

## CHAPTER II

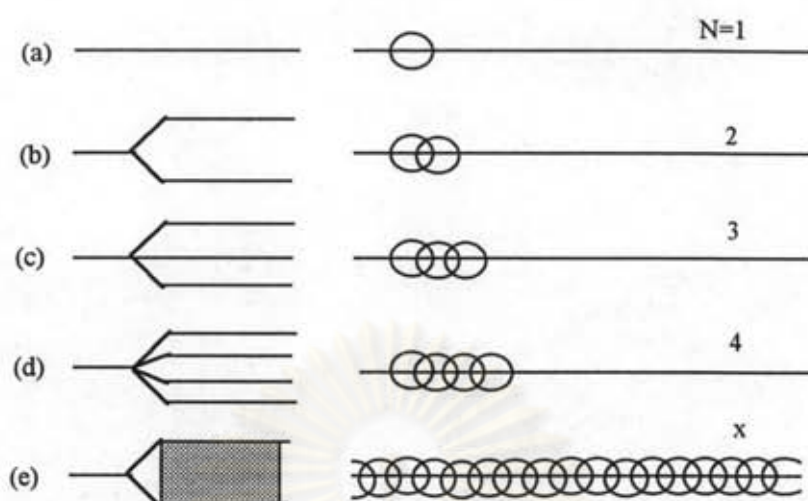
### THEORETICAL CONSIDERATION

#### Electrical Conduction in Polymer

In order to understand the electrical conduction of polymer, a suitable starting point for consideration is band theory which is the essential basic concept for the conduction process in molecular solid.

#### Band Theory

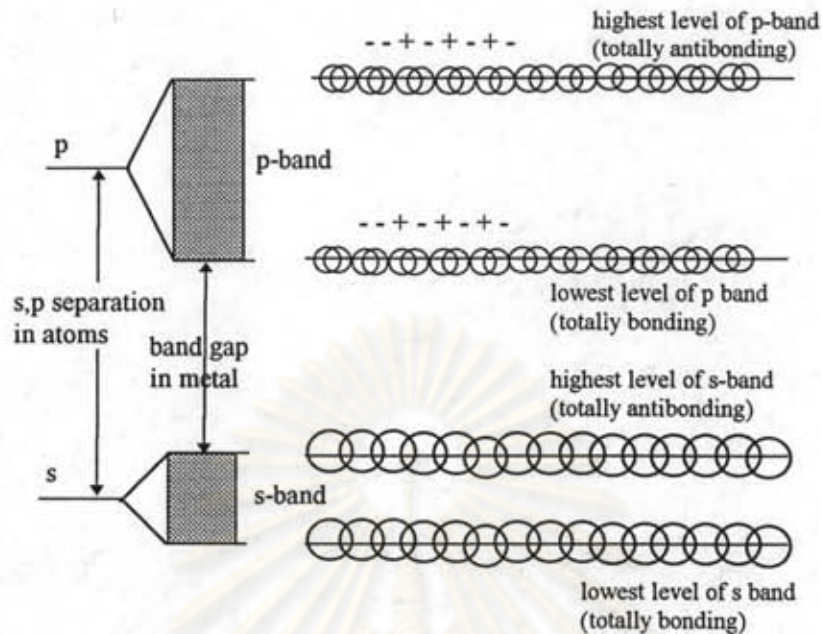
For simplicity, we assume that, one atom provides one atomic s-orbital at some energy, Figure 2.1(a). When the second atom is brought up, it overlaps the first one and forms a bonding orbital and an antibonding orbital, Figure 2.1(b). The third is brought up and overlaps its nearest neighbour (and only slightly its next-nearest) and form these three molecular orbitals are formed as shown in Figure 2.1 (c). The fourth atom leads to the formation of a fourth molecular orbital, and at this stage we can see that the general effect of bringing up successive atoms is slightly to spread the range of energies covered by the orbitals, and also to fill in the range with orbital energies. When  $N$  atoms have been slotted on to the line there are  $N$  molecular orbitals covering a band of finite width. When  $N$  is indefinitely large, the orbital energies are indefinitely close, and form a virtually continuous band. Nevertheless this virtually continuous band consists of  $N$  different molecular orbitals, the lowest-energy orbitals in the band bring predominantly bonding, and the highest-energy predominantly antibonding.



**Figure 2.1** The formation of a band of  $N$  orbitals by the successive addition of atoms to a line.

The band formed from  $s$ -orbitals is called the  $s$ -band. If the atoms carry  $p$ -orbitals, the same procedure may be followed, and the band of molecular orbitals is called the  $p$ -band, Figure 2.2. If the atomic  $p$ -levels lies higher than the atomic  $s$ -level, the  $p$ -band lies higher than the  $s$ -band, unless it is so broad (strong overlap) that the bands overlap.

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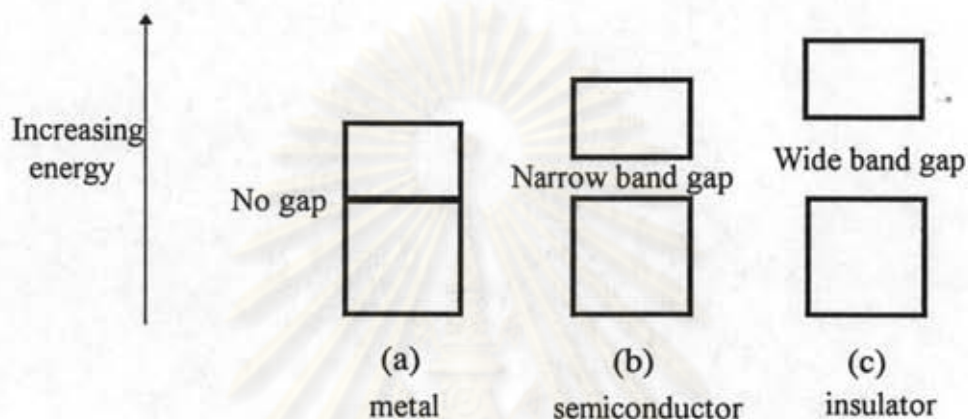
**Figure 2.2** s-band, p-band and the band gap

Energy band diagrams may be used to illustrate the differences between metals, semiconductors and insulators. In metals the electrons completely fill the valence band (VB). The higher energy conduction band (CB) is empty at absolute zero. This is shown in Figure 2.3(a). There is no energy band gap between the VB and CB for metals, above absolute zero, electrons at the top of the highest occupied level can gain thermal energy and move into the low lying empty levels of CB. A substantial fraction of the electrons can be excited into singly occupied energy levels, even at relatively low temperature. Such unpaired electrons contribute to the electrical conductivity of a metal, and the substance is called a conductor.

In semiconductors and insulators, shown in Figures 2.3(b) and (c), the VB is completely filled and an energy gap exists between it and the next higher energy band. If the energy gap is wide (large), there is little chance for electrons to be excited into an empty CB and the material is an insulator. If there is only a small energy gap, the material is an intrinsic semiconductor, electrons being excited



rather easily into the CB. If the gap is wide but impurity atoms are added, it may be possible to establish level within the gap that facilitate the movement of electrons into the CB. These latter systems are known as impurity semiconductors, or extrinsic semiconductors.



**Figure 2.3** The relationship of energy gaps in the three types of solids

Most technologically important semiconductors are the extrinsic type in which the charge carrier production is determined by trace amounts of impurities or by lattice imperfections. However, with the addition of an impurity (between about 0.1% to less than 1 ppm), the charge carrier type, its concentration and the conductivity of the sample can be controlled.

When the crystal lattice is disturbed by the addition of impurities or even by irregularity in the lattice arrangement, isolated centers are generated. Some centers can contribute electrons to the CB of the material. Such defects are called donors or donor centers. If the primary charge carriers are electrons, the material is called an n-type semiconductor. If the centers remove electrons from the chemical bonds, they are called acceptors and produce electron vacancies. These vacancies behave as positive charge carriers in the VB and are called holes. If holes are the predominant charge carriers, a p-type semiconductor results.

Conducting polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Their electrical conductivity can not be explained well by simple band theory. For example, simple band theory can not explain why the charge carriers, usually electrons or holes, in polyacetylene and polypyrrole are spinless. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons and bipolarons, have been applied to conducting polymers since the early 1980s.

### **Nature of the Charges Appearing on the Polymer Chain**

The conductivity of organic polymers is drastically increased by doping. This increase was explained by the following.

In crystal polymer, the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands [1]. The highest occupied electronic level constitutes the VB and lowest unoccupied level, the CB. The width of the forbidden band, or band gap ( $E_g$ ), between the VB and CB determines the intrinsic electronic properties of the material. For all the organic conjugated polymers we have discussed so far, the band gap rather larger so that these materials are intrinsically insulating.

Initially, the high conductivity observed upon doping organic polymers was thought to result from the formation of unfilled electronic bands. It was simply assumed upon p-type or n-type doping that, electrons were respectively removed from the top of the VB or added to the bottom of the CB, in analogy to the mechanism of generation of charge carriers in doped inorganic semiconductors. This assumption was however quickly challenged by the discovery that polypyrrole

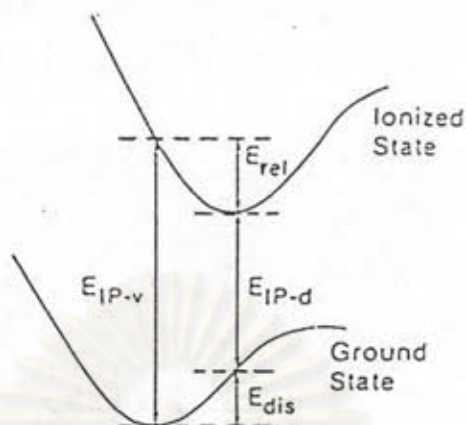


can display conductivity which does not seem to be associated with unpaired electrons but rather with spinless charge carriers.

In organic molecule, it is usually the case that equilibrium geometry in the ionized state is different from that in the ground state, e.g., the geometry of polypyrrole is aromatic-like but becomes quinoid-like in ionized state, Figure 2.4. The energies involved in the ionization process of a molecule are schematically depicted in Figure 2.5. A vertical, Franck-Condon like ionization process costs an energy  $E_{IP-v}$ . If a geometry relaxation then takes place in the ionized state, a relaxation energy  $E_{rel}$  was gained back. Conceptually, going from the ground state to the relaxed ionized state can take place the following way. The geometry of the molecule is first distorted in the ground state in such a way that the molecule adopts the equilibrium geometry of the ionized state. This costs a distortion (elastic) energy  $E_{dis}$ . For one-electron energy levels of the molecule, this distortion leads to an upward shift  $\Delta\varepsilon$  of the highest occupied molecular orbital (HOMO) and a downward shift of the lowest unoccupied molecular orbital (LUMO), as illustrated in Figure 2.6. If we then proceed to the ionization of the distorted molecule, it requires an energy  $E_{IP-d}$ .



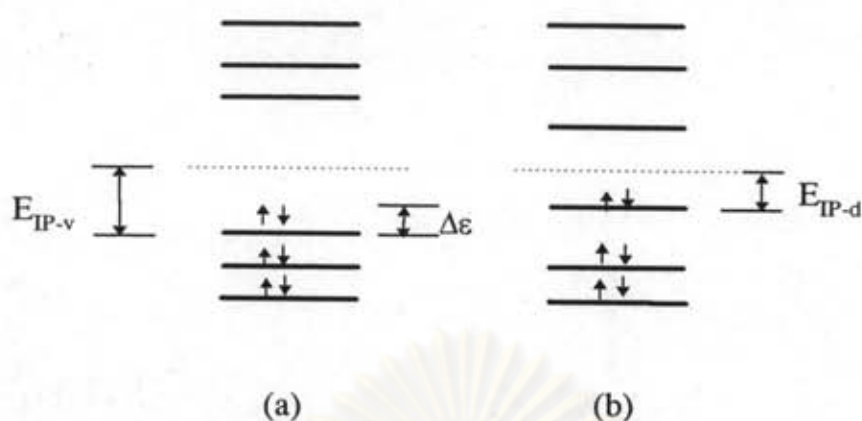
**Figure 2.4** Aromatic (ground-state) and quinoid-like (ionized state) geometric structure for polypyrrole



**Figure 2.5** Illustration of the energies involved in a molecular ionization process.  $E_{IP-v}$  is the vertical ionization energy,  $E_{rel}$ , the relaxation energy gained in the ionized state,  $E_{dis}$ , the distortion energy to be paid in the ground state in order that the molecule adopts the equilibrium geometry of the ionized state, and  $E_{IP-d}$ , the ionization energy of the distorted molecule.

From Figure 2.5, it is clear that it is energetically favorable to have a geometry relaxation in the ionized state when the quantity  $E_{IP-v} - E_{IP-d}$  (which actually corresponds to  $\Delta\epsilon$  as can be inferred from Figure 2.6) is larger than the distortion energy  $E_{dis}$ , or in other words, when the reduction,  $\Delta\epsilon$ , in ionization energy upon distortion is larger than the energy  $E_{dis}$  required to make that distortion.

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**Figure 2.6** The one-electron energy levels for organic molecule in its ground-state electronic configuration.

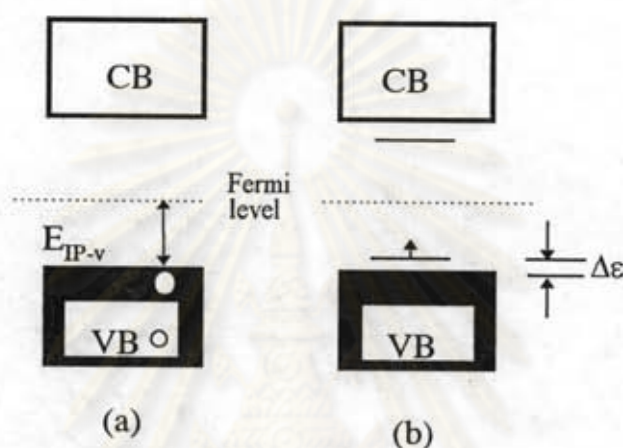
- (a) the equilibrium geometry of the ground state
- (b) the equilibrium geometry of the first ionized state

In a polymer, or any solid, a vertical ionization process  $E_{IP-v}$  results in creating a hole on top of the VB; see Figure 2.7(a). In this case, three remarks can be made. First, by the very definition of the process, no geometry relaxation (lattice distortion) takes place on the chain. Second, the positive charge on the chain is delocalized over the whole polymer chain. Third, the presence of a hole (unfilled level) on top of the VB leads, as discussed above, to the appearance of a metallic character. This situation corresponds to the initial assumption made about the conduction mechanism in doped organic polymers.

However, in an organic polymer chain, it can be energetically favorable to localize the charge that appears on the chain and to have, around the charge, a local distortion (relaxation of the lattice). This process causes the presence of localized electronic states in the gap due to a local upward shift,  $\Delta\epsilon$ , of the HOMO and downward shift of the LUMO, Figure 2.7(b). Considering the case of oxidation, i.e., the removal of an electron from the chain, the ionization energy was lowered by an amount  $\Delta\epsilon$ . If  $\Delta\epsilon$  is larger than the energy  $E_{dis}$  necessary to distort the lattice locally around the charge, this charge localization process is



favorable relative to the band process. It was obtained the formation of what condensed-matter physicists call a polaron [5-7]. In chemical terminology, the polaron is just a radical ion (spin 1/2) associated with a lattice distortion and the presence of localized electronic state in the gap referred to as polaron state.

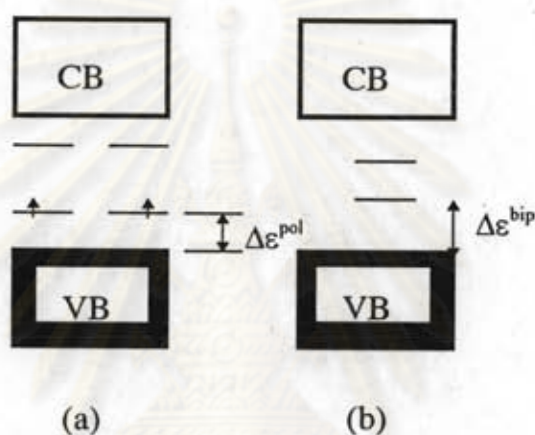


**Figure 2.7** Band structure of a polymeric chain in the case of  
 (a) a vertical ionization process  
 (b) the formation of a polaron

The quantity  $\Delta\varepsilon - E_{\text{dis}}$  ( $= E_{\text{rel}}$ ) corresponds to the polaron binding energy. Calculation (based on Huckel theory with  $\sigma$  bond compressibility) has indicated that polaron formation is energetically favorable in all the organic conjugated polymers. The polaron binding energy is 0.12 eV in polypyrrole. It must be stressed that in the case of polaron formation, the VB remains full and CB empty. There is no appearance of metallic character since the half-occupied level is localized in the gap, Figure 2.7 (b).

If another electron is now removed from the already oxidized polymer containing the polaron two things can happen : This electron could come from either a different segment of the polymer chain, thus creating another

independent polaron, or from the first polaron level (remove the unpaired electron) to create a special dication, which solid-state physicists call a bipolaron. A bipolaron is defined as a pair of like charges associated with a strong local lattice distortion. The formation of a bipolaron implies that energy gained by the interaction with the lattice is larger than the Coulomb repulsion between the two charges of same sign confined in the same location. The two positive charges of the bipolaron are not independent, but act as a pair.



**Figure 2.8** Band structure of a polymer chain containing:

(a) two polarons                      (b) one bipolaron

The electron band structure corresponding to the presence of two polarons and that of one bipolaron is depicted in Figure 2.8. Since the lattice relaxation around two charges is stronger than around only one charge,  $E_{\text{dis}}$  for the bipolaron is larger than  $E_{\text{dis}}$  for the polaron and the electronic states appearing in the gap for a bipolaron are further away from the band edges than for a polaron.

In the comparison of the creation energy of a bipolaron relative to that of two polarons, the calculation for polypyrrole indicates that the distortion energy  $E_{\text{dis}}$  to form one bipolaron is roughly equal to that to form two polarons. On the other hand, the decrease in ionization energy is much more important in the bipolaron case ( $2\Delta\epsilon^{\text{bip}}$ ) than for two polarons ( $2\Delta\epsilon^{\text{pol}}$ ); see Figure 2.8. This is the



reason why one bipolaron is thermodynamically more stable than two polarons in these systems despite of the Coulomb repulsion between two similar charges. Furthermore, the latter is also largely screened by the presence of dopants (counterions) with opposite charges. The bipolaron binding energy is calculated to be larger than that of two polarons by about 0.45 eV in polypyrrole.

In case of p-(n-) type doping, the bipolaron level in the gap is empty (fully occupied); see Figure 2.8(b). The bipolaron is thus spinless. The presence of bipolarons on polymer chains result in the possibility of two optical transitions below the bandgap transition: for p-type doping, such as polypyrrole, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level. In the case of polarons, a third absorption is possible below the gap, corresponding to an optical transition between the two polaron levels, Figure 2.8(a).

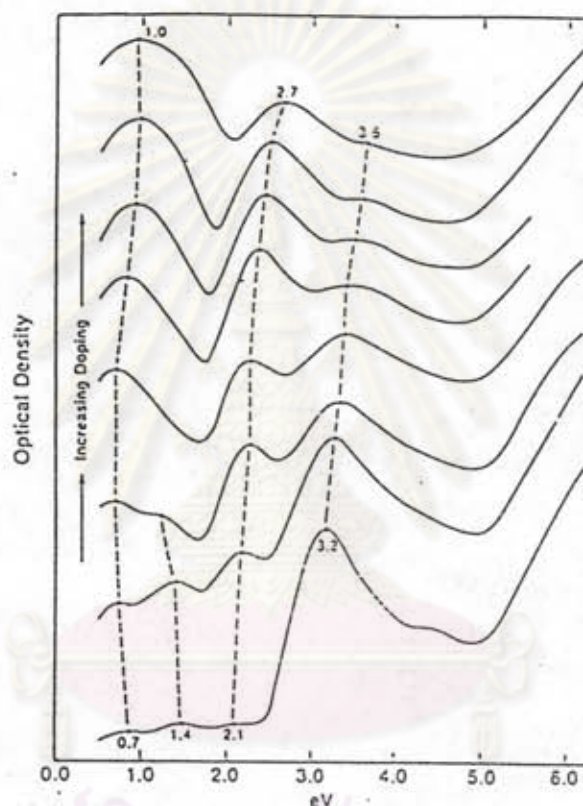
### **Evolution of the Electronic and Transport Properties**

The state of polarons or bipolarons can be observed and explained by the optical absorption data. A consistent description of the electrical transport mechanism in conducting polymers constitutes a critical problem in the understanding of these materials. Band structure calculations on a deformable polypyrrole chain show that polarons and bipolarons are formed upon doping and the current carriers could be explained by relating charge carriers to doubly charged spinless bipolarons. The localized deformation associated with a polaron or bipolaron consists of lengthening the double bonds and shortening the single bonds.

Yakushi, K, et al. have recorded the optical spectra of polypyrrole at various stages of oxidation, from the as-grown highly oxidized film to the almost neutral polypyrrole, Figure 2.9 [8]. At low levels of oxidation (lower curve, Figure 2.9), there is a strong absorption maximum at 3.2 eV, associated with the interband  $\pi$ - $\pi^*$  transition. Within the gap region, there are three additional features at 0.7, 1.4



and 2.1 eV. As the level of oxidation increases, the middle 1.4 eV absorption disappears, and the interband transition weakens and shifts to higher energy. In the fully oxidized sample (upper curve, Figure 2.9), two intense, broad absorption bands are present at 1.0 and 2.7 eV and the interband transition appears as a shoulder at 3.6 eV.



**Figure 2.9** Evolution of the optical-absorption spectrum of polypyrrole as a function of doping level. The concentration of perchlorate anions increased from bottom curve (almost neutral polypyrrole) to top curve (33 mol % doping level).

In order to interpret these experimental results, they present a theoretical study of the energetics of polaron and bipolaron formation on

polypyrrole chains and the band-structure evolution upon oxidation. The result is to demonstrate that the evolution of the absorption spectra upon oxidation can be fully explained in terms of initial polaron formation and then bipolaron formation on the polypyrrole chains. From the ESR measurements, the theoretical studies of the absorption spectra indicate that bipolarons are the spinless charge carriers in the highly conducting regime of doped polypyrrole.

Calculation of the energetics of polaron and bipolaron formation on polypyrrole chains are performed using tight-binding Huckel theory with  $\sigma$  bond compressibility and bond-order-bond lengths relationships. A polaron is formed when the increase in  $\pi$  plus  $\sigma$  energy due to the lattice deformation is more than that compensated by a lowering in ionization energy, the difference corresponding to the polaron binding energy. When a single positive charge on the chain, it was obtained the formation of a polaron with a 0.12 eV binding energy, constituting the difference between the 0.49 eV decrease in ionization energy and the 0.37 eV  $\pi$  plus  $\sigma$  energy needed for the change in geometry. The presence of a polaron on the chain introduces two localized electronic levels in the gap: a singly occupied bonding polaron state, 0.49 eV above the VB edge and an empty antibonding polaron state 0.53 eV below the CB edge, Figure 2.10 (a). The polaron states in the gap account for the three transitions observed within the gap in very slightly oxidized polypyrrole (lower curve, Figure 2.9). The first absorption peak at 0.7 eV can be related to a transition from the VB to the bonding polaron state; the peak at 1.4 eV is associated with a transition from the bonding to the antibonding polaron state; finally, the peak at 2.1 eV corresponds to a transition from the VB to the antibonding polaron state. Exact matching of calculated transitions to the peaks in the absorption spectrum should not necessarily be expected, since the experimental data have not been transformed due to their limited spectral range. Nevertheless, the semiquantitative agreement between calculation and data is quite satisfying. It must be stressed that the sum of the first two peak energies exactly



corresponds to the peak energy for the third transition, as it should be within a one-electron model.

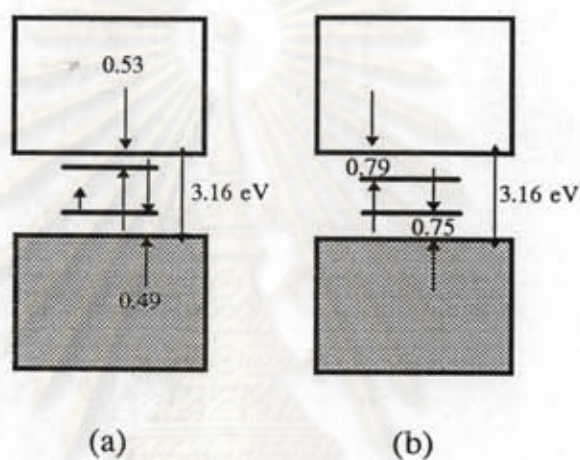
Note that the peak positions indicate that the location of the antibonding polaron state is further away from the CB edge than the location of the bonding state from the VB edge. This asymmetric location arises because of the different nitrogen orbital contributions to the VB and CB states. In the fourth transition, from the bonding polaron state to the CB, should be observed at  $\sim 2.5$  eV. This energy value unfortunately corresponds to the disorder-broadened edge of the band-gap transition.

At higher oxidation levels, polaron state starts interacting. The calculations indicated that two polarons, as they approach each other, become unstable with respect to the pairing of their spins and the formation of a doubly charged spinless bipolaron, Figure 2.10(b). The geometry relaxation is stronger than in the polaron case (i.e., the geometry within the bipolaron is more quinoid-like than within the polaron), so that the empty bipolaron electronic levels in the gap are 0.75 eV above the VB edge and 0.79 eV below the CB edge, Figure 2.10(b). The bipolaron binding energy 0.69 eV means that a bipolaron is favored over two polarons by 0.45 ( $=0.69-2\times 0.12$ ) eV. Very importantly, the bipolaron bonding state, in contrast to the polaron case, is empty. As a result, only two transitions within the gap are now possible. Thus the emptying of the bonding states in the gap accounts for the loss of the middle 1.4 eV absorption peak when going from slightly oxidized to highly oxidized polypyrrole.

The band structure for a doping level of 33 mol % (per polymer repeat unit) is displayed in Figure 2.11. The overlap between the bipolaron states leads to the formation of two  $\sim 0.4$  eV (0.45 and 0.39 eV, respectively) wide bipolaron bands in the gap. The bandgap has widened from 3.16 eV in the neutral state to 3.56 eV in the 33 % doped state, 0.4 eV larger than in the undoped case. This is due to the fact that the bipolaron states coming in the gap are taken from the VB and CB edges. This band structure supports the fact that, upon application of

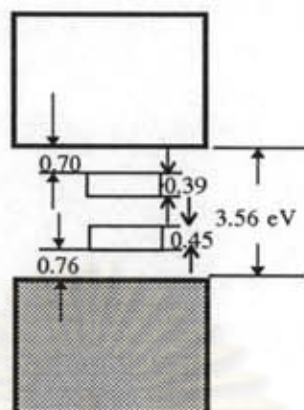


an electric field, the spinless bipolarons (which carry two charges) could become mobile at high dopant concentration, where the Coulomb attraction with the counterions is largely screened. This conduction mechanism would be highly unusual in the sense that all bands are either totally filled or empty (as shown in the band structure in Figure 2.11) and that mobile bipolarons, not electron, transport the current.



**Figure 2.10** Electronic structure diagrams for a polypyrrole chain containing  
 (a) low doping level, polaron formation  
 (b) moderate doping level, bipolaron formation

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**Figure 2.11** Band structure for highly oxidized (33 mol % doping level) polypyrrole, showing the presence of two broad bipolaron bands in the gap.

In summary, conduction by polaron and bipolaron is now thought to be the dominant mechanism of charge transport in polymers. These concepts also explain by the optical absorption changes seen in these polymers with doping, which its data demonstrate that

1. polarons are formed on the chains at low oxidation level.
2. at higher oxidation levels, polarons combine to form spinless bipolaron
3. wide bipolaron bands are present in the gap in the highly conducting regime

However, it should be emphasized that these models were device assuming ideal structure. The actual structures of most conductive polymers, both in the doped and undoped states, are unknown, and all data show that certain polymers have a large number of defects.

## Polypyrrole and Preparation

Among the conducting polymers, one of the most intensively studied polymer is polypyrrole. Polypyrrole is attractive as an electrically conducting polymer because of its relative ease of synthesis, good environmental stability and good electrical conductivity. Polypyrrole was shown to be a conducting polymer in 1968. Dall'Olio et al. prepared it by oxidation of pyrrole in sulfuric acid. The synthesized polypyrrole was a black powder with room temperature conductivity of  $8 \text{ Scm}^{-1}$ . The five membered ring heterocycle of pyrrole polymerizes through  $\alpha, \alpha'$ -coupling (2,5-position) and molecular structure is shown in Figure 2.12.

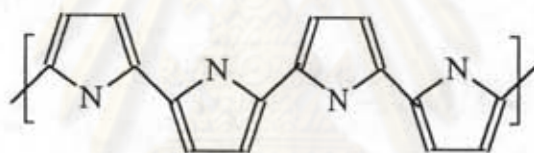


Figure 2.12 Polypyrrole

There were many methods in preparation of polypyrrole. The area of synthesis is extremely fast moving and competitive. Here, they summarize the major types of synthetic techniques used to prepare polypyrrole, such as electrochemical polymerization, chemical vapor deposition and chemical polymerization.



## Electrochemical Polymerization

Typically, conductive polypyrrole are prepared electrochemically by dissolving pyrrole in an appropriate solvent in the presence of an electrolyte. The electrochemical polymerization can be carried out either potentiostatically (constant voltage) or galvanostatically (constant current). The conductive form of polymer is generated directly, incorporating the electrolyte as the counterion, and usually precipitates onto the surface of the anode [9,10].

Polypyrrole was first electrochemically polymerized in aqueous sulfuric acid in 1968 by Dall'Olio and co-workers. They obtained "pyrrole black," as it was called at that time. It formed insoluble powder precipitate on the platinum electrode. Elemental analysis showed that the pyrrole black so obtained consisted of 76% "polypyrrole," the remainder being sulfate ions; therefore the polymer was cationic. It was found to have an electrical conductivity of  $8 \text{ Scm}^{-1}$ .

But it was not until subsequent experiments in 1979 that the importance of the electrochemical approach to the synthesis of conducting polymer became apparent. The key difference between these later and the earlier experiments was that now continuous films were obtained which could be peeled off the platinum electrodes to yield free-standing, easily manageable films that were stable in air and had much higher electrical conductivities than achieved before, namely  $10^2 \text{ Scm}^{-1}$ .

The proposed mechanism for the formation of polymer is shown in Figure 2.13. The initial step involves the oxidation of the monomer unit to the radical cation. Two of these species combine with loss of two protons to form the dimer of pyrrole. Further oxidation of the dimer occurs in preference to the monomer because of the lower half-wave oxidation potential of the dimer. By continued reaction, polymer is generated. The additional loss of an electron, which results in a partial positive charge on the pyrrole ring (from the neutral polymer), is

probably due to further partial oxidation of the polymer. In order to maintain charge neutrality in the polymer, there must be an affiliation of an anionic species which comes from the electrolyte salt.

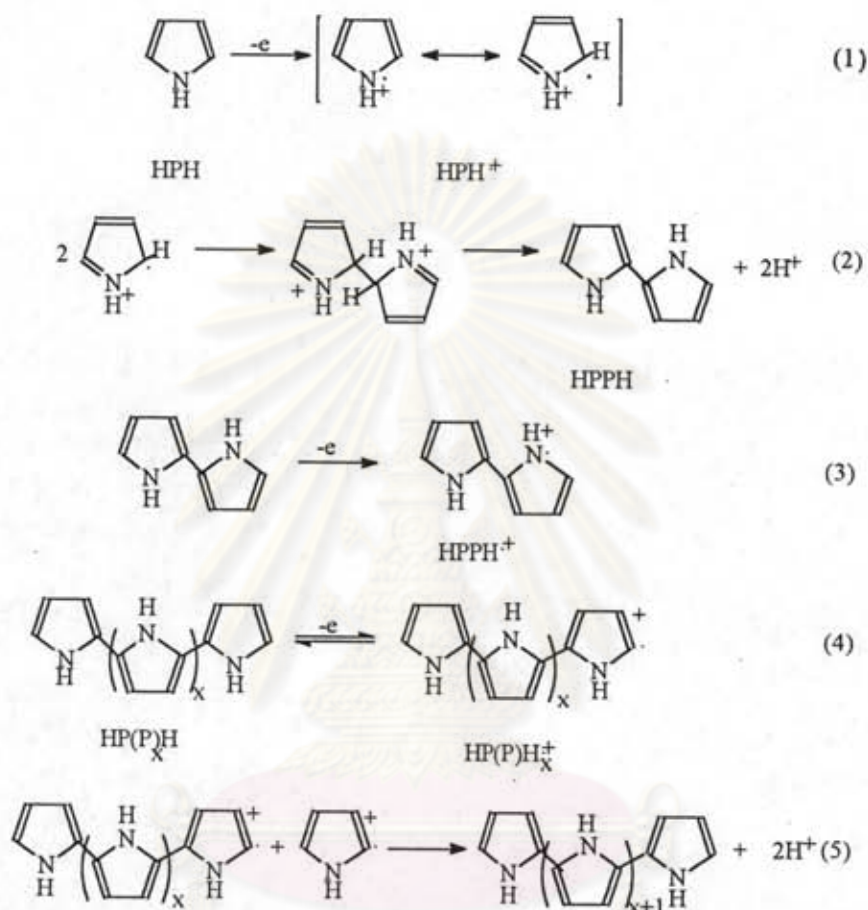


Figure 2.13 Mechanism for polymer formation

From the mechanism, the polymerization reaction proceeds via radical cation intermediates, it becomes apparent that the reaction will be sensitive to the nucleophilicity of the environment in the region near the electrode surface. This then places some limitations of the choice of the solvent and the electrolyte salt. For this reason, many of the reported studies have been performed in aprotic solvents, which are poor nucleophiles. Table 2.1 shows solvent effects of the

conductive polypyrrole obtained by electrochemical polymerization. The conductivities of these material, as determined by the standard four-probe technique are reported in  $\text{Scm}^{-1}$ .

With regards to the electrolyte salt, the main considerations are the solubility, degree of dissociation, and the nucleophilicity. For this reason, most of the salts used are tetraalkylammonium salts, since they are soluble in aprotic solvents and are highly dissociated.

**Table 2.1** Solvent Effects of the Quality of the Generated Polypyrrole Films

Solvent Electrolyte (0.1 M) <sup>a</sup>	Film quality	Conductivity( $\text{Scm}^{-1}$ )
Acetonitrile Tetraethylammonium tetrafluoroborate	Good film	50
Acetonitrile Toluenesulfonic acid	Good film	50
Methylene chloride Tetrabutylammonium tetrafluoroborate	Good film	50
Butanone Tetrabutylammonium tetrafluoroborate	Good film	40
Propylene carbonate Tetrabutylammonium tetrafluoroborate	Good film	50
Dimethylformamide Toluenesulfonic acid	Good film	20
Ethanol Tetrabutylammonium tetrafluoroborate	Rough flaky	0.2
Ethanol Toluenesulfonic acid	Good film	3



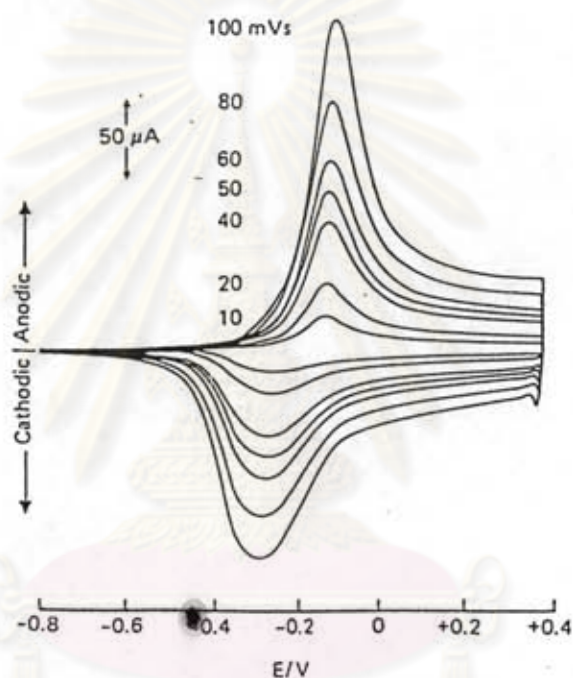
When in the conducting form, the electropolymerized films contain 10-35% anion (by weight) which is affiliated with the cationically charged polymer chains. This polymer-anion compositional balance of the films actually proves to be quite useful, since the properties of the films can be conveniently altered by changing the anion. Since the anion in the film is incorporated from the electrolyte salt in the preparative solution, the modifications can be made by simply changing the electrolyte salt of the solution.

In the case of the polypyrrole films, a wide variety of anions have been used to prepare thick free-standing films, and can be seen in Table 2.2. The anions listed in Table 2.2 are poorly nucleophilic and permit the formation of good-quality films. Tetraalkylammonium salts were used in the preparation of these films. These films are hygroscopic and will lose 5-7% moisture. The level of oxidation of polypyrrole is 0.25-0.32 per pyrrole unit, corresponding to one anion for every 3-4 units. The level of oxidation is an intrinsic characteristic of the polymer and is not sensitive to the nature of the anion. The anion, however does influence both the structural properties and the electroactivities of the films.

**Table 2.2** Polypyrrole films with different anions

Counterion (-)	Conductivity (S $\text{cm}^{-1}$ )
Tetrafluoroborate	30-100
Hexafluoroarsenate	30-100
Hexafluorophosphate	30-100
Perchlorate	60-200
Hydrogen sulfate	0.3
Fluorosulfonate	0.01
Trifluoromethylsulfonate	0.3-1

The electrochemically prepared polypyrrole films are electroactive and can be switched between the neutral and nonconducting state to the oxidized and conducting state. The oxidation reaction is chemically reversible and can be driven repeatedly without loss of electroactivity. This behavior was observed with thin polypyrrole film, 200-400 Å thick, by cyclic voltammetric analysis, Figure 2.14 [13,14].



**Figure 2.14** Cyclic voltammogram for the polypyrrole- $\text{BF}_4$  film, 20 nm thick, prepared and measured in 0.1 M  $\text{Et}_4\text{NBF}_4$  acetonitrile solution [13].

The electrochemical process gives the pure and relatively high molecular weight polymers. They can be prepared from commercially available reagents in a relatively straightforward synthetic procedure. In addition, many of the thick free-standing films are stable in air and show little change in their electrical and mechanical properties when handled in air. But it has the major

drawback of having low yield and limited by the size, shape and the nature of the electrode.

### **Chemical Vapor Deposition**

In 1986, Takeaki Ojio and Seizo Miyata synthesized the conducting composite films of polypyrrole, which can be prepared by exposing polymeric matrix films containing ferric chloride ( $\text{FeCl}_3$ ) to pyrrole vapor. The composite films are, moreover, highly transparent under the appropriate preparation condition. In that communication, the conductivity and the transparency of polypyrrole composite films by the gas state polymerization was discussed.

Poly(vinyl alcohol) (PVA) was used as a polymeric matrix.  $\text{FeCl}_3$  was an oxidizing agent for the polymerization. After dissolving PVA and  $\text{FeCl}_3$  in the water, the solution was casted on a poly(ethylene terephthalate) film substrate. The preparation of polypyrrole-PVA composite films was carried out in a dessicator at  $-15^\circ\text{C}$  by exposing PVA films containing  $\text{FeCl}_3$  on the PET film to the pyrrole and  $\text{H}_2\text{O}$  vapors which had been deoxygenated sufficiently. The polymerization period was from 30 min to 24 hour. The composite films were then dried under vacuum at room temperature. At optimum condition, the composite film shows about  $10 \text{ Scm}^{-1}$  conductivity.

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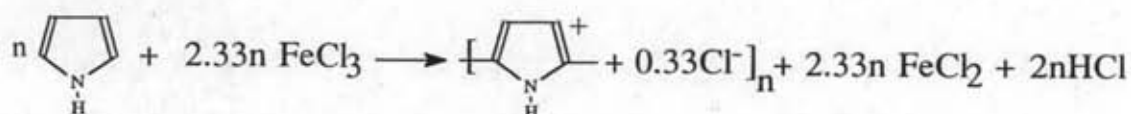


## Chemical Polymerization in Solution

In the past, the synthesis of conducting polymer via chemical method is less popular, even though this method allows a simple preparation of large quantities, more convenient and economical. The majority of the chemical synthesis method involves the polymerization and oxidation with oxidative transition metal ions, for example,  $\text{FeCl}_3$ ,  $\text{AgNO}_3$ ,  $\text{Fe}(\text{NO}_3)_3$  or  $\text{Cu}(\text{NO}_3)_3$  over more, the use of other oxidants such as acid, halogen and organic electron acceptors have also reported [11].

Recently, polypyrrole obtained from chemical polymerization in solution can exhibit very high electrical conductivity when a suitable solvent is selected and the oxidation potential in the solution is controlled.

Polypyrrole has been prepared by chemical polymerization in  $\text{FeCl}_3$  solution. Using methanol as a solvent, along with suitable polymerization conditions, the polypyrrole obtained shows an electrical conductivity as high as  $190 \text{ Scm}^{-1}$ . It is found that the oxidation potential of the solution strongly affects the polymerization process and conductivity. The optimum value of oxidation potential (versus SCE) to produce a highly conductive polypyrrole is approximately 500 mV. When the oxidation potential of  $\text{FeCl}_3$  in methanol solution is controlled by adding  $\text{FeCl}_2$  before the reaction, the conductivity of the polypyrrole can be increased up to  $220 \text{ Scm}^{-1}$ , comparable to values obtained by electrochemical polymerization. From the results of elemental analysis of polypyrrole samples prepared in this method. Reaction stoichiometries have been proposed in Figure 2.14.



**Figure 2.15** Reaction stoichiometries of polypyrrole synthesized from chemical polymerization [4].

From the previous work in this laboratory [17], polypyrrole had been prepared by chemical polymerization using ferric chloride solution. It was found that reaction temperature, concentration of ferric chloride solution, reaction time and solvent affected on the conductivity of the chemically synthesized polypyrrole. However, when 1 ml of pyrrole in 20 ml of methanol was treated with  $\text{FeCl}_3$  2.5 M at  $0^\circ\text{C}$  for 20 mins, the highest electrical conductivity,  $133 \text{ Scm}^{-1}$ , of polypyrrole as recorded. This was thus the best condition of highest electrical conductivity of chemically synthesized polypyrrole.

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## Rechargeable Polymer Battery

A battery is an energy storage device which performs the conversion of chemical energy into electrical energy. Electrical energy is generated as a result of electrochemical reactions operating in a battery. The electrochemical processes involved in primary and secondary batteries are similar, but in a secondary battery a reversible process of chemical-electrochemical reactions occurs; therefore, it has the major advantage of rechargeability over a primary battery. In the charging and discharging processes, a secondary battery acts as an electrolytic and voltage device, respectively [2,12].

A rechargeable or secondary battery is a cell consisting of three main components; positive and negative electrodes, ionically conductive electrolyte, and a separator. In the design and fabrication of a rechargeable battery, a careful consideration of these components is necessary. Some of the practical requirements to be matched are as follows. The electrodes are the backbone of a battery; therefore, the materials for the electrodes should possess high electrical conductivity, good mechanical strength, and inertness to the electrolyte. According to the applicability of the device, the dimensions of the electrodes and their porosity have to be defined. Second, the electrolyte plays an important role, since it governs the process of energy generation. Therefore, the electrolyte that provides the medium for the electrochemical reactions should impart high ionic conductivity and low viscosity. In order to facilitate the electrochemical reactions, an appropriate combination of the electroactive material and electrolyte is the most important requirement in designing a secondary battery. Third, the separator which prevents contact and shorting between electrodes should be made of a nonconducting material. Therefore, taking these factors into account, a rechargeable battery can be designed.

Rechargeable battery makers are always exploring new chemical reactions in hope of finding one that uses cheap, light weight materials and can be



mass produced into a reliable product. The chemical process should run in both directions, so the rechargeable battery can be charged and discharged often without the materials breaking down, and it should run at everyday temperatures. While no one knows which chemical processes will pan out, several companies and industrial research budgets are betting on lithium-polymer batteries.

Lithium polymer battery offers obvious advantages. Lithium is the lightest metal on the atomic chart, in contrast to lead, used in the familiar lead-acid battery, which is one of the heaviest. And the other ingredients, plastics and hydrocarbons, are also light.

Considering the use of electronic devices, potential of an organic conducting polymer as an electroactive material was realized. In 1979 Nigrey et al. first found that the electrochemical doping of polyacetylene is a reversible process. The importance of this reversible electrochemical phenomenon was immediately materialized into designing a rechargeable polymer battery. In polyacetylene, both p- and n- type doping can be accomplished electrochemically; therefore, it can be used as a cathode as well as as anode in a rechargeable battery.

For practical application, polyacetylene has several disadvantages; mainly its poor charge retention capability and thermal stability discouraged its use as an electrode active material. Furthermore, it lacks the processability and environmental stability necessarily required in fabricating an electrochemical device. Some of these problems to some extent have been overcome by other conducting polymers. Considering the suitability of the electroactive material in battery applications, polyaniline, polypyrrole, and poly(p-phenylene) were found to be more promising. These polymers are also interesting due to their ease of synthesis and fabrication, environmental stability, and, at least to some extent, cost.

Theoretically, these polymer electrode batteries have greater advantage over the conventional inorganic rechargeable batteries as summarized in Table 2.3 .

In development of lithium-polymer batteries, a polypyrrole-lithium battery was developed and tested by BASF and VARTA Batterie A.G. of Germany.

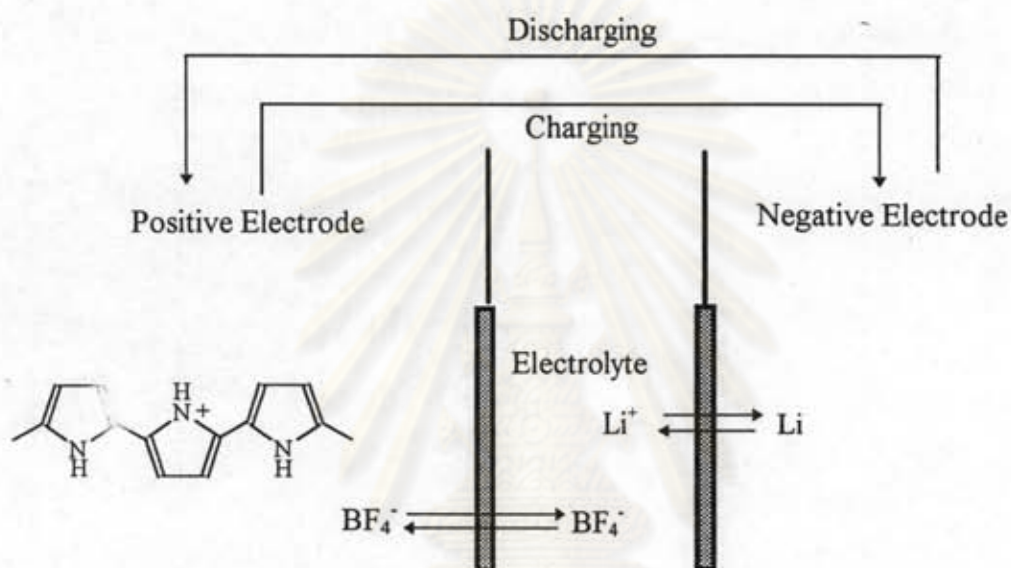
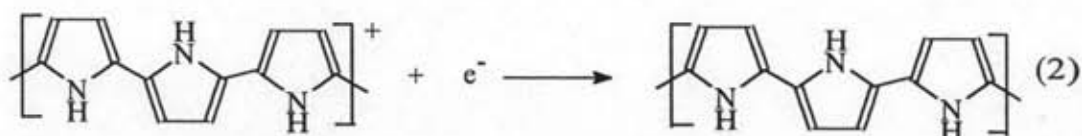
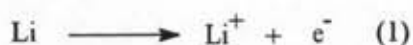
Electrochemically synthesized polypyrrole doped with tetrafluoroborate ( $\text{BF}_4^-$ ) was used as a positive electrode. Elemental analysis showed that three pyrrole monomer units carry one unit of charge. This concludes that the maximum doping level of polypyrrole is 1/12 per carbon atom. When polypyrrole is used with a lithium counter electrode a cell volatage is about 3.5 V.

**Table 2.3** Potential Advantages of Polymer Rechargeable Battery

Conventional rechargeable battery (lead-acid, nickel-cadmium)	Polymer rechargeable battery
Low cell voltage ( about 1 V) material for electrodes are limited due to the electrochemical decomposition in aqueous electrolyte.	Higher cell voltage (about 2-4 V) are possible.
Low energy-to-weight ratio leads to relatively heavy batteries.	Higher energy-to-weight ratio means lighter batteries can be expected.
Shorter lifetime due to the dissolution and redeposition of electrode material that occurs during the charge-discharge cycles (chemical-electrochemical reactions).	Longer lifetime since the ions involved in the delivery and storage of charge come from the solution rather than from the electrodes themselves.
Contains toxic material.	Potentially contains no toxic material.
Can not be easily shaped to fit the device.	Can be easily shaped to fit the device.

In the electrochemical cell, the starting electrolyte is a 0.5 molar solution of lithium perchlorate ( $\text{LiClO}_4$ ) in propylene carbonate. The polypyrrole electrode is used with lithium as a counter electrode. During the discharging process (Figure 2.16), the electrochemical reactions proceed as follows:



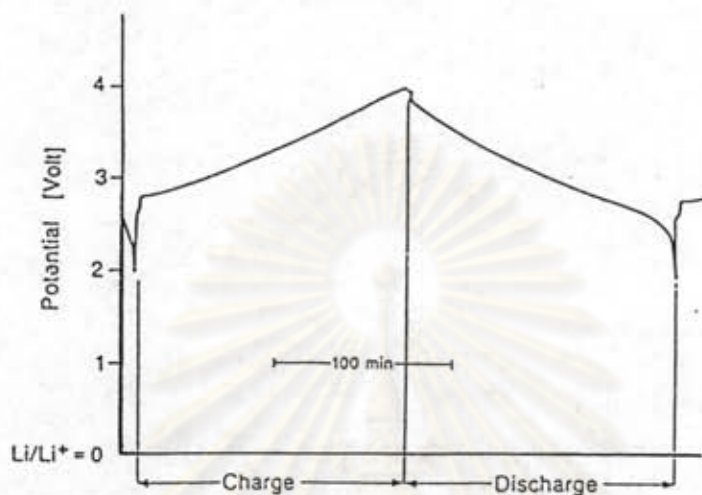


**Figure 2.16** Electrode reactions of a polypyrrole-lithium battery

The electron from the negative lithium electrode moves along a circuit to replace  $\text{BF}_4^-$  in the polypyrrole positive electrode, and the counterion  $\text{BF}_4^-$  is released from polypyrrole to the electrolyte. During the charging process, a reversible electrochemical reaction operates.

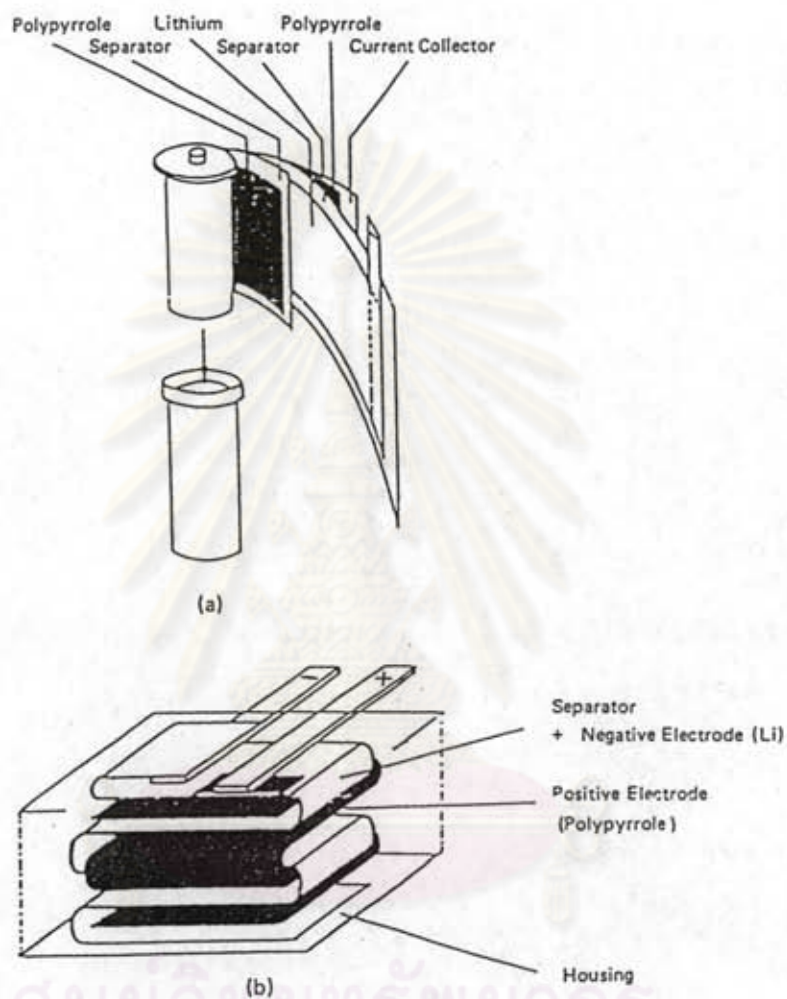
The half-cell charge and discharge curves of polypyrrole electrodes are shown in Figure 2.17. The upper and lower voltage limits of the cell were 2 and 4 V versus  $\text{Li}/\text{Li}^+$ , respectively.





**Figure 2.17** Charge/discharge curves of a polypyrrole electrode. Electrolyte solution was 0.5 M  $\text{LiClO}_4$  in propylene carbonate.

The polypyrrole-lithium rechargeable batteries produced by BASF/VARTA are shown in Figure 2.18a (mignon-size) and Figure 2.18b (sandwich type). The energy densities of the cells at 20 h discharge time are 15 W-h/kg and 30 W-h/kg, respectively. In the latter case, the energy density is equal to that of the Ni-Cd cell. These polypyrrole-lithium batteries can be used in dictaphones, pocket radios, etc.



**Figure 2.18** BASF's polypyrrole-lithium battery  
 (a) mignon-size (b) sandwich type