf life and the long-term durability of the liquid junction.

In electrochromic devices the solid polymer electrolyte can be the same as those extensively studied for lithium-polymer batteries. On the other hand, a solid electrolyte for photoeletrochemical applications requires the additional presence of a redox couple with an adequate standard redox potential adequate to combine with the semiconductor. For this reason, new solid electrolytes for this use have been studied. Recently, Nogueira and co-workers[62] demonstrated that the incorporation of NaI and I_2 to poly(ethylene oxide-*co*-epichlorohydrin) produces an electrolyte with ionic conductivity of 10^{-5} S cm^{-1} and solar cells employing this solid-state electrolyte have yielded solar to electrical energy conversion efficiencies of up to 2.6 % in a dye-sensitized TiO_2 photoeletrochemical cell.[122]

Solid-state photoeletrochemical cells using conjugated polymers as semiconductor electrode have been also investigated. Gazotti and co-workers constructed a photoeletrochemical cell using a film of poly(4,4'-dipentoxy-2,2'-bithiophene) in its reduced form as semiconductor electrode and a polymer solid electrolyte.[59] Auxiliary electrode was a ITO-glass sheet recovered with a Pt layer. Differently from inorganic-based solar cells, this device cell exhibited photocurrent in practically all the visible range with a maximum quantum yield of 0.17% at 450 nm. Figure 6 shows the IPCE (incident photo-to-current conversion efficiency) curve for this solid-state photoelectrochemical cell. Although this value is low when compared to inorganic-based devices, it demonstrates that a conducting polymer device enables the conversion of visible light into electricity.

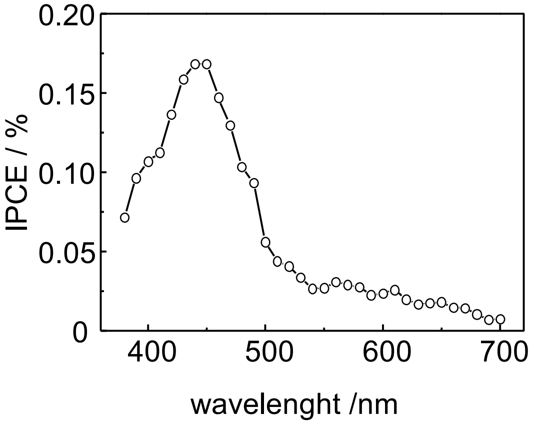

Figure 6. Incident photon-to-current conversion efficiency curve plotted as function of wavelength under short-circuit conditions, for the solid-state phoelectrochemical based on a polythiophene derivative.[59]

Yohannes and Inganäs[123] proposed a new use for polymers in solar cells. They assembled a photoelectrochemical cell by sandwiching, between ITO-glass electrodes, films of poly(3-octylthiophene) (semiconductor electrode), a polyether containing a redox couple (electrolyte) and PEDOT (auxiliary electrode). PEDOT was used in the place of a metal in the auxiliary electrode, to catalyze the redox couple regeneration. According to the authors, the polymer was efficient in this function and the entire cell showed photon-electron conversion efficiency of 0.4% at 500 nm. Gazotti and co-workers assembled a series of flexible dye-sensitized TiO_2 solar cells using different materials to catalyze the redox couple regeneration. The typical solar cell configuration used a TiO_2 nanocrystalline layer covered with a ruthenium complex dye as semiconductor electrode, poly(ethylene oxide-*co*-epichlorohydrin) filled with NaI/I_2 as solid electrolyte. Flexible devices were achieved by the replacement of the conducting substrate, usually a film of indium doped tin oxide (ITO) deposited on glass, by the same coating deposited on PET. Several metals and conducting polymers were tested as auxiliary electrode and poly(4,4'-dipentoxy-2,2'-bithiopphene) shows results comparable to a Au-Pd layer, Figure 7.[60]

Photoelectrochemical cells are simple to fabricate and straightforward in concept. Besides, they present a number of scientific and engineering challenges in conjunction with their potential implementation.[124] As discussed here, polymers in general have potential utilization in all components of a solar cell, comprising the electrical contacts, the semiconductor and auxiliary electrodes, as well as the solid electrolyte. Although a great advance has occurred in the development and improvement of the performance of some polymer-based photoelectrochemical devices, their efficiency is still low in comparison to those based on crystalline and amorphous silicon, gallium arsenide, cadmium telluride, copper-indium-diselenide and dye-sensitized photoelectrochemical cells using nanostructured TiO_2. However, the efficient "all plastic" solar cells are in their infancy and the results here described encourage the research on the use of polymers to assemble solar cells.

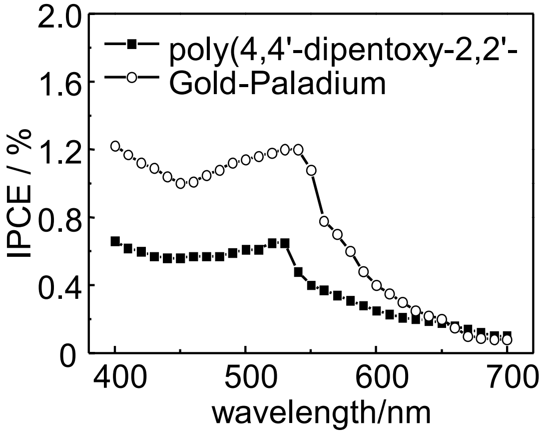

Figure 7. Action spectra of all-solid state photoelectrochemical cells using dye-sensitized TiO_2 as photoactive electrode.[60]

3.3 Light emitting electrochemical cells, LEC

The electroluminescence phenomenon in semiconductors was first observed by Round in the beginning the 20th century[125] and explained in posterior studies carried by Lossev.[126] The term *electroluminescence* was introduced by Destriau[127] and it was initially used only for emission of visible radiation. Nowadays it was extended to include emission in the near-infrared region of the spectrum, because the theoretical and technological approaches involved are similar.

Light emitting diodes, commonly named LED, are the reverse of photovoltaic cells. While in this last the light is used to produce an electrical voltage, in a LED a voltage is applied to produce light.[128] Basically, the electroluminescence occurs when a sufficiently large forward-bias voltage is applied across a *p-n* junction, where minority carrier injection takes place and radiative recombination produces a photon.[129]

When a *p*-type semiconductor is kept in contact with an *n*-type, electrons move from the *n*- to the *p*-doped layer.

At the thermodynamical equilibrium the energy levels of the semiconductors are bent and two regions depleted of majority carriers are formed in both sides of the interface. In this situation, the *p*-semiconductor is depleted of holes, the *n*-semiconductor is depleted of electrons and a potential barrier is formed, which hinders the current flow though the interface. If this junction is forward biased, the potential barrier is lowered and the injected electrons in *p*-type side recombine with the holes and the injected holes in the *n*-type side recombine with the electrons.[130] This current flow usually gives rise to an excitation, which results in a radiative recombination process.[131]

All theoretical considerations about LED involve inorganic semiconductors because of the pioneering works on light emission from GaAs *p-n* junctions.[132-134] The electroluminescence from organic materials was known since 1963,[135] however, the first work describing the use of conducting polymers as emitting material in a LED was only published in 1990, using poly(*p*-phenylene vinylene), PPV, as electroluminescent layer.[8] Polymer-based light emitting diodes are commonly called "polymer, PLED" or "organic LED, OLED".

The light emission process in such devices depends on several parameters, such as charge injection, charge carriers mobility, electron-hole recombination with radiative decay and emission. Charge injection is assigned to the efficiency that the metallic electrodes inject carriers into the polymer film and depends on the Fermi level of the metals. Thus, a hole-injector metal must have high work function, such as: Au or ITO electrodes, and an electron injector metal must posses low work function, such as alkaline or alkaline earth metals.

Polymer based LED present a series of interesting applications, despite their poor light emission properties when compared to inorganic materials. Conducting polymers usually used as electroluminescent material have a band gap between 2 and 3 eV, and the most used are the derivatives of poly(*p*-phenylene-vinylene) and polythiophene, because these materials are usually soluble and can be easily deposited on different substrates.

The aim of using organic materials as electroluminescent component in a LED results from the difficulty of assembling large areas devices with inorganic semiconductors. Additionally, the mechanical properties of conducting polymers open the possibility of constructing flat panel displays. An example of plastic flexible LED was described by Heeger and co-workers,[136] consisting of a free-standing PET film recovered with successive layers as follow: (i) a thin film of polyaniline (emeraldine form, doped with camphor sulphonic acid) as hole-injecting contact; (ii) a film of a PPV derivative as active electroluminescent layer and (iii) a calcium electrode as electron injecting contact.

Polymer LED technology has achieved great advances in the last years, but the preponderance of hole injection over electron injection is a step to be surmounted to reach higher performances because metals with sufficiently low work function are chemically reactive.

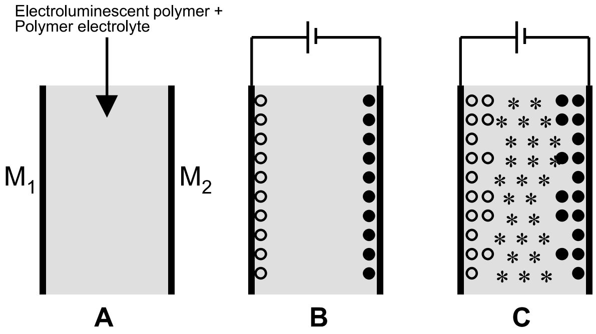

Figure 8. Schematic representation of the electrochemical processes in a LEC. Electrodes are named M_1 and M_2, (○) are the oxidized species, (●) are the reduced species and (*) are the neutral electron-hole pairs. (A) The cell under zero bias, (B) Doping opposite sides as *n*- and *p*-types, (C) Charge migration and radiative decay.[10]

In 1995, Heeger and co-workers proposed an "electrochemical" alternative to solve the operation problems found in heterojunctions: the *light-emitting electrochemical cells*, LEC.[9] A LEC is an electrochemical device composed by a blend of an electroluminescent polymer with a polymeric electrolyte, sandwiched between two ITO electrodes. Its operation is based on the possibility of doping a conducting polymer as both *p*- and *n*-type. By applying sufficient high voltage between the ITO electrodes, cations and anions move in opposite directions. The polymer side adjacent to the anode is oxidized and *p*-type carriers are introduced, while the polymer side closer to the cathode is reduced and *n*-type carriers are introduced. Electrochemical doping occurs when the applied potential is larger than the energy gap of the polymer.[137] The charge balance in this process is provided by cation and anion mobility into the blend. In the bulk an *in-situ p-n* junction is generated, and recombination processes take place with light emission. A schematic representation of a LEC is shown in Figure 8.[10] The electrolyte is needed to provide ions for the occurrence of both *p*- and *n*- doping in the polymer, and the most used in LEC applications is poly(ethylene oxide), PEO, filled with lithium salt.[138]

One limitation in LEC performance comes from the low ionic conductivity of polymeric electrolytes and the phase segregation occurring during LEC operation between the electroluminescent polymer and the solid electrolyte. To improve the ionic conductivity of the blend, Heeger and co-workers included a bifunctional liquid additive to the electroluminescent layer.[139] The resulting LEC has better performance in comparison to the parent LEC without additive: the brightness increased from 10 - 20 to 1000 cd m^2. Besides, the additivated LEC present efficiency of 2.5 %, which is similar to that obtained for a LED-type device using the same electroluminescent polymer.

Finally, the electrochemical generation of an *in-situ* junction in a LEC provides a new kind of light emitting devices. LEC present several interesting properties, such as lower operating voltage and the possibility of using ITO electrodes as electrons injector in the place of the reactive traditional low work function metals.

4. Perspectives and Challenges

The large spectrum of applications of conductive polymers using the variation of its optical properties upon "doping" by redox reactions was discussed in the previous sections. One recent progress in this field is the suitable combination between photoelectrochemical and electrochromic properties. Such devices are called "photoelectrochromic" systems and can change the color under illumination. Basically, the illumination of one part of the cell produces the required photovoltaic potential to drive the current that will produce the electrochromism. As seen, the association of polymers in opto-electronic devices is a promising field of research and the more optimistic people can find that "our imagination is the limit". In part, this affirmation is correct because great advances have been achieved last years in developing new electrochemical devices, after the utilization of polymeric materials in assembling of such devices.

A sign of the potential importance of polymeric opto-electronic devices is that the research is not restricted to the Academy: almost all large companies have specific divisions to do research this field. New conducting polymers with tailored properties are studied, for example, by Du Pont/Uniax (www.dupont.com), Dow Chemical (www.dow.com) and Eastman-Kodak (www.kodak.com). Hewlett-Packard (www.hp.com), Xerox (www.xerox.com) and IBM (www.ibm.com) are studying the deposition of thin films of conducting polymers. Other companies, as Philips (www.philips.com) and Sanyo (www.sanyo.com) announced the use of conducting polymers to construct "flat-thin TV/computer screens" based on LED/LEC technologies.

However, many improvements should be reached to make competitive commercial devices and the researchers are now invited to produce conducting polymers with tailored properties and high stability. The remarkable progress achieved in 30 years encourages us to search these materials because, in a close future, they will certainly be used in niche applications were the use of inorganic materials would be unthinkable.

Acknowledgements

The authors thank FAPESP (96/09983-0), FAPERJ and CNPq for financial supports.

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Received: March 20, 2002
Published on the web: July 10, 2002

FAPESP helped in meeting the publication costs of this article.