

# Charge Transport in Conducting Polymer Film Electrodes

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Review

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The essential features of charge transport in conducting polymer film electrodes are discussed. Selected experimental results are presented, which shed light on the complex nature of the processes occurring in these systems. The problems of the theoretical elucidation and practical consequences are also emphasized.

*Key words:*

Conducting polymers, charge transport, film morphology, relaxation

## Introduction

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 the field. It is also a question of great practical importance, because in the majority of their applications fast charge propagation through the film is needed.<sup>1–14</sup>

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 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 (some nanometers) 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. 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 delocalized electrons

can move through the conjugated systems (electronic conduction). The former mechanism is characteristic of redox polymers that contain covalently attached redox sites, either built in the chain or as pendant groups, or redox-active ions held by electrostatic binding.

Polymers that possess electronic conduction are called conducting polymers. Electrochemical transformation – usually oxidation – of the non-conducting form of these polymers usually leads to a reorganization of the bonds of the macromolecule and the development of an extensively conjugated system. The electron hopping mechanism is likely to be operative between the chains (interchain conduction) and defects even in the case of conducting polymers.

However, attention has to be paid not only to the electronic charging of the polymer film (i.e. to the electron exchange at the metal/polymer interface and the electron transport through the surface layer) since in order to preserve electroneutrality within the film ions will cross the film / solution interface. The motion of counterions (or less frequently that of the co-ions) may also be the rate-determining step. We may regard our 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).

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 extent of the cross-links, reversible elastic deformation or irreversible changes (e.g. dissolution) may occur. Dimerization, ion-pair formation, cross-linking and so forth, should also be considered.

It is evident that all the charge transport processes listed are affected by the physicochemical

properties of the polymer. 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 time characteristic of polymeric systems the equilibrium or steady-state situation often has not been reached within the scale of the experiment.

However, the application of combined electrochemical and non-electrochemical techniques has allowed a very detailed insight into the nature of ionic and electronic charge transfer and charge transport processes.

It is intended here to outline some relevant experiences, to discuss the existing models and theories, as well as to summarize and systematize the knowledge accumulated with respect to the charge transport processes occurring in redox and conducting polymer films.

## Survey of theories and experimental observations

### Electron transport

#### *Electron exchange reaction*

The elementary process is the transfer of an electron from an electron donor orbital on the reductant to the acceptor orbital of the oxidant. The probability of electron transfer (tunneling) depends critically on the distance between species participating in the electron exchange reaction. A reaction can take place between two molecules if they encounter. It follows that the rate-determining step can be either the mass transport (mostly diffusion is considered but the effect of migration cannot be excluded) or the reaction (the actual rate of electron transfer in our case). 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 entirely be restricted. It follows that a diffusion-control is more frequently operative in polymeric systems than that in the case of ordinary solution reactions, because due to the low  $D$  values, the rate coefficients of the diffusion and electron transport,  $k_d$  and  $k_e$  are more likely comparable.

The electron exchange reaction (electron hopping) continuously occurs between the molecules of a redox couple in a random way. A macroscopic

charge transport takes place, however, only when a concentration or potential gradient exists in the phase at least for 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<sup>15–18</sup>

$$D = D_{AB} + D_e = D_{AB} + k_e \delta^2 c / 6 \quad (1)$$

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. Factors 1/4 and 1/2 can be used instead of 1/6 for two- and one-dimensional diffusion, respectively.

As follows from the theory (eq. (1)) the measured charge transport diffusion coefficient should increase linearly with  $c$ , whenever the contribution from the electron exchange reaction is important. There may be several reasons why this model has not fulfilled expectations although the mechanism of electron transport as described might be correct. One of these the uncertainty in determination of  $D$  by potential-step, impedance, or other techniques is substantial due to problems such as the extraction of  $D$  from a  $D^{1/2}c$  product (this combination appears in all the methods), the difficulty arising from the *in situ* thickness estimation, nonuniform thickness, film inhomogeneity, incomplete electroactivity, and ohmic drop effect. It may be forecast, for example, that the film thickness increases, thus  $c$  decreases, due to the solvent swelling of the film, however,  $D_{AB}$  increases, making the physical diffusion of ions and segmental motions less hindered simultaneously. 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 concentration of the redox groups. 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. There are several theories that predict nonlinear  $D(c)$  function which consider an extended electron transfer.<sup>19–21</sup>

In the simple models  $D_e$  is independent of the potential because the effects of both the counterion activity and interactions of charged sites are ne-

glected. 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 interaction between electrons arises. The potential dependence of the electron diffusion coefficient can be expressed as follows:<sup>22</sup>

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

where  $x_e$  is the fraction of sites occupied by electrons,  $z_s$  and  $z_i$  are the charge of the sites and 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 is a diffusion coefficient. In general,  $D_e$  is not constant as the potential, i.e. the film redox composition is changed.  $D_e$  does not vary substantially with potential within the reasonable range of  $g$  and  $z_s$  (e.g. if  $g = 4$ ,  $D_e$  will only be doubled compared with 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.

#### 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 “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 when dopant species of small quantities occupy positions within the lattice of the host material, resulting in a large-scale change in the conductivity of the doped material, as compared to that undoped. 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. The electronic conductivity shows a drastic change (up to 10–12 orders of magnitude) from its low value for the initial (non-charged) state of the polymer corresponding to a semiconductor or even an insulator, to the values within  $\kappa = 1 - 1000 \text{ S cm}^{-1}$  (even up to  $10^5 \text{ S cm}^{-1}$  comparable to metals).<sup>11,14</sup>

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.<sup>6,23</sup> The electron spin resonance (esr) measurements demonstrated the presence of unpaired spins

inside the polymer film. However, the spin concentration passes through a maximum at a low charging level, usually before the high conductivity increase, and then vanishes.<sup>24–26</sup> 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 single charged cation radicals at the polymer chain coupled with local deformations), and bipolarons (two charged defects form a pair, these doubly oxidized, spinless dication usually exist at higher charging levels).<sup>23,27,28</sup>

The intrinsic conductivity, which refers to the conduction process along a conjugated chain, can be described in terms of the band theory which is well-established for solid materials. 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.<sup>29–32</sup> 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, in a good quality polymer the interchain conductivity is rate-determining.<sup>29</sup> 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.<sup>30</sup> 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 conductivity may depend on other factors, for instance on the pH of the contacting solution (proton doping in the case of polyaniline) or on the presence of electron donor molecules in the gas phase. The decrease of the pH of the solution increases the conductivity of polyaniline,<sup>33,34</sup> while the resistance of dry polyaniline or polypyrrole increases in ammonia atmosphere.<sup>35</sup> The electron conducting polymers can easily be switched between conducting and insulating states just by changing the potential, by electrochemical (or chemical) oxidation and reduction, respectively, or by varying the composition of the contacting fluid media ( $\text{H}^+$  – ion activity of the solution or the  $\text{NH}_3$ ,

NO concentration in the gas phase). This is a unique property in comparison with the majority of electron conducting materials (e.g. metals). When the oxidation state of the polymers is varied not only their conductivity is altered but other properties (e.g. color) also change. It is the very feature that can be exploited in many practical applications.<sup>14</sup> The charging/discharging (or redox switching) processes are usually fast, but their nature is rather complex. The cyclic voltammograms represent in most cases a combination of broad anodic and cathodic peaks with a plateau of the current at higher potentials. The current is proportional to the scan rate, i.e. from electrical point of view the film behaves like a capacitor.<sup>36–41</sup> However, this simple result is the consequence of a complicated phenomenon which includes the faradaic process (generation of charged electronic entities at the polymer chains near the electrode surface by electron transfer to the metal), the transport of those species throughout the film, as well as the ion exchange at the film / solution interface. Slow heterogeneous electron transfer, effects of local rearrangements of polymer chains, slow mutual transformations of various electronic species, phase transition of first order due to an S-shaped energy diagram, dimerization, insufficient conductivity of the film at the beginning of the anodic process have been proposed as possible origins of the hysteresis.<sup>27,34,42–48</sup>

### Ion transport

In the course of electrochemical oxidation or reduction of the surface polymer films or membranes the overall electroneutrality of the polymer phase is retained by ion exchange processes between the polymer film and the bulk electrolyte solution.<sup>3,49</sup> Not only ion transport has to be considered but solvent and other neutral molecules may enter or leave the film during the charging/discharging processes.<sup>50–55</sup> In order to maintain electroneutrality in the simplest case either counterions enter the film or co-ions leave it. The relative contributions of the ions carrying different charge to the overall charge transport may depend on their physical properties (e.g. size) and/or on their chemical nature (e.g. specific interactions with the polymer), as well as on other parameters (e.g. potential).<sup>1–4,50–69</sup>

Oxidation of organic polymers is often coupled with deprotonation instead of or beside anion incorporation.<sup>3,42</sup>

The results obtained by different techniques (radiotracer,<sup>57,61</sup> quartz crystal microbalance,<sup>50–53,55,62–64,67,69–83</sup> probe beam deflection<sup>65–67</sup> etc.) have revealed that the situation may further be complicated. It has been found that the relative contribution of anions and cations to the overall ionic

charge transport process depends upon several factors, such as the oxidation state of the polymer (potential), the composition of supporting electrolyte as well as on film thickness.<sup>3,50–69</sup> These phenomena can be elucidated in terms of morphological changes, mobility of ions, interactions between the polymer and mobile species, size exclusion and so forth.<sup>50–88</sup> If large size counterions are used during the film deposition (electropolymerization), mostly co-ion exchange can be found. Diffusion-migration transport equations have been solved mostly for one-dimensional transport.<sup>3–5</sup>

### Coupling of electron and ionic charge transport

Electronic and ionic charge transport processes are coupled by electroneutrality condition.<sup>89–103</sup> Typically, two mobile species are considered, assuming that a Donnan exclusion exists. However, a theoretical model involves diffusion and the migration charge transport mechanism with three charge carriers has also been developed.<sup>101</sup> A fundamental feature of all these analyses is that electron transport is not only driven by a concentration gradient, but migration also plays a role.

The ion association effect has been also considered.<sup>104–105</sup> The advanced models elaborated for the low-amplitude potential perturbation of metal/conducting polymer film/solution systems also take into account the different mobilities of electronic (polarons) and ionic species within the uniform film. An important feature of this approach is that the difference in the electric and ionic mobilities ( $D_e \neq D_i$ ) leads to a non-uniformity of the electric field inside the bulk film which increases as the  $D_e/D_i$  ratio increases and vanishes when  $D_e = D_i$ .<sup>89,90,92</sup>

### Other transport processes

Beside the counterions' sorption/desorption the exchange of solvent and in some cases that of the salt (acid) molecules between the polymer film and background electrolyte is theoretically expected and has indeed been found experimentally.

#### Solvent transport

The equilibrium distribution of neutral molecules depends on the difference of their standard chemical potentials in the polymer and solution phases, respectively. The free energy of transfer is higher that is the sorption of neutral molecules in the polymer phase is larger if the character of the neutral species and the polymer is similar.<sup>49</sup> For instance, more water will be incorporated in hydrophilic polymers containing polar groups. Because in many cases a neutral polymer is converted into a polyelectrolyte as a function of potential the parti-

tioning of water into the polymer film will change during the charging/discharging processes. It may cause a swelling or deswelling of the layer. The extent of swelling is strongly affected by the electrolyte composition (both the nature and concentration of the electrolyte) and temperature.<sup>3,49,53,54,60,106</sup>

The expansion and contraction of the polymer network which is in conjunction with the sorption/desorption of solvent molecules and ions can be described in terms of mechanical work. This mechanical contribution should be considered in the calculation of the equilibrium electrode potential. For a range of neutral polymer films freshly deposited on metal substrates by solvent evaporation technique several potential sweeps are required for the films to become fully electroactive.<sup>3,54,57,106,107</sup> This phenomenon has been referred to as the break-in effect. A secondary break-in effect may be observed when the film is in its neutral form for a longer period of time before a repeated charging process. Both break-in effects are attributed to the incorporation of solvent molecules and ions into the film phase during electrolysis, as well as to potential-dependent morphological changes.

### Dynamics of polymeric motion

The rate of chain and segmental motions is of the utmost importance since these processes may determine the rate of the diffusional encounter and consequently the rate of electron transport process within the polymer film. Below the glass-transition temperature ( $T_m$ ) the polymeric motion is practically frozen-in. Above  $T_m$  the frequency of the chain and segmental motions strongly increase with temperature.<sup>3,108</sup> The plasticizing effect of solvent enhances the rate of all kinds of motions in the polymer phase. At high electrolyte concentrations the ionic shielding of the charged sites of the polymer increases, and the polymer film will adopt a more compact structure. In this case the activity of the solvent is also low, consequently the film swelling is less.<sup>3,56,106</sup> In the more compact structure the molecular motions become more hindered. Covalent or electrostatic cross-linking diminishes the rate of all the physical diffusion processes.

### Film structure and morphology

In the general sense the swollen polymer films can be considered as a polymer, polyelectrolyte gel.<sup>3</sup> Various microscopic techniques have revealed a pronounced heterogeneity of the surface layer.<sup>109–113</sup> In this respect, one should distinguish between macropores (of which diameter exceeds considerably 10 nm) and nanopores (which represents solvent molecules and ions between the polymer chains). Inside the macropores the thermodynamic and transport

properties of ions and solvent molecules practically do not differ from that of the contacting bulk solution. The space-charge regions (electric double layers) are formed at the interface between the polymer and solution phases the thickness of which is much lower than the characteristic sizes of macromolecules (fibrils, grains and pores). The polymer phase itself consists of a polymer matrix with incorporated ions and solvent molecules which do not form a separate continuous phase. Strong coulombic attractions between electronic and ionic charges prevent their separations at the distance significantly exceeding the Debye screening length of the medium (ca. 0.1 – 0.3 nm in charged state). There are three principal approaches to modeling the structure of the polymer phase.<sup>14,93</sup> One may consider a uniform, homogeneous film,<sup>9,89,90,93</sup> or a porous medium<sup>27,38,114,115</sup> or an inhomogeneous homogeneous phase where the properties of the first layer differ from those of the bulk film.<sup>116,117</sup> Despite seemingly opposite ways of describing the polymer phase in these approaches, the results concerning the responses to *dc* and *ac* perturbations often turned out to be often similar or even identical.

Porosity effects in the charging process have been implicated for a long time in the discussion of the faradaic and capacitive contributions to the current especially in the case of electronically conducting polymers. The peaks of the cyclic voltammograms are attributed to the faradaic process while the plateaus of the current are considered as the indication to the capacitive term.<sup>37,40,118</sup> However, this straightforward analogy to the metal/solution interface does not work in reality the faradaic process of redox transformation of the redox species in the surface layer does not lead to a direct current, unlike similar reaction for solute species.

### Thickness

According to the theory of metastable adsorption of de Gennes,<sup>119</sup> when an adsorbed polymer layer is in contact with a pure solvent the layer density diminishes from the substrate (e.g. a metal) surface. The behavior of several polymer film electrodes (e.g. poly(tetracyanoquinodimethane),<sup>120</sup> poly(vinylferrocene),<sup>69</sup> polypyrrole<sup>121</sup> and polyaniline<sup>26,122,123</sup>) has been explained by the assumption that the film density decreases with film thickness, that is from the metal surface to the polymer/solution interface.

### Synthesis conditions, nature of electrolyte

Although the region close to the electrode surface shows a more or less well-defined structure, in general the polymer layer can be considered as an amorphous material. The film morphology is

strongly dependent on the composition of the solution and the current density used in the course of electrodeposition.<sup>32,42,51,53,69,109,124–127</sup>

#### *Effect of electrolyte concentration and temperature*

The swelling and shrinking of a polyelectrolyte gel are strongly affected by the concentration of the contacting electrolyte solution and temperature.<sup>3,50,51,54,60</sup> The thermodynamic theory predicts a gel shrinkage as the salt concentration is increased or temperature is decreased.<sup>128</sup> Usually, the shrinking process occurs smoothly, but under certain conditions the process becomes discontinuous, and a tiny addition of salt leads to the collapse of the gel that is a drastic decrease of the volume to a fraction of its original value. The onset of shrinking and swelling substantially depends on temperature. The abrupt deterioration of the charge transport rate in poly(tetracyano-quinodimethane) or poly(vinyl-ferrocene) films at high electrolyte concentrations and its temperature dependence can be interpreted on the basis of the thermodynamic theory.<sup>54,56</sup> In a more compact structure, the rate of electron hopping may increase since the concentration of redox sites is high, however, simultaneously a deterioration of the film permeability concerning the counterions due to the decrease of the free volume is expected. The maximum observed in the peak current versus salt concentration curves is the result of the balanced effects of the enhanced electron-exchange process and the hindered counterion motion. The abrupt change in the free volume of solvent-filled cavities causes a sharp decrease in the charge transport diffusion coefficient.<sup>3</sup>

#### **Relaxation and hysteresis phenomena**

Owing to the long relaxation times characteristic to polymeric systems the equilibrium or steady-state situation often has not been reached within the time scale of the experiment. Consequently, even slow sweep rate cyclic voltammetry does not supply reliable thermodynamic quantities which otherwise can be derived by analyzing the changes in the peak potentials. The manifestation of the polymeric nature of these systems is most striking in the relaxation phenomena in the case of conducting polymers which are in connection with the changes of the conditions (potential, temperature, etc.) and appear in different effects, such as hysteresis, “first cycle” and memory effects.<sup>34,42,46,54,128–131</sup>

The first cycle or waiting time effects (the shape of the cyclic voltammograms and the peak potentials depend on the delay time at potentials where the polymer is in its neutral (discharged) state – see also secondary break-in) have been interpreted in terms of slow morphological changes and/or with

the difficulty of removing remaining charges from an insulating surrounding.<sup>129</sup> This problem also arises in the case of redox polymers.<sup>54,56–58</sup> The results of fast scan rate voltammetry, chronoamperometry and chronopotentiometry have been explained also by a model assuming an instantaneous two-dimensional nucleation and growth of conducting zones and it has been concluded that the oxidation and reduction must proceed by different pathways and involve different degree of disorder.<sup>42</sup> For the conducting-to-insulating conversion the slow relaxation effect has been interpreted within the framework of the percolation theory<sup>130</sup> and by the electrochemically stimulated conformational relaxation (ESCR) model,<sup>46</sup> respectively. Both theories predict logarithmic time dependence. The hysteresis effect and the non-nernstian behavior for polyaniline have also been elucidated with the help of the polaron models considering that the formation energies of both polarons and bipolarons increase with the degree of oxidation.<sup>27</sup> An intermolecular coupling of two  $\pi$ -radical centers has also been proposed.<sup>44,45</sup> The considerable difference between the anodic and cathodic peak potentials of the cyclic voltammograms in the case of polytetracyanoquinodimethane redox electrode has been explained by the formation of dimeric species i.e. a slow formation of mixed valence dimer during reduction (charging) and fast reoxidation of dimer dianion resulting in the mixed valence dimer during the discharging process.<sup>4,59</sup>

While the effect of the potential-induced relaxation phenomena has been extensively studied fewer efforts have been made concerning the temperature effect. A notable exception is a temperature shock experiment on poly(tetracyanoquinodimethane) electrode. It was found that when the electrode returned from elevated temperature to room temperature, a relatively long time was needed to restore the original voltammetric response characteristic for room temperature. Apparently, the polymer adopts an extended, perhaps solvent swollen conformation at the elevated temperatures that requires a long time for the restoration of the room temperature structure.<sup>54</sup> Such behavior is observed in the studies of polymer gels, when the variation of temperature results in the hysteresis of macroscopic polymer properties such as swelling, elasticity, turbidity and so forth.

#### **Measurements of the rate of charge transport**

The rate of charge transport within an electrochemically active polymer film has been successfully studied by transient electrochemical techniques. One may distinguish methods using large and small potential or current perturbations, respectively. For

the basic characterization cyclic voltammetry, and potential (less often current) step and pulse techniques have been applied.<sup>1–10</sup> With the help of these techniques average values for the charge transport diffusion coefficient can be obtained since the properties of the polymer continuously change and large amounts of ions and/or solvent molecules are exchanged between the polymer phase and the bulk solution during the experiments. Owing to the marginal perturbation from equilibrium (steady-state) by low amplitude (< 5 mV) sinusoidal voltage the advantage is evident of electrochemical impedance spectroscopy (EIS) over other techniques involving large perturbations.<sup>3,4,25–27,38,89–103,109–112,114–117,132,133</sup>

The radiotracer technique<sup>41,54,57,61</sup> is well suited to the investigation of the motion of counterions and coions coupled to the electron transfer and transport processes, and offers the opportunity of studying the attainment of equilibrium and steady states in regard to the sorbed ions at any potential that is at any ratio of oxidized and reduced sites in the film without disturbing the original experimental conditions. Piezoelectric microgravimetry at electrochemical quartz crystal microbalance (EQCM) with nanogram sensitivity has also emerged as an important technique for monitoring the surface mass change.<sup>50–54,60,2–64,67–83,106,107,131,134,135</sup> A comparison of the change of the surface mass with the charge consumed in the course of the redox transformations may shed light on the mechanism of the electrochemical reactions. It may also supply information on the sorption of neutral species and protonation equilibria. Conclusions can be drawn concerning the relative contribution of different anions and cations to the overall ion exchange process as well as the rate of the mass transport processes.

Probe beam deflection (PBD) involves the measurement of the deflection of a light beam, aligned parallel to the electrode surface.<sup>65–67,136</sup> This in-situ method is also a very convenient tool for the study of ion transport and the reaction mechanism. The combination of a radiotracer and EQCM or EQCM and PBD techniques is especially useful because it allows access to individual ion and solvent flux contributions to the mass transport dynamics.<sup>67</sup>

In situ conductivity measurements,<sup>33,34,131,137–140</sup> luminescence techniques,<sup>141</sup> different spectroscopies in combination with electrochemical methods<sup>25,26,59,86,110–112,142–144</sup> and surface plasmon resonance<sup>145</sup> have also supplied valuable information about the ionic and electronic charge transfer and charge transport processes. Microscopies have given new insights into the structure and morphology of surface polymer film, as well as their changes with experimental conditions.<sup>109–113,146–150</sup>

## Experimental

The details of the experiments can be found in the references cited.

## Illustrative experimental results

### Transition from insulating to conduction state

The main difference between the redox and the electronically conducting polymers is that the latter systems can conduct electricity even in dry state. By the help of an appropriate experimental arrangement<sup>34</sup> the changes of the conductivity can be measured even in contact with an electrolyte, when the oxidation state of the polymer can easily be varied by varying the potential. Fig. 1 shows this effect in the case of polyaniline (PANI).

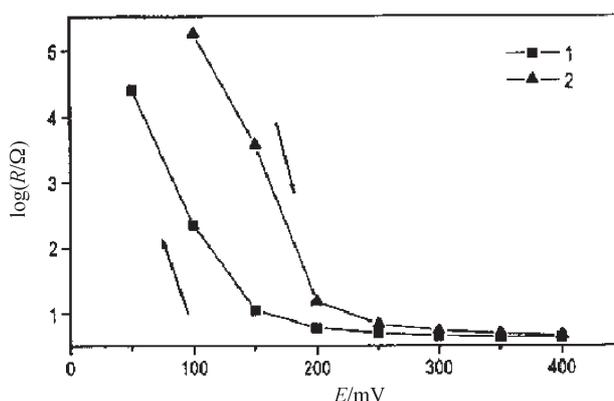


Fig. 1 – Changes of the resistance of a polyaniline film in contact with  $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  as a function of the potential. The waiting times after each potential step were from 6 to 30 min depending on the nature of relaxation.  $U_{\text{film}} = 5 - 25 \text{ mV}$  depending on the value of  $R$ .<sup>34</sup>

As seen in Fig. 1 the resistance of the PANI film changes ca. five orders of magnitude during its redox transformation from leucoemeraldine to emeraldine form. The changes of the resistance depend considerably on the direction of potential variation especially in the region where the conducting to insulating transition occurs. It can be shown that there is a connection between the hysteresis and relaxation phenomena. A comparison with the cyclic voltammograms reveals that there is a close relationship between the hysteresis shown above and the shape of the cyclic voltammogram.

### Ion transport

Fig. 2 shows typical cyclic voltammograms and the simultaneously detected EQCM frequency responses for a PANI electrode in acid media.<sup>131</sup>

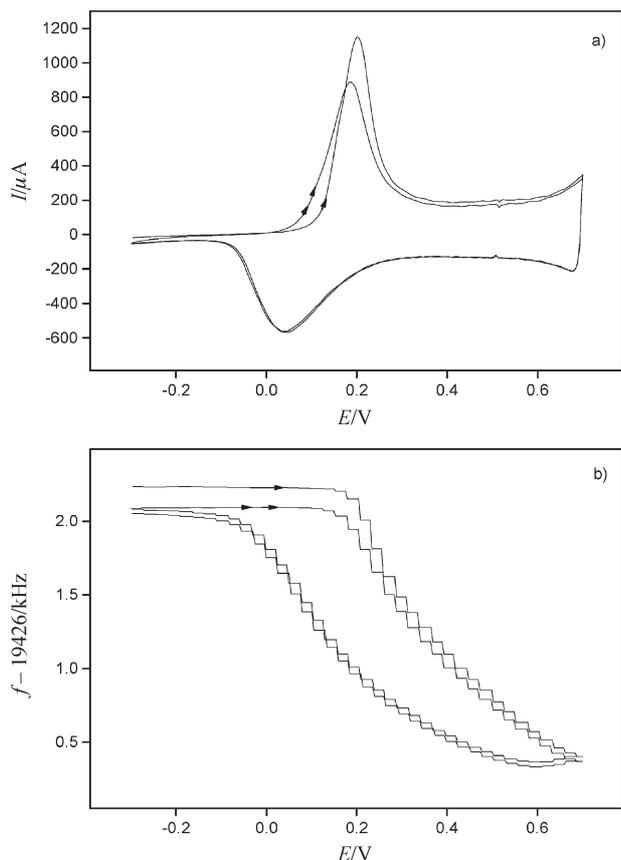


Fig. 2 – (a) Cyclic voltammograms (two cycles) and (b) Simultaneously detected EQCM frequency changes for a polyaniline film ( $l=2.9 \mu\text{m}$ ) in contact with  $1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ . Sweep rate:  $100 \text{ mV s}^{-1}$ .<sup>131</sup>

The difference between the first and the second cycles ('first cycle effect') is clearly seen in the figure. The frequency decrease indicates the incorporation of anions into the oxidized PANI film. However, a closer inspection of the curves reveals that the mass increase starts at potentials when a certain amount of charge was already injected. This can be explained as follows. The leucoemeraldine form is partially protonated and the polymer film contains an equal amount of anions. In the first stage of oxidation these sites will deprotonate and the protons leave the film. Owing to the very low molar mass of hydrogen ions only a very small decrease can be expected.

### Break-in effect

The effect, which is in connection with the gradual swelling by solvent molecules and ionic species, depends on the film thickness, the composition of the contacting electrolyte and temperature. Fig. 3 shows the results obtained for the poly(tetracyanoquinodimethane) electrode (PTCNQ).<sup>106</sup>

At high electrolyte concentrations the break-in period last longer, and due to the low water activity the film remains stable even in dianion state, i.e., no fast hydrolysis reaction takes place.

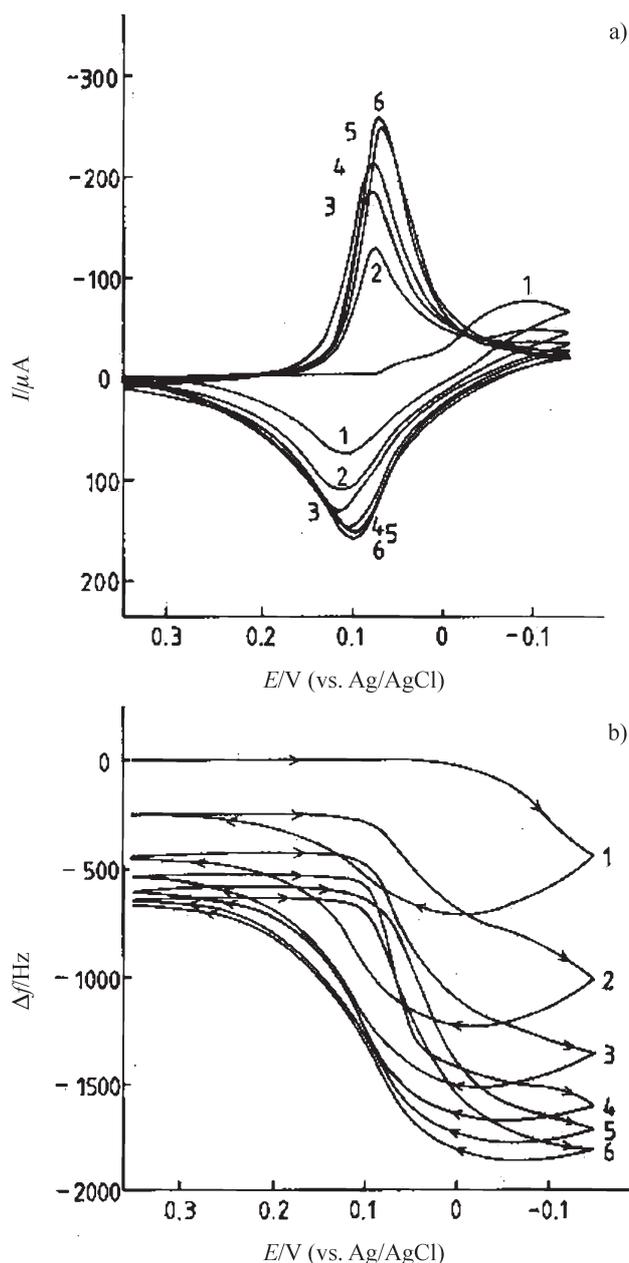


Fig. 3 – Cyclic voltammetric break-in of a poly(tetracyanoquinodimethane) electrode.  $\Gamma = 7 \times 10^{-8} \text{ mol cm}^{-2}$ . Electrolyte:  $2.5 \text{ mol dm}^{-3} \text{LiCl}$ . Sweep rate:  $6 \text{ mV s}^{-1}$ . (a) Consecutive cyclic voltammograms, (b) Simultaneously obtained EQCM frequency curves.<sup>106</sup>

### Dynamics of polymeric motion, effect of temperature

Fig. 4 shows the temperature dependence of the voltammetric response of a PTCNQ electrode.<sup>54</sup>

The fast chain and segmental motions enhance the rate of the electron transport via electron hopping. At the first wave the gradual development of the more symmetrical shape is a consequence of the regress of dimerization, which process is also temperature dependent.

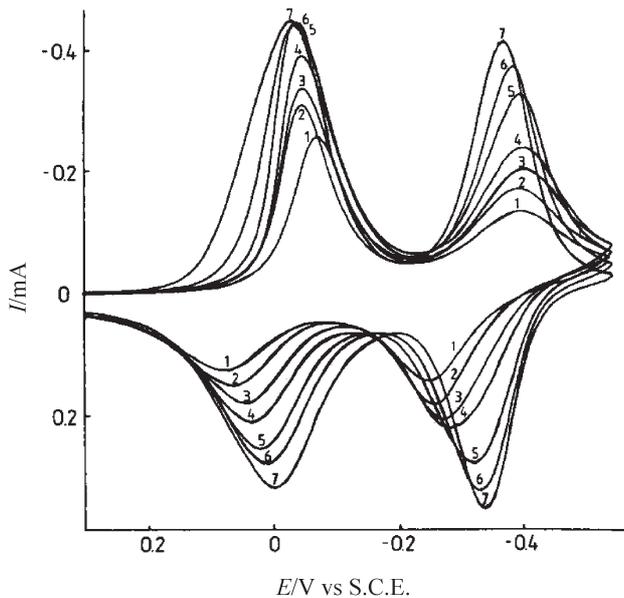


Fig. 4 – Cyclic voltammograms of a PTCNQ electrode ( $\Gamma = 5.1 \times 10^{-8} \text{ mol cm}^{-2}$ ) in contact with aqueous  $10 \text{ mol dm}^{-3} \text{ LiCl}$ . Scan rate:  $6 \text{ mV s}^{-1}$ . Temperature: (1) 22, (2) 34, (3) 44, (4) 50, (5) 61, (6) 66 and (7) 77 °C.<sup>54</sup>

Temperature causes no drastic changes in the case of PANI since the chain and segmental motion is less important for electronically conducting polymers.

The charge transport rate is high even at low temperatures, which extends the application range of PANI.<sup>151</sup>

Electrochemical impedance spectroscopy provides information on the rate of charge transfer and charge transport processes beside other important

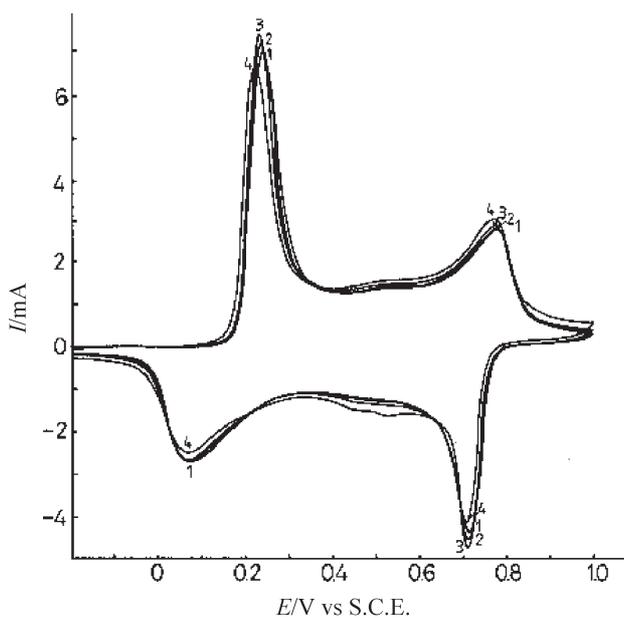


Fig. 5 – Cyclic voltammograms of a PANI electrode in contact with  $1 \text{ mol dm}^{-3} \text{ HCl}$  at different temperature: (1) -1.5, (2) 1.25, (3) 2.5 and (4) 5.0 °C. Scan rate:  $60 \text{ mV s}^{-1}$ .<sup>151</sup>

quantities such as film resistance, double layer capacitance, redox capacitance of the film. The variation of the ohmic resistance ( $R_s$ ), the charge transfer resistance ( $R_{ct}$ ) and the charge transport diffusion coefficient ( $D_{ct}$ ) as well as that of other quantities as a function of temperature ( $T$ ) have been analyzed in detail.<sup>152</sup> The decrease of  $R_s$  with  $T$  manifests itself in the shift of the spectra along the x-axis. The temperature dependence of  $R_{ct}$  appears in the decrease of diameter of the Randles semi-circle.

### Polyelectrolyte behavior, effect of electrolyte concentration

Fig. 6 shows a series of cyclic voltammograms obtained for a PTCNQ electrode in contact with aqueous lithium chloride of different concentrations.

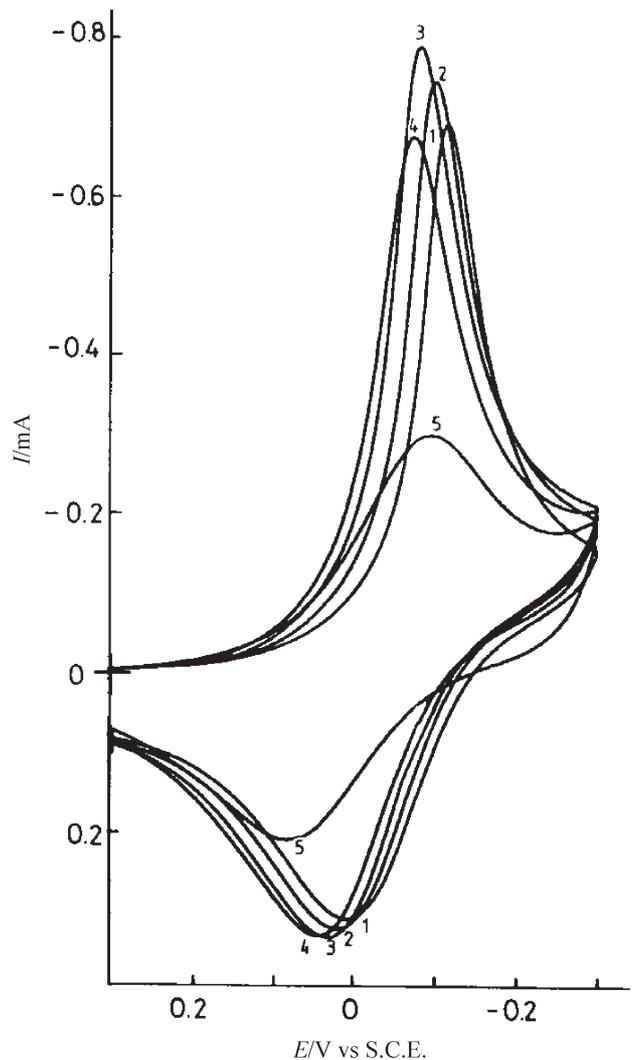


Fig. 6 – Cyclic voltammograms of a poly(tetracyanoquinodimethane) electrode ( $\Gamma = 13 \text{ nmol cm}^{-2}$ ) in contact with lithium chloride solution at different concentrations: (1) 0.625, (2) 1.25, (3) 2.5, (4) 5.0 and (5) 10.0  $\text{mol dm}^{-3}$ . Scan rate:  $60 \text{ mV s}^{-1}$ .<sup>54</sup>

It is a rather surprising result since the peak currents ( $I_p$ ) should not depend on the electrolyte concentration ( $c_s$ ) and the shift of the peak potentials ( $E_p$ ) becomes irregular at high concentrations. However, if we consider that polyelectrolyte gels shrink when they are placed into concentrated solutions the phenomena observed can be elucidated. There are two effects regarding the charge transport rate. As the polymer shrinks the site concentration

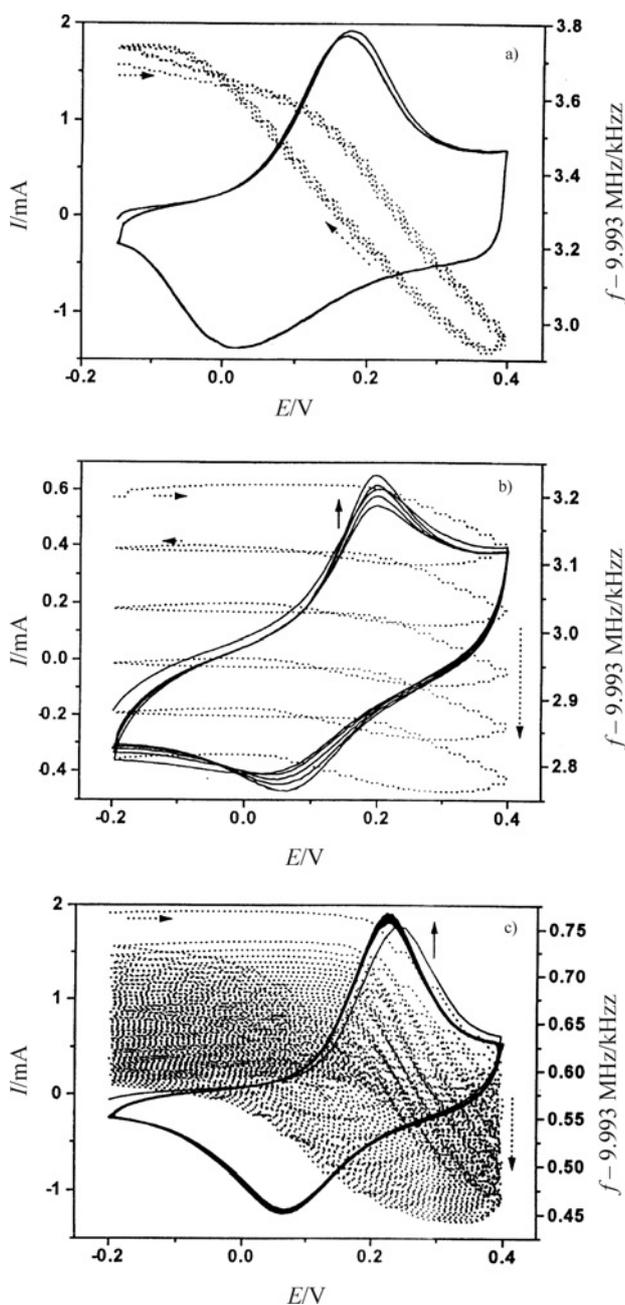


Fig. 7 – Cyclic voltammograms and the simultaneous EQCM curves recorded for a PANI electrode in (a)  $1 \text{ mol dm}^{-3} \text{ HClO}_4$ , (b) and (c) in  $1 \text{ mol dm}^{-3} \text{ HSSA}$  after exchanging  $\text{HClO}_4$  for HSSA. Curves shown on (b) were taken during the first five cycles after the solution replacement, while those of (c) display the responses from 135<sup>th</sup> to 175<sup>th</sup> cycles. Scan rate:  $100 \text{ mV s}^{-1}$ .<sup>53</sup>

( $C_p$ ) increases which enhances the electron exchange reaction. On the other hand the size of the solvent-filled cavities will be smaller which will hinder the motion of counterions.<sup>54</sup>

The charge transport rate also depends on the morphology in the case of electronically conducting polymers. The morphology of these polymer films is related to the composition of the solution used during the electropolymerization. However, the electrolyte exchange causes a structural change, and eventually the full electroactivity will be regained even when relatively small anions are replaced by bulky ones. Fig. 7 shows the effect when  $\text{HClO}_4$  is replaced by 5-sulfosalicylic acid (HSSA).

### Potential dependence of the charge transport diffusion coefficient

While from the results of the methods using large perturbations only an average  $D_{ct}$  value can be derived, from the data of electrochemical impedance spectroscopy (EIS) the potential dependence of  $D_{ct}$  can also be calculated. Such a result is shown in Fig. 8.

At low potentials when poly(o-phenylenediamine), PPD is in its reduced state, the transference number of ions ( $t_i$ ) is much higher than that of electrons ( $t_e$ ), while at high potentials  $t_e \gg t_i$ , i.e., the  $D$  values determined in the previous case are characteristic of electron transport ( $D_e$ ) while in the latter case  $D_i$  for the ion transport can be determined. There is a potential region when  $t_e \sim t_i$ .

The maximum curve can be explained on the basis of interactions within the film between the charged sites and also between the charged sites and counterions [see eq. (2)].

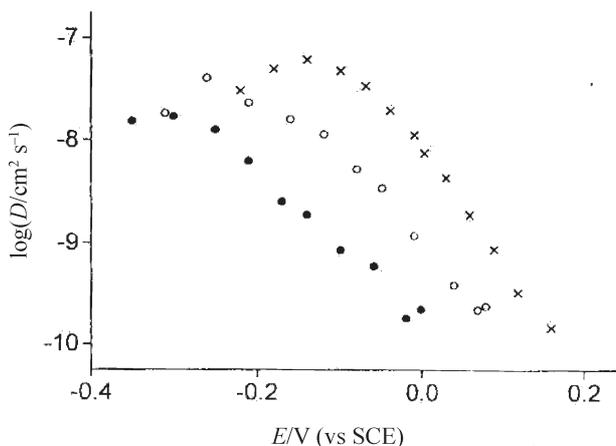


Fig. 8 – Log  $D$  vs. potential plot calculated from the EIS spectra of an Au\PPD electrode in contact with  $\text{HClO}_4$  solutions of different concentrations:  $0.01 \text{ mol dm}^{-3}$  (●),  $0.1 \text{ mol dm}^{-3}$  (○) and  $1 \text{ mol dm}^{-3}$  (x), respectively. The total concentration of perchlorate ions was  $1 \text{ mol dm}^{-3}$  by adding an appropriate amount of  $\text{NaClO}_4$  to the more dilute solutions.<sup>153</sup>

## Relaxation phenomena

Figure 9 shows the simultaneous changes of the current ( $I$ ) and the resistance ( $R$ ) of the polymer film after a potential-step for a PANI electrode. At high potential step amplitude the relaxation period may last for tens of minutes especially when the polymer is switched between insulating and conducting states.

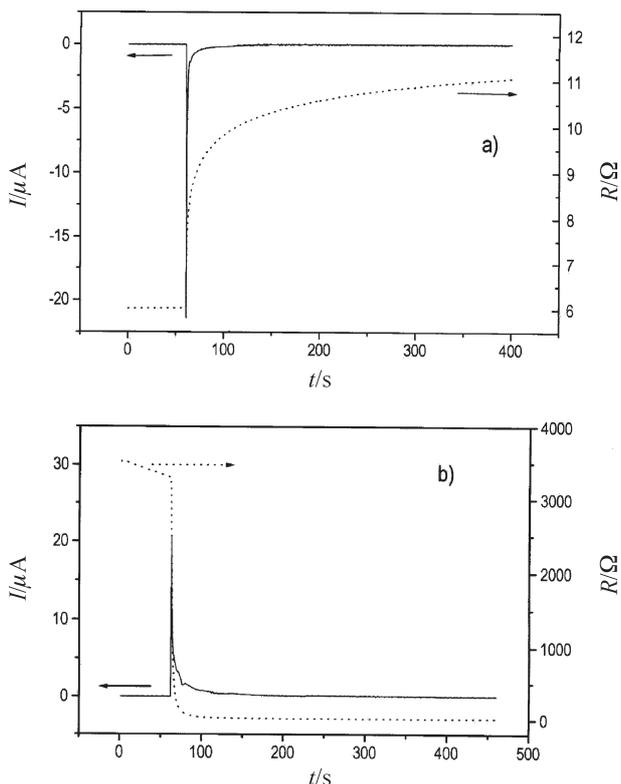


Fig. 9 – Current transients and respective resistance-time curves obtained for a polyaniline film following potential steps (a) from 0.2 to 0.15 V; and (b) from 0.15 to 0.2 V. Solution:  $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ .<sup>34</sup>

## Conclusions

In summary, the application of new and powerful techniques has allowed a detailed insight into the nature of charge transport and charge transfer as well as of the chemical and physical processes occurring in these systems. Therefore, the production of electrochemically active polymers, polymeric films, and composites with desired properties has become a well established area of electrochemical and material sciences. Considering the pace of the ever growing applications of polymers in electrochemical cells it may be declared that electrochemistry is in transition from its bronze age (i.e. typically using metals) to the era of polymers.

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## List of symbols

$C$	– site concentration
$c_e$	– electrolyte concentration, $\text{mol dm}^{-3}$
$c$	– concentration of redox center
$D$	– diffusion coefficient, $\text{cm}^2 \text{ s}^{-1}$
$E$	– potential, V, mV
$g$	– occupied site interaction energy
$I$	– current, mA
$k_d$	– mass transfer coefficient, $\text{m s}^{-1}$
$k_e$	– electron transfer coefficient, $\text{m s}^{-1}$
$l$	– length, $\mu\text{m}$
$R$	– resistance, $\Omega$
$r$	– half thickness, $\mu\text{m}$
$T$	– temperature, K
$t$	– transference number
$\chi$	– site fraction
$z$	– site charge
$\delta$	– electron hopping distance
$\kappa$	– conductivity, $\text{S cm}^{-1}$

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