

Chapter 6

Redox Transformations and Transport Processes

The elucidation of the nature of charge transfer and charge transport processes in electrochemically active polymer films may be the most interesting theoretical problem of this field. It is also a question of great practical importance, because in most of their applications fast charge propagation through the film is needed. It has become clear that the elucidation of their electrochemical behavior is a very difficult task, due to the complex nature of these systems [1–8].

In the case of traditional electrodes, the electrode reaction involves mass transport of the electroactive species from the bulk solution to the electrode surface and an electron transfer step at the electrode surface. A polymer film electrode can be defined as an electrochemical system in which at least three phases are contacted successively in such a way that between a first-order conductor (usually a metal) and a second-order conductor (usually an electrolyte solution) is an electrochemically active polymer layer. The polymer layer is more or less stably attached to the metal, mainly by adsorption (adhesion).

The fundamental observation that should be explained is that even rather thick polymer films, in which most of the redox sites are as far from the metal surface as 100–10,000 nm (this corresponds to surface concentrations of the redox sites $\Gamma = 10^{-8} - 10^{-6} \text{ mol cm}^{-2}$), may be electrochemically oxidized or reduced.

According to the classical theory of simple electron-transfer reactions, the reactants get very close to the electrode surface, and then electrons can tunnel over the short distance (tenths of a nanometer) between the metal and the activated species in the solution phase.

In the case of polymer-modified electrodes, the active parts of the polymer cannot approach the metal surface because polymer chains are trapped in a tangled network, and chain diffusion is usually much slower than the time-scale of the transient electrochemical experiment (e.g., cyclic voltammetry). Although we should not exclude the possibility that polymer diffusion may play a role in carrying charges, even the redox sites may get close enough to the metal surface when the film is held together by physical forces. It may also be assumed that in ion-exchange polymeric systems, where the redox-active ions are held by electrostatic binding [e.g.,

$\text{Ru}(\text{bpy})_3^{3+/2+}$ in Nafion], some of these ions can reach the metal surface. However, when the redox sites are covalently bound to the polymer chain (i.e., no free diffusion of the sites occurs), and especially when the polymer chains are connected by chemical cross-linkages (i.e., only segmental motions are possible), an explanation of how the electrons traverse the film should be provided.

Therefore, the transport of electrons can be assumed to occur either via an electron exchange reaction (electron hopping) between neighboring redox sites, if the segmental motions make it possible, or via the movement of delocalized electrons through the conjugated systems (electronic conduction). The former mechanism is characteristic of redox polymers that contain covalently attached redox sites, either built into the chain or included as pendant groups, or redox-active ions held by electrostatic binding.

Polymers that possess electronic conduction are called conducting polymers, electronically conducting polymers, or intrinsically conducting polymers—ICPs (see Chap. 2). Electrochemical transformation—usually oxidation—of the nonconducting forms of these polymers usually leads to a reorganization of the bonds of the macromolecule and the development of an extensively conjugated system. An electron-hopping mechanism is likely to be operative between the chains (interchain conduction) and defects, even in the case of conducting polymers.

However, it is important to pay attention to more than just the “electronic charging” of the polymer film (i.e., to electron exchange at the metal|polymer interface and electron transport through the surface layer), since ions will cross the film|solution interface in order to preserve electroneutrality within the film. The movement of counterions (or less frequently that of co-ions) may also be the rate-determining step.

At this point, it is worth noting that “electronic charging (or simply charging) the polymer” is a frequently used expression in the literature of conducting polymers. It means that either the polymer backbone and/or the localized redox sites attached to the polymeric chains will have positive or negative charges as a consequence of a redox reaction (electrochemical or chemical oxidation or reduction) or less often protonation (e.g., “proton doping” in the case of polyaniline). This excess charge is compensated for by the counterions; i.e., the polymer phase is always electrically neutral. A small imbalance of the charge related to the electrochemical double layers may exist only at the interfacial regions. “Discharging the polymer” refers to the opposite process where the electrochemical or chemical reduction or oxidation (or deprotonation) results in an uncharged (neutral) polymer, and, because the counterions leave the polymer film, in a neutral polymer phase.

The thermodynamic equilibrium between the polymer phase and the contacting solutions requires $\tilde{\mu}_i(\text{film}) = \tilde{\mu}_i(\text{solution})$ for all mobile species, as discussed in Chap. 5. In fact, we may regard the film as a membrane or a swollen polyelectrolyte gel (i.e., the charged film contains solvent molecules and, depending on the conditions, co-ions in addition to the counterions).

A simple model of the charge transfer and transport processes in a polymer film electrode is shown in Fig. 6.1.

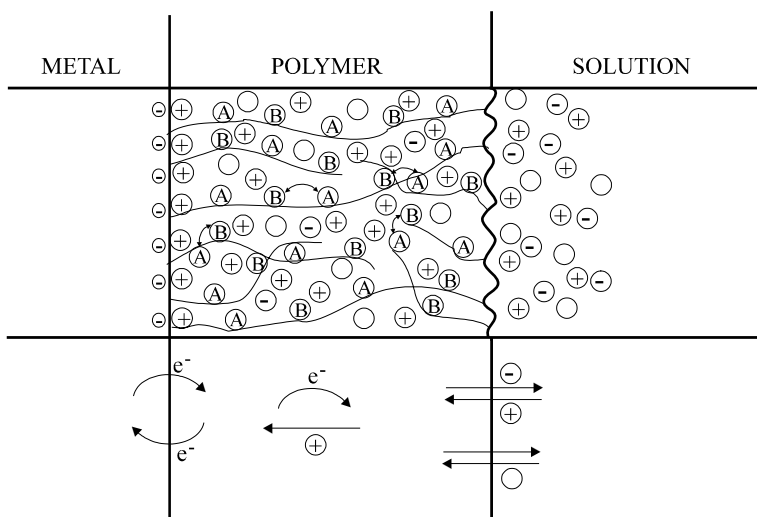


Fig. 6.1 A schematic picture of a polymer film electrode. In an electrochemical experiment the electron transfer occurs at the metal|polymer interface that initiates the electron propagation through the film via an electron exchange reaction between redox couples A and B or electronic conduction through the polymer backbone. (When the polymer reacts with an oxidant or reductant added to the solution, the electron transfer starts at the polymer|solution interface.) Ion-exchange processes take place at the polymer|solution interface; in the simplest case counterions enter the film and compensate for the excess charge of the polymer. Neutral (solvent) molecules (O) may also be incorporated into the film (resulting in swelling) or may leave the polymer layer

As a consequence of the incorporation of ions and solvent molecules into the film, swelling or shrinkage of the polymer matrix takes place. Depending on the nature and the number of crosslinks, reversible elastic deformation or irreversible changes (e.g., dissolution) may occur. Other effects, such as dimerization, ion-pair formation, crosslinking, and so forth, should also be considered.

We have already mentioned several effects that are connected with the polymeric nature of the layer. It is evident that all the charge transport processes listed are affected by the physicochemical properties of the polymer. Therefore, we also must deal with the properties of the polymer layer if we wish to understand the electrochemical behavior of these systems. The elucidation of the structure and properties of polymer (polyelectrolyte) layers as well as the changes in their morphology caused by the potential and potential-induced processes and by other parameters (e.g., temperature, electrolyte composition) set an entirely new task for electrochemists. Owing to the long relaxation times that are characteristic of polymeric systems, the equilibrium or steady-state situation is often not reached within the time allowed for the experiment.

However, the application of combined electrochemical and nonelectrochemical techniques has allowed very detailed insights into the nature of ionic and electronic charge transfer and charge transport processes.

In this chapter we intend to outline some relevant experiences, to discuss existing models and theories, as well as to summarize and systematize the knowledge accumulated on charge transport processes occurring in redox and conducting polymer films.

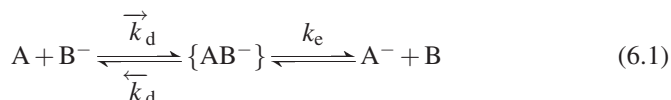
6.1 Electron Transport

As has already been mentioned, electron transport occurs in redox polymers—which are localized state conductors—via a process of sequential electron self-exchange between neighboring redox groups. In the case of electronically conducting polymers—where the polymer backbone is extensively conjugated, making considerable charge delocalization possible—the transport of the charge carriers along a conjugated strand can be described by the band model characteristic of metals and semiconductors. Besides this intrachain conduction, which provides very high intrinsic conductivity, various hopping and tunneling processes are considered for nonintrinsic (interstrand and interfiber) conduction processes.

6.1.1 Electron Exchange Reaction

The elementary process is the transfer of an electron from an electron donor orbital on the reductant (e.g., Fe^{2+}) to the acceptor orbital of the oxidant (e.g., Fe^{3+}). The rate of electron transfer is very high, taking place within 10^{-16} s; however, bond reorganization may require from 10^{-13} to 10^{-14} s, reorientation of the solvent dipoles (e.g., water molecules in the hydration sphere) needs 10^{-11} to 10^{-12} s, and the duration of the rearrangement of the ionic atmosphere is ca. 10^{-8} s. The rate coefficients are much higher for electron exchange reactions occurring practically without structural changes (outer sphere reactions) than for reactions that require high energies of activation due to bond reorganization (inner sphere mechanism).

However, the probability of electron transfer (tunneling) depends critically on the distance between the species participating in the electron exchange reaction. A reaction can take place between two molecules when they meet each other. It follows that the rate-determining step can be either the mass transport (mostly diffusion is considered, but effect of migration cannot be excluded) or the reaction (the actual rate of electron transfer in our case). For an electron exchange process coupled to isothermal diffusion, the following kinetic scheme may be considered:



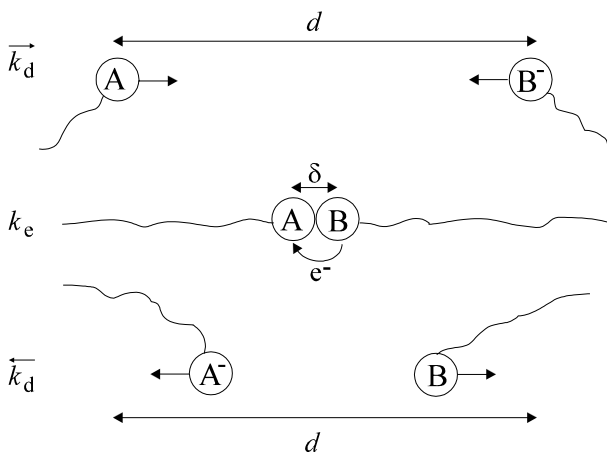


Fig. 6.2 A microscopic-level schematic of the electron exchange process coupled to isothermal diffusion. The *upper part* shows that species A and B[−] start to diffuse towards each other from their average equilibrium distance (d) with diffusion rate coefficient, k_d . The next stage is the “forward” electron transfer step after the formation of a precursor complex, characterized by rate coefficient k_e , and the mean distance of the redox centers $\delta = r_A + r_B$ or for similar radii $\delta \cong 2r_A$. The *lower part* depicts the separation of the products, A[−] and B

where $\overrightarrow{k_d}$, $\overleftarrow{k_d}$ and k_e are the rate coefficients for diffusive approach, for separation, and for the forward reaction, respectively. Note that $\overrightarrow{k_d}$ is a second-order rate coefficient, while $\overleftarrow{k_d}$ and k_e are first-order. The overall second-order rate coefficient can be given by

$$k = \overrightarrow{k_d} k_e / \overleftarrow{k_d} + k_e. \quad (6.2)$$

Figure 6.2 schematically illustrates the microscopic events that occur during an electron exchange reaction.

If the reaction has a small energy of activation, so k_e is high ($k_e \gg \overleftarrow{k_d}$), the rate-determining step is the approach of the reactants. Under these conditions it holds that $k = \overrightarrow{k_d}$. The kinetics are activation-controlled for reactions with large activation energies ($\Delta G^\ddagger > 20 \text{ kJ mol}^{-1}$ for reactions in aqueous solutions), and then

$$k = k_e \overrightarrow{k_d} / \overleftarrow{k_d}. \quad (6.3)$$

Since $\overrightarrow{k_d} / \overleftarrow{k_d}$ is the equilibrium constant, K for the formation of the precursor complex k can be expressed as

$$k = k_e K. \quad (6.4)$$

The rate of the collision, k_d , can be estimated using Smoluchowski's equation:

$$k_d = 1000 \times 4\pi N_A \delta D_{AB} \quad (6.5)$$

where N_A is the Avogadro constant, δ is the mean distance between the centers of the species involved in the electron exchange ($\delta \approx 2r_A$ for identical species where r_A is the radius of the reactant molecule) and D_{AB} is the relative diffusion coefficient of the reacting molecules. The diffusion coefficients of ions in aqueous solutions at 298 K are typically $1\text{--}2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, except $D_{\text{H}^+} = 9.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{OH}^-} = 5.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. For a small ion $\delta = 0.5 \text{ nm}$. By inserting these values into (6.5), we obtain $k_d = 8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Consequently, if $k_e > 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ the reaction is diffusion-controlled. In aqueous solutions fast electron transfer and acid–base reactions fall within this category. On the other hand, if the viscosity (η) of the solvent is high, due to the inverse relationship between D and η , k_d may be smaller by orders of magnitude. Similarly, the diffusion of macromolecules is also slow, $D = 10^{-10} \text{--} 10^{-16} \text{ m}^2 \text{ s}^{-1}$. In the case of polymer film electrodes where the polymer chains are trapped in a tangled network, rather small values for the diffusion coefficient of the chain and segmental motions can be expected. If the latter motions are frozen-in (e.g., at low temperatures or without the solvent-swelling, which has a plasticizing effect on the polymer film), the electron transport may be entirely restricted.

It follows that diffusion control is more frequently operative in polymeric systems than that in ordinary solution reactions, because k_d and k_e are more likely to be comparable due to the low D values [9–16]. If the electron exchange reaction occurs between ionic species (charged polymer sites), the coulombic forces may reduce or enhance both the probability of the ions encountering each other and the rate of electron transfer. For the activation-controlled case, k_e can be obtained as follows [17]:

$$\ln k_e = \ln k_e^0 - \frac{z_A z_B e^2}{2r_A \epsilon k_B T} \quad (6.6)$$

where z_A and z_B are the charges of the ions and ϵ is the dielectric permittivity of the medium. If z_A and z_B have the same sign k_e decreases; in the opposite case k_e increases. The effect can be modified by using a solvent with high or low ϵ values or by adding a large amount of inert electrolyte to the solution. In the latter case the effect of ionic strength (I) is approximately given by

$$\ln k = \ln k^0 + z_A z_B A \sqrt{I} \quad (6.7)$$

where A is the constant of the Debye–Hückel equation, and k^0 is the rate coefficient in the absence of electrostatic interactions.

The electron exchange reaction (electron hopping) continuously occurs between the molecules of a redox couple in a random way. Macroscopic charge transport takes place, however, only when a concentration or potential gradient exists in the phase for at least one of the components of the redox couple. In this case the hydrodynamic displacement is shortened for the diffusive species by $\delta \sim 2r_A$, because the electron exchange (electron diffusion) contributes to the flux. The contribution of the electron diffusion to the overall diffusion flux depends on the relative magnitude of k_e and k_d or D_e and D_{AB} (i.e., the diffusion coefficients of the electron and ions, respectively).

According to the Dahms–Ruff theory of electron diffusion [9–12]

$$D = D_{AB} + D_e = D_{AB} + k_e \delta^2 c / 6 \quad (6.8)$$

for three-dimensional diffusion where D is the measured diffusion coefficient, c is the concentration of redox centers, and k_e is the bimolecular electron-transfer rate coefficient. The factors $1/4$ and $1/2$ can be used instead of $1/6$ for two- and one-dimensional diffusion, respectively.

This approach has been used in order to describe the electron propagation through surface polymer films [2, 6, 18–26]. In these models it was assumed that transport occurs as a sequence of successive steps between adjacent redox centers of different oxidation states. The electron hopping has been described as a bimolecular process in the direction of the concentration gradient. The kinetics of the electron transfer at the electrode-polymer film interface, which initiates electron transport in the surface layer, is generally considered to be a fast process which is not rate-limiting. It was also presumed that the direct electron transfer between the metal substrate and the polymer involves only those redox sites situated in the layer immediately adjacent to the metal surface. As follows from the theory (6.8), the measured charge transport diffusion coefficient should increase linearly with c whenever the contribution from the electron exchange reaction is important, and so the concentration dependence of D may be used to test theories based on the electron exchange reaction mechanism. Despite the fact that considerable efforts have been made to find the predicted linear concentration dependence of D , it has been observed in only a few cases and for a limited concentration range.

There may be several reasons why this model has not fulfilled expectations although the mechanism of electron transport as described might be correct.

6.1.1.1 Problems with the Verification of the Model

The uncertainty in the determination of D by potential-step, impedance, or other techniques is substantial due to problems such as the extraction of D from the product $D^{1/2}c$ (this combination appears in all of the methods), the difficulty arising from the in situ thickness estimation, nonuniform thickness [27–29], film inhomogeneity [30–32], incomplete electroactivity [19, 23, 33], and the ohmic drop effect [34]. It may be forecast, for example, that the film thickness increases, and thus c decreases, due to the solvent swelling the film; however, D_{AB} simultaneously increases, making the physical diffusion of ions and segmental motions less hindered. In addition, the solvent swelling changes with the potential, and it is sensitive to the composition of the supporting electrolyte. Because of the interactions between the redox centers or between the redox species and the film functional groups, the morphology of the film will also change with the concentration of the redox groups. We will deal with these problems in Sects. 6.4–6.7. It is reasonable to assume that in many cases $D_{AB} \gg D_e$ (i.e., the electron hopping makes no contribution to the diffusion), or the most hindered process is the counterion diffusion, coupled to electron transport.

6.1.1.2 Advanced Theories Predicting a Nonlinear $D(c)$ Function

According to the theory of *extended electron transfer* elaborated by Feldberg, δ may be larger than $2r_A$, and this theory predicts an exponential dependence on the average site–site distance (d) (i.e., on the site concentration) [26]:

$$k_e = k_0 \exp \frac{-(d - \delta)}{s} \quad (6.9)$$

where s is a characteristic distance (ca. 10^{-10} m).

An alternative approach proposed by He and Chen to describe the relationship between the diffusion coefficient and redox site concentration is based on the assumption that at a sufficiently high concentration of redox centers several electron hops may become possible because more than two sites are immediately adjacent. This means that the charge donated to a given redox ion via a diffusional encounter may propagate over more than one site in the direction of the concentration gradient. This is the case in systems where the electron exchange rate is high, and therefore the rate of the electron transport is determined by the physical diffusion of redox species incorporated into the ion-exchange membrane or those of the chain and segmental motions. This enhances the total electron flux. Formally, this is equivalent to an increase in the electron hopping distance by a certain factor, f , so D can be expressed as follows [35]:

$$D = D_0 + \frac{k_e c (\delta f)^2}{6} . \quad (6.10)$$

Assuming a Poisson distribution of the electroactive species, the enhancement factor can be expressed as a power series of a probability function which is related to the concentration. At low concentrations the probability of finding more than one molecule in a hemisphere with a radius of the molecular collision distance is nearly zero and $f = 1$. The factor f , and therefore D_e , increases noticeably at higher concentrations.

Another model introduced by Fritsch-Faules and Faulkner suggests that k_e or D_e should first have an exponential rise with increasing c and then flatten at high concentrations. The exponential rise occurs because d becomes smaller as the concentration increases, which promotes intersite electron transfer. As the minimum center-to-center separation is approached, when each redox center has a nearest neighbor that is practically in contact, k_e or D_e asymptotically approaches its theoretical maximum value. A similar result has been obtained by a microscopic model which describes electron (or hole) diffusion in a rigid three-dimensional network. This concept is based on simple probability distribution arguments and on a random walk [36].

6.1.1.3 Transition Between Percolation and Diffusion Behaviors

Blauch and Savéant systematically investigated the interdependence between physical displacement and electron hopping in propagating charge through supramolecular redox systems [37]. It was concluded that when physical motion is either non-existent or much slower than electron hopping, charge propagation is fundamentally a percolation process, because the microscopic distribution of redox centers plays a critical role in determining the rate of charge transport [37,38]. Any self-similarity of the molecular clusters between successive electron hops imparts a memory effect, making the exact adjacent-site connectivity between the molecules important. The redox species can move about their equilibrium positions at which they are irreversibly attached to the polymer (in the three-dimensional network the redox species are either covalently or electrostatically bound); this is referred to as “bounded diffusion.” In the opposite extreme (free diffusion), rapid molecular motion thoroughly rearranges the molecular distribution between successive electron hops, thus leading a mean-field behavior. The mean-field approximation presupposes that $k_d > k_e$, and leads to Dahms–Ruff-type behavior for freely diffusing redox centers, but the following corrected equation should be applied [37]:

$$D = D_{AB} (1 - x) f_c + D_e x \quad (6.11)$$

where x is the fractional loading, which is the ratio of the total number of molecules to the total number of lattice sites. The factor $(1 - x)$ in the first term accounts for the blocking of physical diffusion and f_c is a correlation factor which depends on x . When D_{AB} becomes less than D_e , percolation effects appear. If $D_e \gg D_{AB}$ a characteristic static percolation behavior ($D = 0$ below the percolation threshold and an abrupt onset of conduction at the critical fractional loading) should be observed. The mechanistic aspects of the charge transport can be understood from D versus x plots. When D_{AB} is low, that is in the case of bounded diffusion [26, 38],

$$D = D_e x = k_e \delta^2 x^2 c / 6 . \quad (6.12)$$

Thus D varies with x^2 when the rate of physical diffusion is slow.

In the case of free diffusion, the apparent diffusion coefficient becomes

$$D = D_{AB} f (1 - x) . \quad (6.13)$$

Accordingly D will decrease with x . This situation originates in the decreased availability of vacant sites (free volume) within the polymer film. When both electron hopping and physical diffusion processes occur at the same rate ($D_{AB} = D_e$), D becomes invariant with x .

6.1.1.4 Potential Dependence of the Diffusion Coefficient

In the simple models, D_e is independent of the potential because the effects of both the counterion activity and interactions of charged sites (electron–electron interactions) are neglected. However, in real systems the electrochemical potential of counterions is changed as the redox state of the film is varied, the counterion population is limited, and interactions between electrons arise. According to Chidsey and Murray, the potential dependence of the electron diffusion coefficient can be expressed as follows [39]:

$$D_e = k_e \delta^2 \left\{ 1 + \left[z_i^{-1} (x_e - z_s)^{-1} + g/k_B T \right] x_e (1 - x_e) \right\} \quad (6.14)$$

where x_e is the fraction of sites occupied by electrons, z_s and z_i are the charges of the sites and the counterions, respectively, and g is the occupied site interaction energy. (The g parameter is similar to that of the Frumkin isotherm.) In the case of noninteracting sites ($g = 0$), and in the presence of a large excess of supporting electrolyte ($z_s = \infty$), $D_e = k_e \delta^2$ and this is a diffusion coefficient. In general, D_e does not remain constant as the potential (that is, the film redox composition) is changed. D_e does not vary substantially with potential within the reasonable ranges of g and z_s (e.g., if $g = 4$, D_e will only be double that of its value at $g = 0$), and a maximum (if $g > 0$) or a minimum (if $g < 0$) will appear at the standard redox potential of the system.

The details of other theoretical models, including electric field effects [13, 14, 40–46], can be found in [3, 7, 18].

6.1.2 Electronic Conductivity

Electronically conducting polymers consist of polyconjugated, polyaromatic, or polyheterocyclic macromolecules, and these differ from redox polymers in that the polymer backbone is itself electronically conducting in its “doped” state. The term “doping,” as it is often applied to the charging process of the polymer, is somewhat misleading. In semiconductor physics, doping describes a process where dopant species present in small quantities occupy positions within the lattice of the host material, resulting in a large-scale change in the conductivity of the doped material compared to the undoped one. The “doping” process in conjugated polymers is, however, essentially a charge transfer reaction, resulting in the partial oxidation (or less frequently reduction) of the polymer. Although conjugated polymers may be charged positively or negatively, studies of the charging mechanism have mostly been devoted to the case of p-doping. The electronic conductivity shows a drastic change (up to 10–12 orders of magnitude) from its low value for the initial (uncharged) state of the polymer, corresponding to a semiconductor or even an insulator, to values of 1–1000 S cm^{−1} (even up to 10⁵ S cm^{−1} comparable to metals) [47–66]. The range of conductivities of conducting polymers in charged and

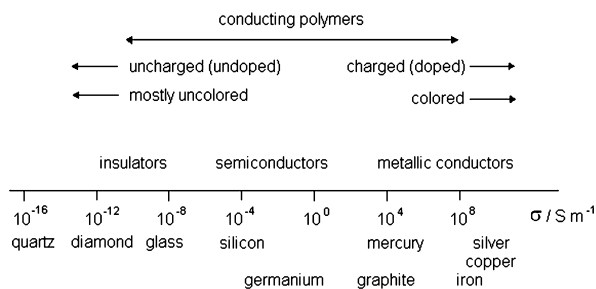


Fig. 6.3 Illustration of the range of electronic conductivities of conducting polymers in comparison with those of other materials

uncharged states in comparison with different materials (insulators, semiconductors, and metallic conductors) is displayed in Fig. 6.3.

In general, the mobility of initial portions of the incorporated electronic charge is rather low. At higher charging levels the conductivity increases much more rapidly than the charge and then levels out, or even decreases. This onset of conductivity has been interpreted as an insulator–metal transition due to various electron–electron interactions [67]. The temperature dependence of the conductivity in the highly charged state does not correspond in most cases to the metallic type [68]. In agreement with quantum-chemical expectations, electron spin resonance (ESR) measurements have demonstrated the presence of unpaired spins inside the polymer film. However, the spin concentration passes through a maximum at a relatively low charging level, usually before the high conductivity increase, and then vanishes [52, 69–77]. The variation of the ESR signal intensity (in arbitrary units) during a potential cycle and the corresponding cyclic voltammogram are shown in Fig. 6.4.

As observed in ESR measurements, the generation of polarons (see below) at an early stage of oxidation is widely accepted. However, at higher oxidation levels, the decrease in spin density with increasing conductivity is found to be a challenging feature. The following conclusions were drawn based on the correlation between the mobilities and the ESR signal. The variation in mobility as a function of oxidation level (Figs. 6.5 and 6.6) can be explained by the polaron lattice model [78].

The mobilities were calculated from the relation $\mu = \sigma / \rho_{cc} F$, where σ is the conductivity and ρ_{cc} is the density of charge carriers. The charge-carrier density was estimated from the charge measured by coulometry (Q), the density of the polymer (ρ , which was assumed to be 1 g cm^{-3}), the molar mass of the aniline monomer unit (M), and the weight of the polymer film (W): $\rho_{cc} = \rho Q / FW$.

The sharp rise in the mobility suggests the evolution of metallic conduction, and this is attributed to the formation of Pauli spins. The decrease in ESR intensity at higher charging levels is due to the transformation between Curie spins (unpaired electrons are localized or poorly delocalized) and Pauli spins (unpaired electrons are delocalized in a conduction band). (As well as the number of spins, the linewidth

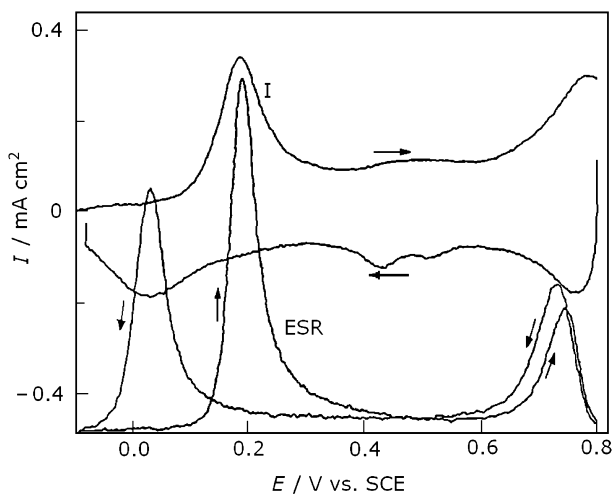


Fig. 6.4 Simultaneous measurements of ESR absorption and current (I) for a 100-nm PANI film on Pt in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The potential was scanned from -0.1 V to $+0.8 \text{ V}$ and back. Scan rate: 10 mV s^{-1} [69]. (Reproduced with the permission of The Electrochemical Society)

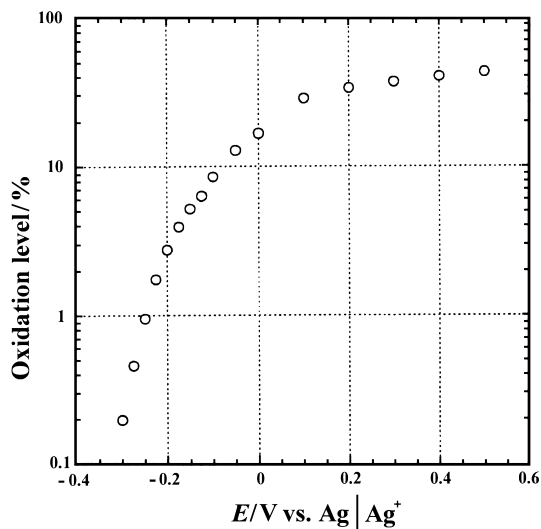


Fig. 6.5 Oxidation levels of the PANI film on Pt as a function of electrode potential. Electrolyte: 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile. (Reproduced from [78] with the permission of Elsevier Ltd.)

and the g -factor as a function of the oxidation level have also been analyzed.) The optical spectra indicate that the small mobility decrease during the early phase of oxidation can be ascribed to a change in the polymer conformation from a simple coil to an expanded coil [78].

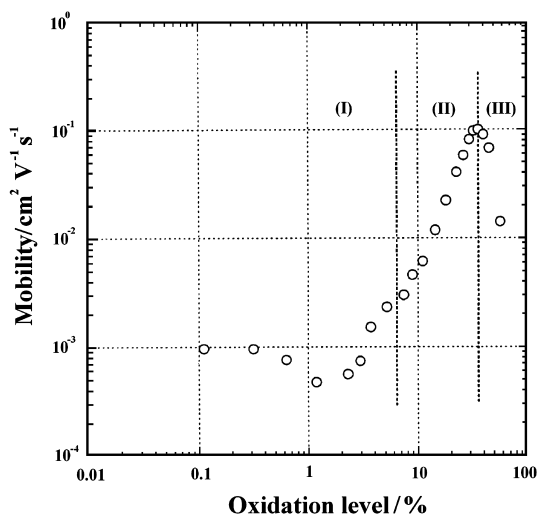


Fig. 6.6 Mobilities of positive charge carriers in the PANI film at different oxidation levels. Electrolyte: 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile. (Reproduced from [78] with the permission of Elsevier Ltd.)

Various models have been developed to explain the mechanism of charge transport in conducting polymer film electrodes. Two extreme approaches exist. According to the delocalized band model, the charges and unpaired electrons are delocalized over a large number of monomer units [57, 69, 79, 80], while in the chemical model the charge is localized in the polymer chain [75], or at most only some monomer units are involved. Because the approach assuming localized charges does not differ essentially from that applied for redox polymers, and the semiconductor or one-dimensional metal models [48, 51, 81] have generally been accepted, we will deal with the latter theories. Although the precise nature of charge carriers in conjugated systems varies from material to material, in general the following delocalized defects are considered: solitons (neutral defect state), polarons (a neutral and a charged soliton in the same chain, which are essentially singly charged cation radicals at the polymer chain coupled with local deformations), and bipolarons (two charged defects form a pair; these doubly oxidized, spinless dications usually exist at higher charging levels) [48, 68, 82–88].

The macroscopic charge transport in a conducting polymer matrix represents a superposition of the local transport mechanism. The intrinsic conductivity, which refers to the conduction process along a conjugated chain, can be described in terms of band theory, which is well-established for solid materials. Metallic conductors are characterized by either a partially filled valence band or an overlap between the valence and conduction bands. Semiconductors and insulators possess a band gap between the top of the valence band and the bottom of the conduction band. The band gap energy is relatively small for a semiconductor but rather large for

an insulator. The neutral (reduced, undoped) polymer has a full valence and empty conduction band separated by a band gap (insulator).

Chemical or electrochemical doping (oxidation and incorporation of counterions) results in the generation of a polaron level at midgap. Further oxidation leads to the formation of bipolaron energy bands in the band gap. Electronic conductivity is rationalized in terms of bipolaron hopping. Because the overall size of the polymer is limited, interchain electron transfer must also be considered. The intrachain conductivity of the polymer is usually very high if the polymer chain is long, and contains no defects; therefore, the interchain conductivity is rate-determining in a good-quality polymer [83]. (If the polymer morphology is fibrillar, the fiber-to-fiber electron transport may also be the most hindered process.) The essential aim is to synthesize conducting polymers where the mean free path is limited by intrinsic scattering events from the thermal vibrations of the lattice (phonons). One of the problems is that quasi-one-dimensional electronic systems are prone to localization of electronic states due to disorder. In the case of electronic localization, the carrier transport is limited by phonon-assisted hopping, according to the Mott model [89]. The Mott model of variable range hopping gives the following equation for the conductivity (σ):

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^\gamma \right] \quad (6.15)$$

where σ_0 and T_0 are constants and γ is a number related to the dimensionality (d) of the hopping process ($\gamma = (d + 1)^{-1}$).

The σ_0 value depends on the electron–phonon coupling constant, while T_0 is connected to the localized density of states near the Fermi level and the decay length of the wavefunction, respectively. It can be seen that conductivity increases with temperature, in contrast to the situation for metals. This type of conductive behavior has been verified for many conjugated polymer systems. The problem of localization is less important if the molar mass of the polymer is high and only a few defects are present, and a relatively intense interchain coupling prevails. In this case, the mean free path becomes quite large and is determined by phonon-scattering, as in true metals. Under such conditions the conductivity is high, and its value increases with the molar mass of the polymer and decreases with the temperature.

The mechanism of fluctuation-induced tunneling is expected for the electrical conductivity if large regions of a highly conductive (“metallic”) phase in an inhomogeneous material are separated from each other by an insulating phase. The latter acts as a potential barrier. Due to the exponential dependence of the tunneling probability, tunneling will effectively occur only in the regions of closest approach of the metallic segments.

The parabolic barrier approximation for the fluctuation-induced tunneling gives the following relationship in terms of the temperature dependence of conductivity [85, 90]:

$$\sigma = \sigma_0 \left[- \frac{T_1}{T - T_0} \right] \quad (6.16)$$

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