Chapter 7
Applications of Conducting Polymers

7.1 Material Properties of Conducting Polymers

For practical reasons, electronically conducting polymers that can be prepared from cheap compounds such as aniline, pyrrole, thiophene, and their derivatives by relatively simple chemical or electrochemical polymerization processes attract the most interest [1–26]. However, redox polymers are also applied in special cases, such as in biosensors or electrochromic display devices. Nevertheless, in this chapter, we focus our attention on the applications of electronically (intrinsically) conducting polymers, which we will refer to as "conducting polymers," or by the abbreviations "ECPs" and "ICPs." The most interesting property of conducting polymers is their high (almost metallic) conductivity, which can be changed by simple oxidation or reduction, and also by bringing the material into contact with different compounds. Conducting polymers usually have good corrosion stabilities when in contact with solution or/and in the dry state. For instance, polyaniline is stable in its leucoemeraldine and emeraldine states, even in 10 mol dm^{-3} acid solutions. Furthermore, ICPs can be deposited from a liquid phase, even in complex topographies. Redox processes combined with the intercalation of anions or cations can therefore be used to switch the chemical, optical, electrical, magnetic, mechanic, and ionic properties of such polymers. These properties can be modified by varying the anion size and preparation techniques, by including other chemical species, for example. A qualitative summary of the relationship between the properties of a conducting polymer and its charge state is given in Table 7.1.

Typical areas in which conducting polymers are applied can be described using a double logarithmic plot of ionic resistance vs. electronic resistance, as shown in Fig. 7.1. The positions of ideal metals, semiconductors, and insulators in the diagram are shown at the top. Constant properties exist at high ionic resistances, i.e., toward the top of the diagram. Here, ICPs can be applied in the dry state in an inert atmosphere. Contact with an electrolyte leads to a much wider field of applications, depending on the specific ionic and electronic resistances associated with the charge state, such as in batteries, displays, sensors, etc.

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Table 7.1 Qualitative properties of conducting polymers that conduct in their oxidized state, as a function of their charge state

Properties/charging state	Reduced	Oxidized
Stoichiometry	Without anions (or with cations)	With anions (or without cations)
Content of solvent	Smaller	Higher
Volume	Smaller	Higher
Color	Transparent or bright	Dark
Electronic conductivity	Insulating, semiconducting	Semiconducting, metallic
Ionic conductivity	Smaller	High
Diffusion of molecules	Dependent on structure	
Surface tension	Hydrophobic	Hydrophilic

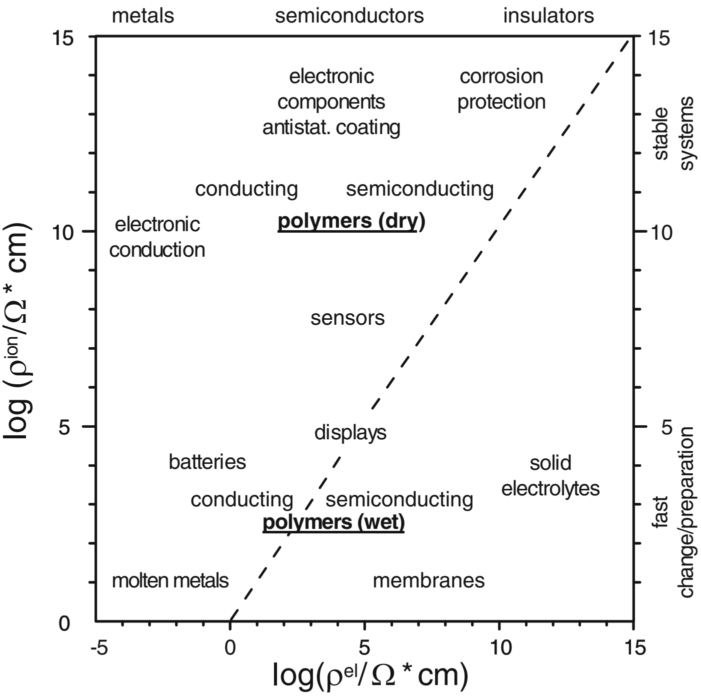

Fig. 7.1 Double logarithmic plot of ionic resistance vs. electronic resistance for conducting polymers, showing areas of application (Reproduced from [10] with the permission of Elsevier Ltd.)

Special properties, such as wettability, optical, or membrane properties, can be utilized in special systems (e.g., displays) or processes (e.g., metallization of holes). Conducting polymers can therefore be grouped according to their technological field of application (e.g., energy technology, sensors, and others). For more on this topic, see the reviews in [1–26].

7.2 Applications of Conducting Polymers in Various Fields of Technologies

7.2.1 *Thin-Film Deposition and Microstructuring of Conducting Materials (Antistatic Coatings, Microwave Absorption, Microelectronics) [27–38]*

Before polymers can be applied in advanced systems, their mechanical and topographic properties must first be checked. The filling of molds, holes, and gaps often is a problem, depending on the preparation process. However, ICPs have an advantage in this context. For instance, electrochemical polymerization can be carried out in a hole or mold. Sometimes, the growth preferentially takes place at the edges, which can be an advantage when depositing chemicals [27]. The minimum size of the holes to be filled is given by the molecular size of the polymer and the hydrophilicity of the holes. Even nanosized channels of porous silicon or Al_2O_3 can be filled [33, 34]. Chemical polymerization by soluble (Fe^{3+}) or solid oxidants (MnO_2, $RuCl_3$ [32]) can also be used.

A detailed review of the use of conducting polymers for microsystem technologies and silicon planar technology was given in [36]. Local deposition of polybithiophene is possible on n-type silicon using laser-assisted deposition. The production of negative and positive microstructures with high aspect ratios and precisions is possible. Various concepts such as direct laser writing, prestructuring of the silicon substrates by mask techniques, or poststructuring of predeposited polymer films have also been realized [36].

For micro- and nanostructures with negative aspect ratios, successful filling can only be realized if the reaction starts at the bottom of the pore (see Fig. 7.2b). This can be achieved if the bottom of the negative microstructure is conducting while the wall is insulating. A homogeneous reaction may also take place all over the pore wall when an inhibiting layer (e.g., a high-field oxide) is formed at the wall.

Potential approaches to microstructuring are illustrated in Fig. 7.3.

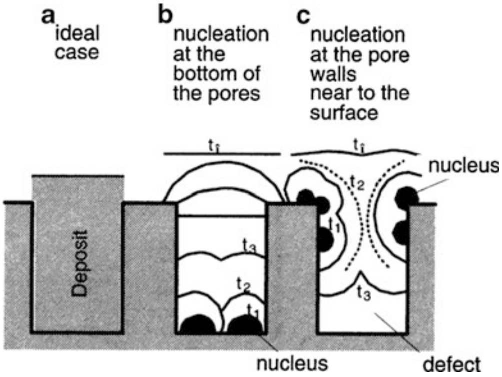

Fig. 7.2 Scheme for polymerization in pores. (**a**) Ideal case, (**b**) nucleation at the bottoms of the pores, (**c**) nucleation at the walls of the pores (Reproduced from [36] with the permission of Elsevier Ltd.)

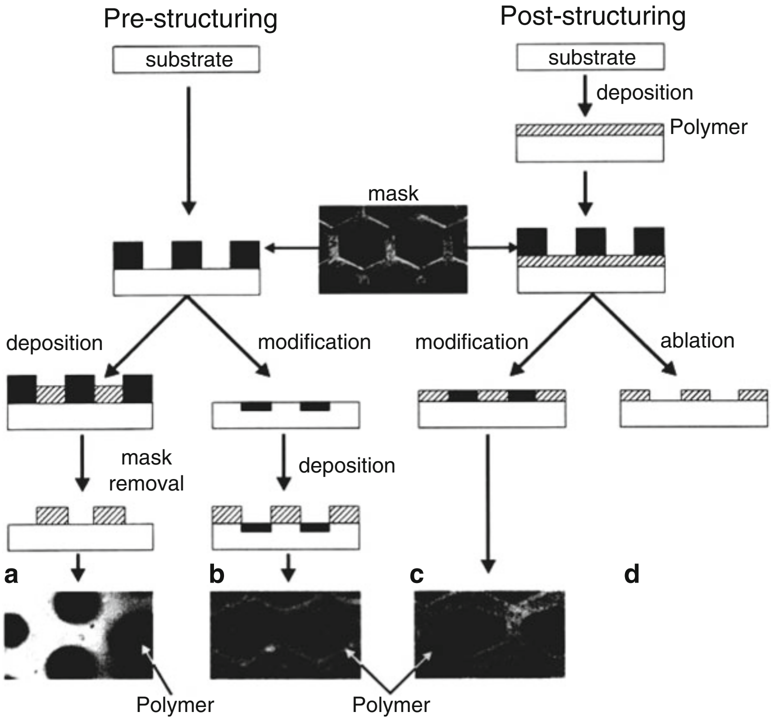

Fig. 7.3 Schemes for pre- and poststructuring conducting polymers (Reproduced from [36] with the permission of Elsevier Ltd.)

Prestructuring can be achieved through the usual photoresist technique (Fig. 7.3a) or by ion implantation through a mask (Fig. 7.3b). The prestructuring yields an insulating region of the semiconductor's surface, and so polymerization only occurs over the rest of the surface. In the case of poststructuring, a polymer film is prepared at the surface and then microstructuring is carried out using a chemical reaction, such as by oxidation (Fig. 7.3c), using a photoreaction (laser ablation; Fig. 7.3d) or by mechanical removal of the polymer film. Positive microstructures are usually obtained by poststructuring.

In thin-film technologies, ICPs can be used as conducting layers. Two application fields of great technical importance are antistatic protection [28, 30] and electromagnetic interference shielding by conducting polymers [29, 37]. For instance, a 0.54-mm-thick polypyrrole–textile composite absorbs ca. 50% of the incident 30–35 W microwave radiation [29]. PANI, PP, and PT derivatives are predominant in these fields. They are incorporated as fillers into common polymeric materials such as poly(vinylchloride) or poly(vinylacetate) in order to substitute carbon-black-filled materials. Poly(3,4-ethylenedioxythiophene) (PEDOT) is used as a protective layer for photographic films [30].

A large-scale technological process was realized with the through-hole plating of printed circuit boards [31, 35]. The insulating epoxy board is oxidized by $KMnO_4$. The resulting thin film of MnO_{2-x} is used as an oxidizer for the oxidative polymerization of EDT. The thin film of PEDOT is conductive even at low potentials in acidic solution. Therefore, the hole covered with conducting polymer can be directly electroplated with copper.

In microelectronics, ICPs can be applied as charge dissipators for electron-beam lithography. Electron-beam lithography is a direct writing method with a very high resolution in the submicrometer range. The charging of the insulating electron-beam resist can lead to the deflection of the electron beam, resulting in image distortion. Conducting resists or layers must therefore be applied to negate this problem. Water-soluble PANI was introduced by IBM as a discharge solution [38].

7.2.2 Electroluminescent and Electrochromic Devices [17, 19, 39–87]

Electrochromic devices have been realized with ICPs [17, 19, 39–87]. Many conducting polymers exhibit redox states with distinct electronic absorption spectra. When the redox transformations generate new or different visible region bands, the material is said to be electrochromic [19, 64]. The color changes from either a transparent ("bleached") state, where the polymer absorbs in the ultraviolet region, to a colored state, or from one colored state to another (see Chap. 2). In several cases, more than two redox transformations can take place, which are accompanied by more than two color changes. The usual color change is from pale yellow or colorless (the reduced state) to green or blue (the oxidized state); for example, PANI absorbs at $\lambda \leq 330$ nm in its reduced state, the absorbance at ~440 nm increases during the oxidation, and a broad free carrier electron band appears at $\lambda \sim 800$ nm at more positive potentials (oxidation state; see Fig. 4.7). During the oxidation of PP, the following color changes can be observed: yellow $\leftrightarrow$ green ($\lambda = 420$ nm), blue $\leftrightarrow$ violet ($\lambda = 670$ nm). However, colorless $\leftrightarrow$ red (PPD), orange $\leftrightarrow$ black [69], or red ($\lambda = 470$ nm) $\leftrightarrow$ blue ($\lambda = 730$ nm) (PT), etc., also occur. This effect can be used in light-reflecting or light-transmitting devices for optical information and storage (displays) or for glare-reduction systems and "smart windows" in cars and buildings. To be applicable in this context, the response time of the conducting polymer must be fast enough (<100 ms [64]), and it must be highly reversible upon charging/discharging (for up to 10^5 cycles or more) [19, 64]. Smart windows based on a sandwich structure of ITO/PEDOT–PSS/ITO between glass have been developed [51, 73].

Tuning the color states via modification of the polymer structure has become a basic method in order to achieve multicolor electrochromic displays [40]. The color (i.e., the color change) can be tuned by using different derivatives of the same parent monomer. For instance, 3-methylthiophene, 3-hexylthiophene, and

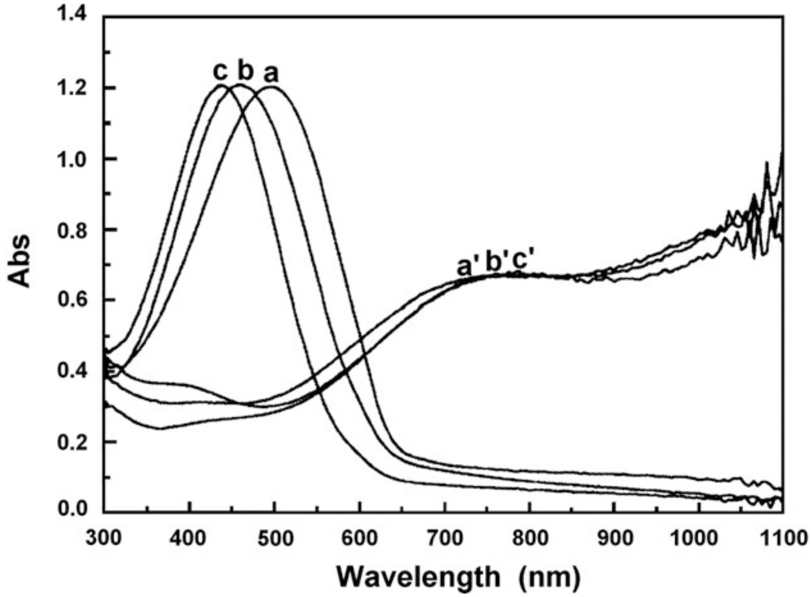

Fig. 7.4 Normalized absorption spectra of poly(3-methylthiophene) (*a* and *a*′), poly(3-hexylthiophene) (*b* and *b*′), and poly(3-octylthiophene) (*c* and *c*′) in their fully reduced and oxidized states, respectively (Reproduced from [68] with the permission of Elsevier Ltd.)

3-octylthiophene have been electropolymerized in a room-temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$), and the resulting polymers (PMeT, PHexT, and POcT) exhibit slightly different color changes during reversible redox switching [68]. Figure 7.4 shows the spectra of these polymers in their oxidized and reduced states, respectively. The respective color changes during oxidation are bright red → bright blue (PMeT), orange red → blue (PHexT), and orange yellow → black blue (POct). Thiophene and pyrrole derivatives are good examples concerning the effect of the structure modification. For instance, the following color changes can be observed at different compounds: PEDOT and poly(3,3-dimethyl-3,4-dihydro-2*H*-thieno-[3,4-*b*]dioxepine) deep blue ↔ transparent blue [80], poly(3,4-ethylenedioxypyrrole) red ↔ transmissive blue [50, 74], poly(3,4-propylenedioxypyrrole) orange ↔ brown ↔ gray blue [77], poly (*N*-sulfonatopropoxy-dioxypyrrole) colorless ↔ gray [77]. Poly(benzo[*c*]thiophene-*N*-2-ethylhexy-4,5-dicarboxylic imide) and poly(thieno[3,4-*b*]thiophene) absorb only in the near-infrared region [63, 76]. Polymers prepared either by using comonomers (monomers containing two or more different rings) or by copolymerization exhibit several distinct redox transformations and consequently multicolor electrochromism. Copolymers are versatile systems in this respect, even a change of the relative concentrations of the monomers influences the color changes: poly(bis-EDOT-*N*-methylcarbazole) yellow ↔ green ↔ blue [78], poly-(bis-EDOT-pyridine) blue ↔ red ↔ light blue in neutral, radical cation, and dication states [49, 56], respectively. Even four colors can be achieved if the materials are capable of undergoing both p- and n-doping. Poly-(bis-EDOT-pyridopyrazine) has two n-doped states, a neutral state, and a p-doped state, and the respective color changes are as follows: black ↔ red ↔ green ↔ light green [49]. Near-infrared switchable electrochromic polymer has been prepared by the electropolymerization of 2,5-bis-dithienyl-1*H*-pyrrole containing carbazole pendant groups. An electrochromic device based on this polymer has been constructed [75]. A series of *N*-alkylated-2,7-di(2-furyl)carbazoles, *N*-butyl-2,7-di(2-thienyl)carbazole, and *N*-butyl-2,7-di(2-(3,4-ethylenedioxthienyl))carbazole were synthesized by electropolymerization in order to obtain polymers with more extended conjugation lengths and lower energy bandgaps than poly(3,6-carbazole)s. They have low oxidation potentials [<0.57 V vs. ferrocene (Fc/Fc^+)], and the corresponding polymers exhibit good redox properties. The energy bandgaps of the polymers obtained from optical absorption spectra range from 2.1 to 2.3 eV. Among the polymers, poly[*N*-butyl-2,7-di(2-(3,4-ethylenedioxthienyl))carbazole] shows the lowest bandgap energy of 2.1 eV, which is lower than that of previously reported poly(3,6-carbazole) analogs (2.4 eV). This polymer exhibits a significant color change from red in the oxidized state to blue in the reduced state during an electrochemical redox process. The electrochemical and optical properties of the monomers are dependent on external heteroaromatic rings attached to the 2 and 7 positions of the carbazole unit [57]. Electrochromic devices based on poly(3,4-ethylenedioxypyrrole) (PEDOP)–Ag and PEDOP–Au nanocomposites showed a large coloring efficiency in the visible region, for an orange/red to blue reversible transition, and also in the near-infrared region [58].

The photoluminescence of polyaniline has been studied as a function of the polymer redox state. It was stated that each of the three PANI species has fluorescent emissions with different quantum yields. When conductive domains are present, the emission from excitons located either inside these domains or near to them is efficiently quenched [39]. Organic electroluminescent devices (LEDs) are a possible alternative to liquid crystal displays and cathodic tubes, especially for the development of large displays. The principal setup for a polymeric LED is ITO/light-emitting polymer/metal. A thin ITO electrode on a transparent glass or polymeric substrate serves as the anode, while metals such as Al, Ca, or Mg are used as cathode materials. After applying an electric field, electrons and holes are injected into the polymer. The formation of e^-/h^+ pairs leads to the emission of photons. One of most important opportunities to follow from the use of polymeric LEDs is the chemical tuning of the HOMO–LUMO gap of the light-emitting polymers via tailored synthesis. Typical materials used in this context are poly(*p*-phenylenevinylene) (PPPV) [42] and its derivatives or substituted polythiophenes. Heeger collaborating with Wudl started to work with polythiophene and derivatives such as poly (iso-*p*-thionaphthene), with the objective of probing how to tune electronic properties via the molecular structure. Heeger's team had made the first inroads into device applications—making a diode by casting a polythiophene from solution onto electrodes. Heeger remained a major player in the field of light-emitting polymer diodes [53].

The use of PANI as a first layer on the ITO electrode is reported to increase the efficiency of the LED [84, 85] and prevents the degradation of the polymer because

PANI acts as a hole blocker [62]. Quantum efficiencies of 3%, light densities of up to some 1,000 cd m^{-2}, and light efficiencies of 5 lm W^{-1} are made possible using this approach. Polyfluorene is an important blue-light-emitting polymer which has been studied for applications in the emissive layers in LEDs because of its high chemical and thermal stability as well as its high fluorescence quantum yield [86].

Poly(alkylbithiazoles) have received considerable attention because of their n-doping capabilities and applications in LEDs. The nonyl derivative has unusual optical properties due to its crystallinity and π–π stacking behavior. The combination of this n-type electron-accepting compound with a p-type electron-donating monomer (comonomer) was recently attempted [45]. The electropolymerization of bis 3,4-ethylenedioxythiophene (EDOT)–(4,4′-dinonyl-2,2′-bithiazole) leads to a homogeneous and high-quality polymer film (PENBTE) which shows fast electrochromic behavior when switched between its neutral and oxidized states. Both p-doping and n-doping of the polymer are possible, as shown in Fig. 7.5.

The band gap (E_g) was calculated from the difference in the onset potentials. The p-doping involves the thiazole unit, while both the thiazole and EDOT moieties participate in the n-doping [45]. The changes in the visible spectra of PENBTE as function of the potential are displayed in Fig. 7.6.

The color change is illustrated in Fig. 7.7. It is interesting that the oxidized form is transmissive, while the reduced, neutral state shows intense absorption.

Among the various electroluminescent polymers available, poly(1-methoxy-4-(2-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH–PPPV) seems to be a good material to apply in LEDs and also in light-emitting electrochemical cells (LECs). In LECs, the electronically conductive electroluminescent polymer is blended

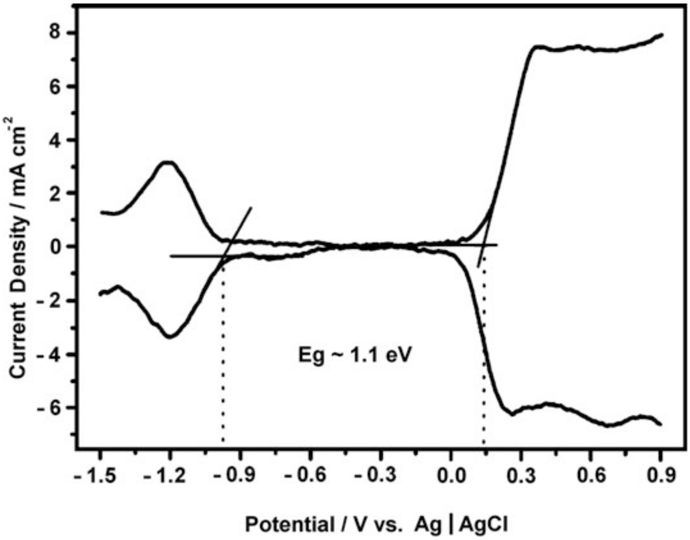

Fig. 7.5 Differential-pulse voltammetry of PENBTE in 0.1 mol dm^{-3} Et_4NBF_4–CH_2Cl_2 (Reproduced from [45] with the permission of Elsevier Ltd.)

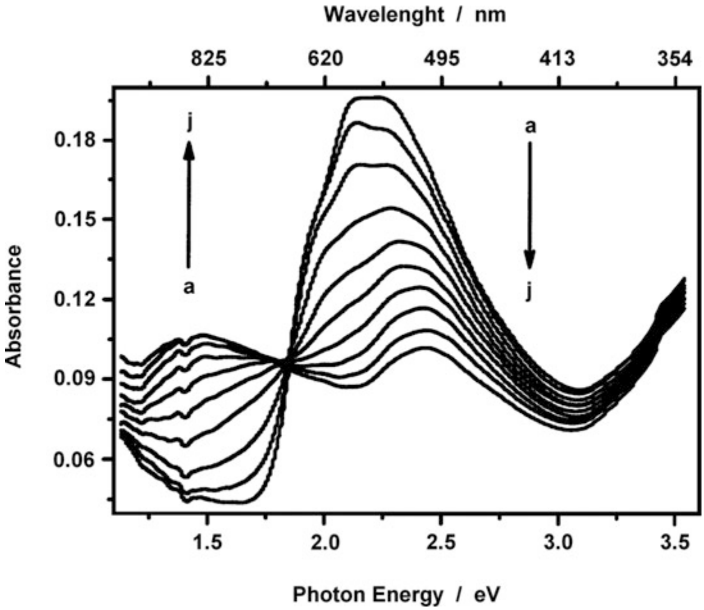

Fig. 7.6 The spectra of a PENBTE film measured at different potentials from 0.4 V (*a*) to 0.8 V (*j*) vs. Ag–AgCl. The potential was stepped up by 100 mV each time (Reproduced from [45] with the permission of Elsevier Ltd.)

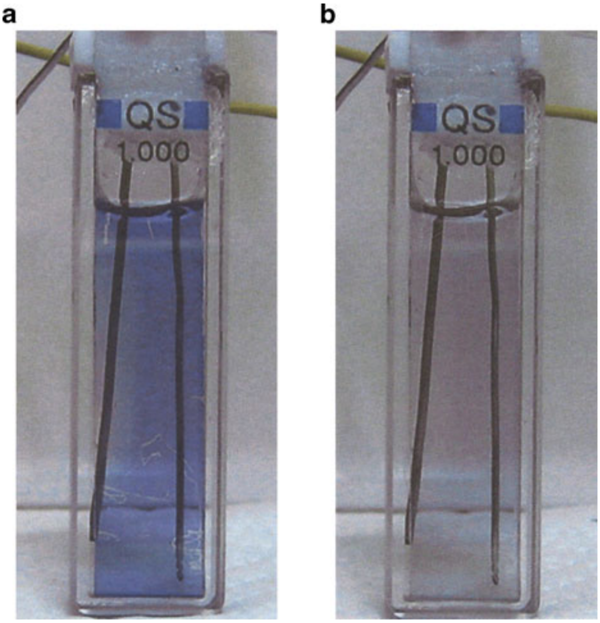

Fig. 7.7 The change in the color of a PENTBE film deposited onto ITO-coated glass: (**a**) reduced state (at −0.4 V) and (**b**) oxidized state (at 0.8 V vs. Ag–AgCl) (Reproduced from [45] with the permission of Elsevier Ltd.)

with an ionically conductive polymer [e.g., poly(ethylene oxide) complexed with CF_3SO_3Li] sandwiched between an anode (typically ITO) and a cathode (e.g., Al). The quantum yield of LECs is generally higher than those of most LEDs due to the better balance of both charge carriers upon injection into the active layer, which takes place when an insulating region is created between n- and p-doped layers (a p–i–n junction).

MEH–PPPV has an advantage over PPP in that it is soluble in several organic solvents and so can easily be prepared as a spin-cast film. A detailed characterization of MEH–PPPV using spectroelectrochemistry and EQCN has been carried out by Goncalves et al. [71].

The electrochemical energy gap was calculated from the difference between the onset potentials of reduction and oxidation (ϕ_n and ϕ_p), which is the usual procedure used to calculate this (see also earlier). In this case, $E_g = 2.35$ eV (see Fig. 7.8).

Note that a probably more accurate method is to derive E_g values from the respective redox potentials; however, in many cases, due to the ill-defined peaks involved, this is a difficult task to execute, and the difference between the values obtained using the two approaches is usually not more than 10–20%. MEH–PPPV also exhibits a reversible color transition, as seen in the UV–VIS spectra displayed in Fig. 7.9.

The in situ absorption spectra of MEH–PPPV show a well-defined isosbestic point around 570 nm, which permits the determination of the optical bandgap, $E_g = 2.18$ eV (λ_{edge}). Using the maximum absorption of the excitonic band, $E_g = 2.51$ eV can be derived, i.e., the electrochemically determined value is exactly intermediate between the minimum and maximum values of the optical bandgaps of MEH–PPPV.

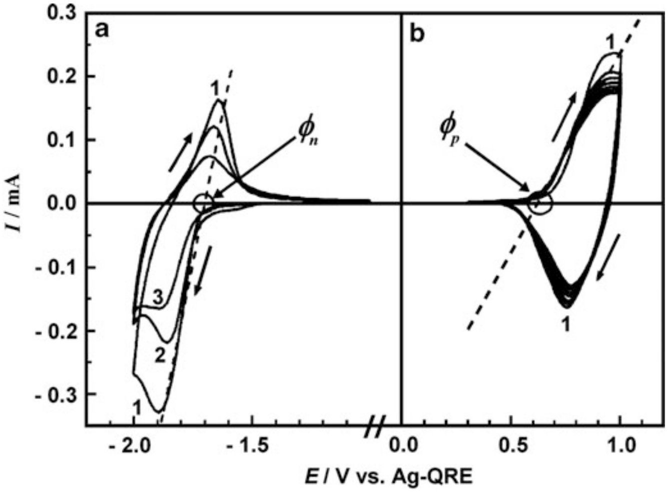

Fig. 7.8 Multicyclic voltammograms of MEH–PPPV films in 0.01 mol dm^{-3} TBAP–acetonitrile with a scan rate of 50 mV s^{-1}. (**a**) Negative and (**b**) positive potential ranges, i.e., *n*-doping and *p*-doping of the polymer (Reproduced from [71] with the permission of Elsevier Ltd.)

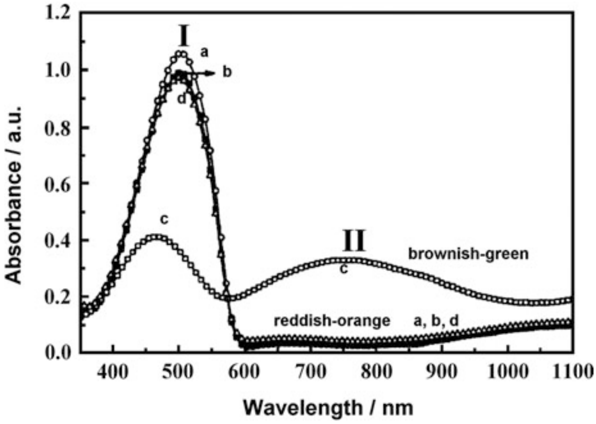

Fig. 7.9 Absorption spectra of MEH–PPPV films in the dry state (*a*) original sample, (*b*) after three voltammetric cycles, (*c*) oxidized at 1 V vs. Ag-quasireference electrode, and (*d*) cycled back to the original form (Reproduced from [71] with the permission of Elsevier Ltd.)

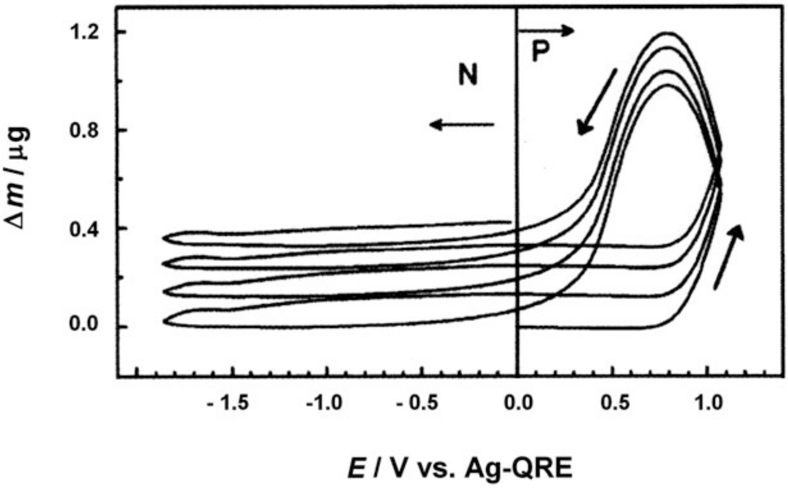

Fig. 7.10 Mass changes observed during the oxidation of MEH–PPPV using the EQCN technique. *P* and *N* indicate positive and negative regions, respectively (Reproduced from [71] with the permission of Elsevier Ltd.)

Results from EQCN studies have revealed that ClO_4^- counterions and two acetonitrile molecules enter the layer in a reversible process during oxidation (Fig. 7.10).

The mass change increases with the number of cycles due to the gradual swelling of the film. In the negative potential region (N), irreversible mass and charge increases occur due to the sorption of solvent molecules [71].

A positively charged ruthenium metal complex ($[Ru(bpy)_3]^{2+}$) was immobilized by ion pairing with a sulfonated conducting polymer poly(2-methoxyaniline-5-

sulfonic acid) (PMAS). The electron transport between the ruthenium metal centers was greatly enhanced due to the interaction with the conducting polymer. Electron transport appears to be mediated through the PMAS conjugated structure, contrasting with the electron-hopping process typically observed in nonconducting metallopolymers. This increased regeneration rate causes the ruthenium-based electrochemiluminescence (ECL) efficiency to be increased, which is of importance concerning the ECL detection of low concentrations of disease biomarkers [47]. The incorporation of $[Os(bpy)_3]^{2+}$ in polyaniline and polypyrrole results in a faster electron transport rate between metal centers and enhanced ECL efficiency [48]. Polymers of carbazole and its derivatives can also be utilized in light-emitting devices. It was found that the anion size strongly affects the performance of the device [61]. Peripheral carbazole substituted ruthenium(II) complexes were prepared and used in organic light-emitting diodes [87]. Electrogenerated chemiluminescence (ECL) of a series of star-shaped donor–acceptor molecules consisting of an electron acceptor 1,3,5-triazine core with three fluorene arms substituted with diarylamino or carbazolyl electron donors has been studied. These compounds exhibit large solvatochromic effects with emissions ranging from deep blue to orange red, as well as high quantum yields [66]. Poly(2,5-di-(thienyl)-furan), which is black in its oxidized state and orange in neutral state according to the fluorescence measurements, is a good yellowish-green light emitter [54]. Poly(*N*-phenyl-2-naphtylamine) exhibited excellent blue-light-emitting and blue-green-light-emitting properties [60].

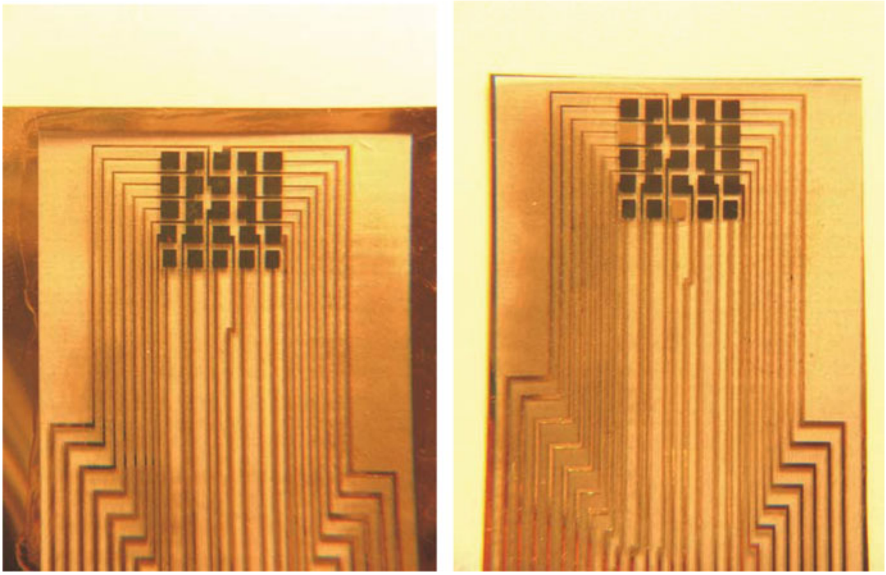

Fig. 7.11 Photos of a PANI-based flexible electrochromic display device containing 25 pixels. The display region and the connections were made by depositing gold on a plastic sheet using an appropriate mask and an evaporation technique. Each pixel can be driven separately. *Left*: PANI is in its oxidized state in all pixels. *Right*: PANI is reduced in two pixels (the bleached ones)

Due to its many advantageous properties (low cost, fast color change, good contrast, stability, etc.), PANI is also a favorite material for use in electrochromic display devices. Pictures of a PANI-based flexible device are shown in Fig. 7.11. The display pattern, which consists of 25 pixels and the connections that allow each pixel to be driven separately, was fabricated by depositing gold onto a plastic sheet. Another plastic sheet covers the display. The electrochemical switching is executed using a counterelectrode, which also serves as a reference electrode, and an acidic gel electrolyte is placed between the two sealed plastic sheets.

7.2.3 Membranes and Ion Exchanger [88–98]

Conducting polymers can be regarded as membranes due to their porosity [88–98]. They could therefore be used to separate gas or liquids. Free-standing (on supporting substrates) chemically prepared PANI films are permeated selectively by gases. In general, the larger the gas molecule, the lower the permeability through the film.

Several studies have reported a switchable permeability for water and organics that is dependent on the redox state. For electrochemically formed PANI and PP on metal or conducting grids, a large increase in water permeability was observed for doped films compared with undoped (reduced) films. This can be explained by structural changes and an increase in hydrophilicity during oxidation [94]. Membranes of 3-hexyl-PT show a decrease in permeability for dopamine with increasing oxidation [95]. Different permselectivities for anions were found and studied [90]. Polypyrrole–polystyrene sulfonate electrodeposited on porous carbon was prepared for water softening by removal of Ca^{2+} ions [93]. Composites of polypyrrole and Cladophora cellulose have been investigated in order to use those for desalting and extraction of proteins and DNA from biological samples [91]. Despite the ability to switch the selectivity and the excellent separation effects observed for some systems, technical applications of these effects are relatively scarce due to low stability and a lack of pinhole-free materials. A method for coating membranes with polypyrrole (PP) has been developed, recently. Different membranes, such as microfiltration as well as ion exchanger membranes, have been coated with PP to yield electrical conductivity of the membranes. PP can be tailored as cation or anion exchanger, and its porosity can be controlled to avoid any impairment of the membrane by the polymer layer. These PP-coated membranes can be applied as electrochemically switchable, functionalized membranes with controllable and variable separation properties [96].

7.2.4 Corrosion Protection [88, 99–148]

Conducting polymers can be deposited as a corrosion protection layer [3, 24, 25, 88, 99–148]. Work in this area is partly motivated by the desire to replace coatings that are hazardous to the environment and to human health. Since the equilibrium potentials of several electronically conducting polymers are positive relative to those of iron and aluminum, they should provide anodic protection effects similar to those provided by chromate(VI) or similar inorganic systems. Either electropolymerization or chemical oxidation of the respective monomer can be used to form the coating. An alternative approach is to use preformed polymers that had been rendered soluble by applying substituted (e.g., alkylsulfonated) monomers. Conducting polymer colloids have also been tried. The cheap and effective polymers PANI, PP, and PT (and their derivatives) have mostly been used [25, 133, 144, 147]. The favorite substrate used in such investigations is mild steel, but aluminum, copper, titanium, or even dental materials have also been discussed [24, 25]. Figure 7.12 shows the Tafel plots obtained for bare steel and PANI-coated steel, respectively, in contact with a 3% NaCl solution [141].

The conducting materials are applied directly by electrodeposition onto the active material [3] or by coating with formulated solutions of these polymers. The efficiency and mechanism of the corrosion protection provided are not yet fully clarified. Anodic protection on iron has been discussed [24, 99]. Several authors have proposed that the passivation is achieved because the doped emeraldine salt form of PANI keeps the potential of the underlying stainless steel in the passive region [107, 138, 140]. However, other authors claim that the mechanism by which PANI protects the underlying metal surface from corrosion is independent of the doping level [114]. Due to the redox processes taking place, thick layers of iron oxide are formed and are stabilized against dissolution and reduction. Inhibition is also reasonable due to geometric blocking and reduction of the active surface. The effects of the different polymer layers on the corrosion protection may be rather diverse. For instance, EIS and polarization resistance

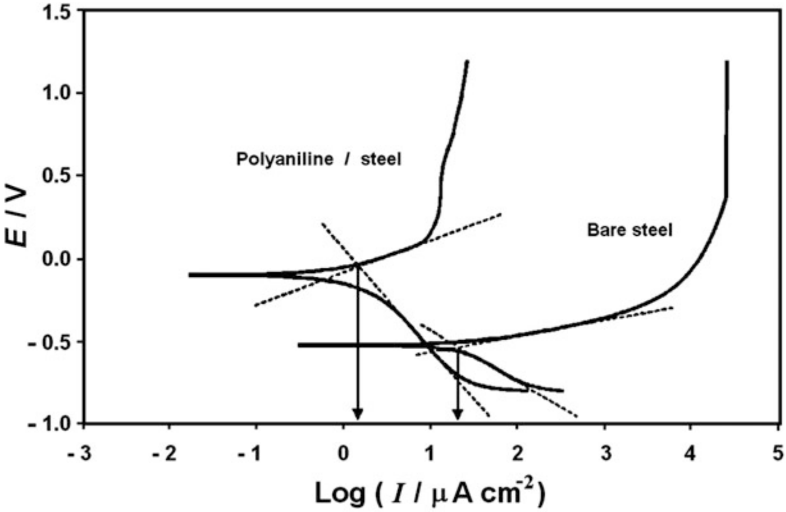

Fig. 7.12 Tafel plots (potential vs. log current) for PANI-coated steel and for bare steel in 3% NaCl (Reproduced from [141] with the permission of Elsevier Ltd.)

measurements have shown that polypyrrole film reduces the corrosion protection efficiency of epoxy coating on mild steel in 3.5% NaCl solution when it is used as the primary film under the epoxy layer. On the other hand, a PANI coating significantly improved the protection efficiency of the epoxy coating against mild steel corrosion. It was related to the healing effect of PANI upon surface passivation along a defect (scratches) [142]. Polyaniline–poly(*o*-phenylenediamine) copolymer shows a better performance than polyaniline itself concerning the protective properties of stainless steel in chloride containing media due to the hindered anion sorption [148]; however, poly(*o*-phenylenediamine) alone has also been recommended [116].

Poly(*o*-phenylenediamine) coating effectively inhibits the adhesion of biofilm on aluminum aeronautical alloy due to its biocidal property; therefore, it can be used for the protection of fuel storage tanks [134]. Polyindole lowered the permeability against the attack of corrosive environment [143]. Poly(*o*-toluidine)–CdO nanoparticle composite was prepared for the corrosion protection of mild steel [104]. Films of polyaniline and poly(methylmethacrylate-*co*-acrylic acid) offer a better corrosion protection to the aluminum alloy used in the Brazilian can industry than the commercial epoxy resin films [131]. Poly(vinylcarbazole) was also proposed as anticorrosion coatings on steel coupons or indium–tin oxide [110]. Poly (pyrrole-*co*-phenol) from solutions containing dodecyl benzene sulfonic acid and oxalic acid was deposited on steel, and the effective barrier of the coating was investigated [121].

Another strategy for corrosion prevention using conducting polymers is to incorporate inhibitor anions into the polymer coatings. This approach has been trialed by coating mild steel and zinc substrates with PP containing anions as such molybdates or 3-nitrosalicylate [132]. However, as well as the corrosion of metals, that of semiconductor electrodes can also be decreased by using conducting polymers that fill holes, thus preventing the oxidation of the semiconductors. For instance, it has been found that ferrocene polymers enhance the stability of Si [102, 145], GaAs [102], and Ge [142]. Nafion/TTF was used successfully in the case of Si [129]. Polypyrrole protects n-Si [122, 130], n-CdS, n-CdSe, and n-GaAs [130]. Good results have been obtained by using PANI to protect n-Si, N-CdS, n-CdSe, and n-GaAs [129] and PT to protect n-CdSe and n-CdS [115], while polycarbazole diminished the corrosion of InSe [109], and polyindole was effective in the case of n-MoSe$_2$ [106].

7.2.5 Sensors [8, 149–308]

The use of conducting polymers in sensor technologies involves employing the conducting polymers as an electrode modification in order to improve sensitivity, to impart selectivity, to suppress interference, and to provide a support matrix for sensor molecules [1, 5, 8, 9, 12, 18, 21, 149–305]. All electrochemical transducer principles can also be realized with conducting-polymer-modified electrodes.

The role of the conducting polymer may be active (for instance, when used as a catalytic layer, as a redox mediator, as a switch, or as a chemically modulated resistor, a so-called chemiresistor) or passive (for instance, when used as a matrix) [5, 8, 12, 18, 21, 22, 197, 210, 224, 228, 235, 294].

7.2.5.1 Gas Sensors

Gas sensors made of conducting polymers have high sensitivities and short response times, and—a great advantage compared with most commercially available sensors based on metal oxides—work at room temperature [1, 9, 149–190]. Polyaniline [149, 152, 157, 160, 163, 165, 167, 168, 170, 172–175, 177, 181, 184, 185, 188], polypyrrole [150, 151, 154, 156, 161, 166, 169, 180], and polythiophene [155, 164, 171, 178, 179, 186, 187, 189] have usually been used in gas sensor devices. The sensing principles employed in gas sensors using conducting polymers as active sensing materials vary. The principle used depends on the variables (resistance, current, absorbance, mass, etc.) measured and the type of interaction between the gas (analyte) and the polymer. Although the interaction mechanism is not entirely clear for every case, the electron-donating or electron-withdrawing ability of the gas usually plays the determining role. The oxidation state (the charge or doping level) of the polymer is altered by the transfer of electrons from the analyte to the polymer, which causes a change in the properties (resistance, color, work function, etc.) of the polymer.

Electron-donor gases such as NH_3 increase the resistance of PANI [149, 153, 159, 160, 163, 165, 167, 168, 172, 177, 188, 273] or PP [150, 151] because the electrons transferred neutralize the positive sites (polarons), and the polymer becomes neutral. Interestingly, this is a reversible process; after flushing the polymer with air, the conductivity of the polymer (sensing layer) is recovered (Fig. 7.13). Electron acceptor gases or vapors such as NO_2 and I_2 usually enhance the electrical conductivity by removing electrons from the polymer, resulting in the formation of a p-type conducting polymer.

However, the situation is more complicated; for example, ammonia causes an increase in the conductivity of polycarbazole [134, 158]. In the case of PANI, it is most likely that NH_3 also causes deprotonation and contributes to increasing its resistance. This mechanism is supported by the observation that gases or vapors that are able to transfer protons to PANI (e.g., HCl, H_2S, or H_2O) are able to enhance the conductivity of this polymer [160, 162, 171, 175, 188].

Chemiresistors consist of one or several pairs of electrodes and a layer of polymer possessing variable conductivity connecting the electrodes (see Figs. 7.14 and 7.15). Interdigitated electrode arrangements are also widely used. Chemiresistors are the most popular device configuration for gas sensors. In some cases, ac current is also applied. Diode and transistor arrangements can also be fabricated. The transistors consist of an active semiconductor layer (e.g., p-Si) in contact with two electrodes (the "source" and the "drain") and a third electrode (the "gate"), which is separated from the semiconductor layer by an insulator. In this

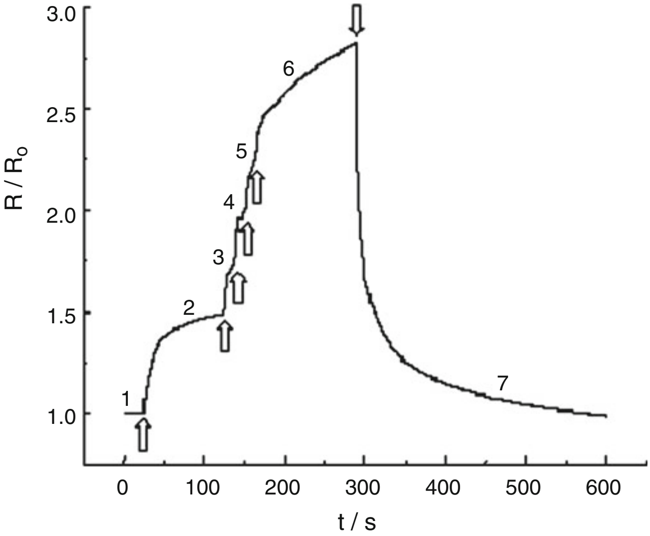

Fig. 7.13 The response of a PANI gas sensor (relative resistance vs. time curves at 20°C). 10 ppm ammonia was injected into the air at times indicated by the *arrows*. The total concentrations were (*1*) 0, (*2*) 10, (*3*) 20, (*4*) 30, (*5*) 40, (*6*) 50 ppm, and (*7*) after flushing with clean air again [163]

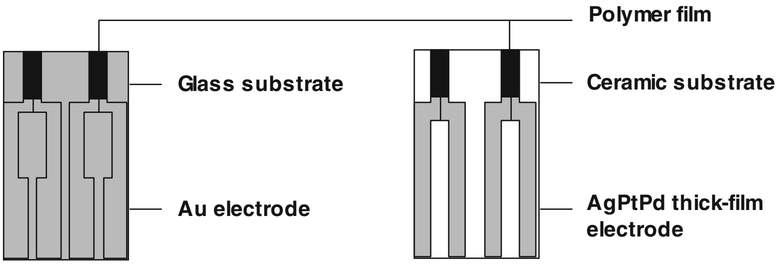

Fig. 7.14 Layout designs of thin-film and thick-film polymer gas sensors [163]

device, the conducting polymer acts as a gate that reacts with the gases, causing its work function to change and therefore modulating the source–drain current. Another widely used arrangement is the field effect transistor (FET). Such an arrangement is shown in Fig. 7.15.

In the case of gas sensing, the charge level of the conducting polymer (e.g., polyaniline) layer will change (this can also be varied by changing its potential with a potentiostat, as shown in Fig. 7.15).

Until the source–drain voltage (V_D) is smaller than the difference between the gate voltage (V_G) and the threshold potential (V_T), i.e., $V_D < V_G - V_T$, the source–drain current (I_D) is linearly dependent on V_D:

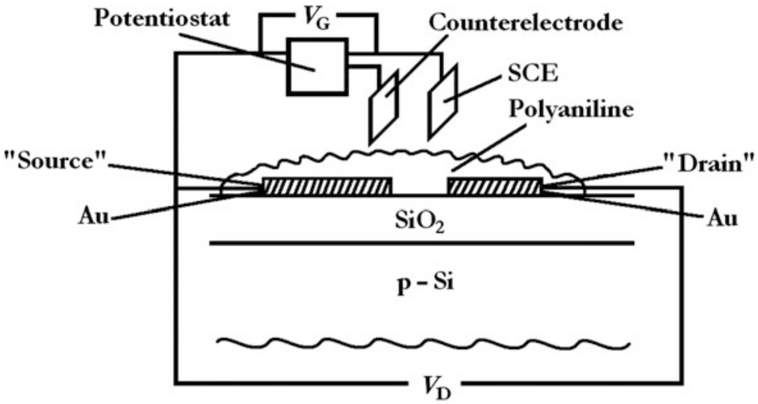

Fig. 7.15 Configuration of a polyaniline-based microelectrode device [273] (Reproduced with the permission of the American Chemical Society.)

$$I_{\mathrm{D}} = \frac{\mu CW}{L}\left(V_{\mathrm{G}} - V_{\mathrm{T}} - \frac{V_{\mathrm{D}}}{2}\right)V_{\mathrm{D}}, \tag{7.1}$$

where μ is the mobility of the minority charge carrier, C is the gate capacitance, and W and L are the width and the length of the channel, respectively. In the saturation region $V_{\mathrm{D}} > V_{\mathrm{G}} - V_{\mathrm{T},}$

$$I_{\mathrm{D}} = \frac{\mu CW}{2L}(V_{\mathrm{G}} - V_{\mathrm{T}}). \tag{7.2}$$

Chemically sensitive FETs are called CHEMFETs. If the coating of the gate of the FET is gas sensitive, the term GASFET is used instead. When the polymer acts as an ion exchanger with protons or other ions, it results in a pH-sensitive or ion-sensitive device called a pH-FET or ISFET. For instance, a potassium-sensitive device is called a K-ISFET.

In diodes, the conducting polymer (usually a p-type semiconductor) is in contact with an n-type semiconductor or a metal. In the former case, a heterojunction can form at the interface, while in the latter case, a Schottky barrier can be created. The relation between the current density and the voltage is described by Richardson's equation [273]:

$$J = A^{*}T^{2}\exp\left(-\frac{\varphi_{\mathrm{B}}}{k_{\mathrm{B}}T}\right)\exp\left(\frac{eV}{nk_{\mathrm{B}}T}\right), \tag{7.3}$$

where A^{*} is the effective Richardson's constant, φ_{B} is the effective barrier height, k_{B} is the Boltzmann constant, n is the ideality factor, e is the elementary charge, and T is the temperature. The charge level of the polymer will change under the influence of the analyte, which causes a variation in φ_B. Consequently, either the current (J) or the voltage (V) can be measured.

The conductivity of the polymer layer may also depend on the physical state of the polymer. For instance, the sorption of organic vapors (e.g., alcohol) [152, 161, 164, 184] or acetone [180] causes a swelling of the polymer that alters the rate of interchain electron hopping. The mass change caused by the sorption can be followed by a piezoelectric quartz-crystal nanobalance (QCN) or by surface acoustic wave (SAW) sensors. Optical changes can also be detected, although this effect is less frequently utilized in gas sensors.

Gas sensors based on conducting polymers have high sensitivities but (usually) low selectivities. They respond to different gases (NH_3, CO_2, CO, HCl, H_2S) and vapors, for example, alcohols, acetone, or nitroaromatic explosives [186]; water (humidity) [170, 174] also influences their properties. However, the composition of gas mixture can be calculated by using an array of several units containing different polymers possessing different sensitivities for different gases (an artificial nose). Amperometric sensors have also been used for the detection of gases; however, proton-conducting membranes like Nafion are usually utilized in these systems.

7.2.5.2 Electroanalysis and Biosensors

Another large field of application for conducting polymers in chemical analysis is the detection of ions and molecules in the liquid phase [5, 182, 194, 227, 234, 246, 294, 296, 306]. The development of biosensors has been an especially significant field over the last two decades [5, 8, 18, 21, 192, 194, 196–199, 203, 206, 207, 209, 212, 213, 218, 219, 225, 226, 228, 229, 234, 238, 249, 250, 258–260, 268, 272, 274, 276, 280, 281, 283, 288, 290, 292, 297, 302, 307]. Conducting polymers show sensitivities toward anions or cations since Nernstian behavior is expected in relation to the counterions. However, their selectivities are usually not very good. Therefore, EDTA [227] or ionophores have been attached to the polymers in order to detect small cations. Polythiophenes have been modified by acyclic and cyclic polyethers [22, 264], and similar compounds based on PP have also been tested [267]. Calixarene with built-in PT and PP has been investigated [206, 213]. Anion detection using polymers with positively charged groups or polymers functionalized with such groups has been attempted. Determination of chloride in fuel ethanol using a polyaniline chemically modified electrode in flow injection analysis has been reported [215].

The use of conducting polymers as amperometric sensors, where the detection signal is amplified due to the catalytic properties of the polymer and/or built-in catalytic entities, is straightforward, although the application of these systems as ion-selective electrodes in potentiometry is problematic because redox state and acid–base or ionic equilibria need to be controlled simultaneously. Nevertheless, several attempts have been made to fabricate ion-selective electrodes based on conducting polymers [244, 257]. Chemiresistors based on conducting polymers have been reviewed, recently. This review covers the development of measurement configurations: beside the usual two- and four-electrode methods, the simultaneous application of the two- and four-electrode measurement configurations is also evaluated. An incorporation of two additional electrodes controlling the redox state of chemosensitive polymers and connecting to the measurement electrodes through liquid or (quasi)solid electrolyte results in a six-electrode technique: an electrically driven regeneration of such sensors allows one to perform fast and completely reversible measurements [254].

Conducting polymers have attracted much interest as suitable matrices for entrapping enzymes. The conducting polymers used in this context must be compatible with biological molecules in aqueous solutions over the physiological pH range. The conducting polymers can transfer the electric charge produced by the biochemical reaction to an electronic circuit. Enzymes such as glucose oxidase (GOD), nicotinamide adenine dinucleotide-dependent dehydrogenases, horseradish peroxidase (HRP), and urease have been immobilized in conducting polymer films via electrostatic interactions, complex formation, van der Waals forces (adsorption), or covalent bonds. The formation of cross-links and covalent binding may cause a decrease in the enzymatic activity. Enzymes can be incorporated as counterions into the conducting polymer network during electropolymerization or into the positively charged film later on, since the surface charges of most enzymes at physiological pH are negative. A redox mediator (e.g., ferrocene or quinone) is usually also applied in order to ensure the transfer of electrons from the electrode to the enzyme [228]. The scheme for such an electroanalytical sensor is shown in Fig. 7.16.

The detection of biologically active molecules with high selectivity is a very important task for researchers working in the field of analytical electrochemistry. Biosensors fabricated from conducting polymers and enzymes can be utilized in various fields, such as in medical diagnosis and food analysis in order to detect glucose, fructose, lactate, urea, cholesterol, ascorbic acid, etc.; in immunosensors and DNA sensors; and also for monitoring hazardous chemicals, for example,

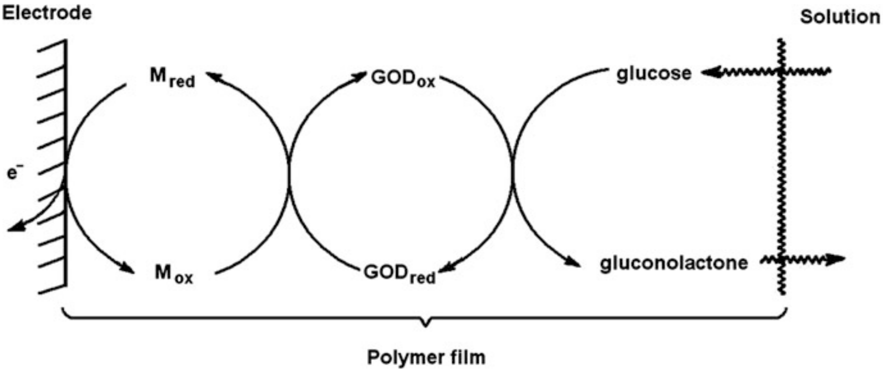

Fig. 7.16 Scheme for an amperometric electrode for glucose determination where GOD is immobilized in a conducting polymer film which contains a redox mediator (M)

peroxides, formaldehydes, phenols, etc. We will present typical examples below. An intense search for effective glucose sensors is underway. Polypyrrole has usually been used for the immobilization of GOD [199, 212, 225, 249, 258, 260, 292]; however, PANI [196, 260], poly(*o*-phenylenediamine) [258], and poly(neutral red) [274] have also been applied. PANI is less frequently used in biosensors because at low pH values, where the formation of polyaniline takes place and where this polymer is conductive, enzymes are usually less stable. Amperometric biosensors for glucose have also been prepared by immobilizing GOD onto ferrocene containing a siloxane-based copolymer (Fig. 7.17), which acts as an electrocatalyst for either the oxidation or the reduction of H_2O_2 that arises during the enzyme-catalyzed reaction [194]. The structure of the siloxane-based copolymer containing pendant dendritic wedges that possess electrically conducting ferrocene moieties and electrocatalytic activity toward the oxidation of H_2O_2 is presented in Fig. 7.17.

Figure 7.18 shows a calibration plot for H_2O_2 obtained when a Pt electrode was covered with a layer of the ferrocene-containing copolymer.

A calibration plot for amperometric glucose determination using a Pt–ferrocene polymer–GOD electrode is displayed in Fig. 7.19. An efficient electrochemiluminescent sensor for H_2O_2 determination was proposed, which was based on poly (luminol-3,3′,5,5′-tetramethylbenzidine) electrode. It can be used for the determination of oxidase substrates in single-use biosensors [195].

A polyaniline-based, electron-conducting, glucose-permeable, redox hydrogel was formed in one step at pH 7.2 by cross-linking polymer acid-templated polyaniline with a water-soluble diepoxide, poly(ethyleneglycol diglycidyl ether). Coimmobilization of GOD in the hydrogel, by co-cross-linking in the same step, led to the electrical wiring of the enzyme and to the formation of a glucose electrooxidation catalyst, allowing the electrocatalytic oxidation of glucose at a steady-state current [263].

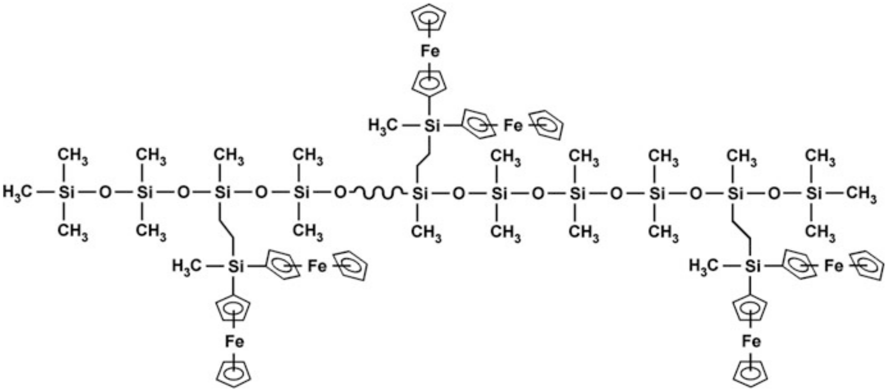

Fig. 7.17 The structure of the siloxane-based copolymer containing pendant dendritic wedges that possess ferrocenyl moieties (Reproduced from [194] with the permission of Elsevier Ltd.)

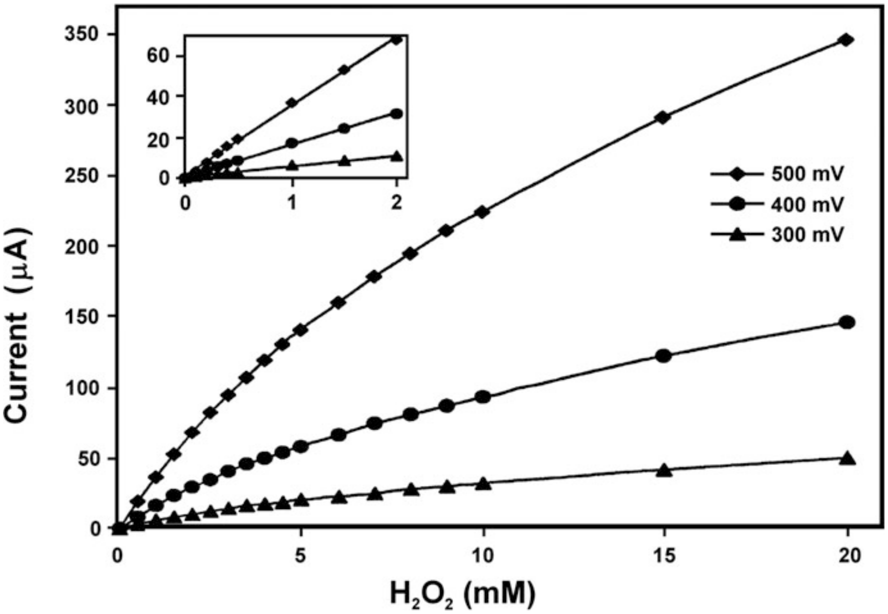

Fig. 7.18 Calibration plots for hydrogen peroxide oxidation obtained using Pt coated with a ferrocene-containing siloxane-based copolymer at three different potentials, as indicated in the figure. The surface concentration of the copolymer was 1.7×10^{-9} mol cm^{-2}. Solution: deaerated 0.1 mol dm^{-3} pH 7 phosphate buffer (Reproduced from [194] with the permission of Elsevier Ltd.)

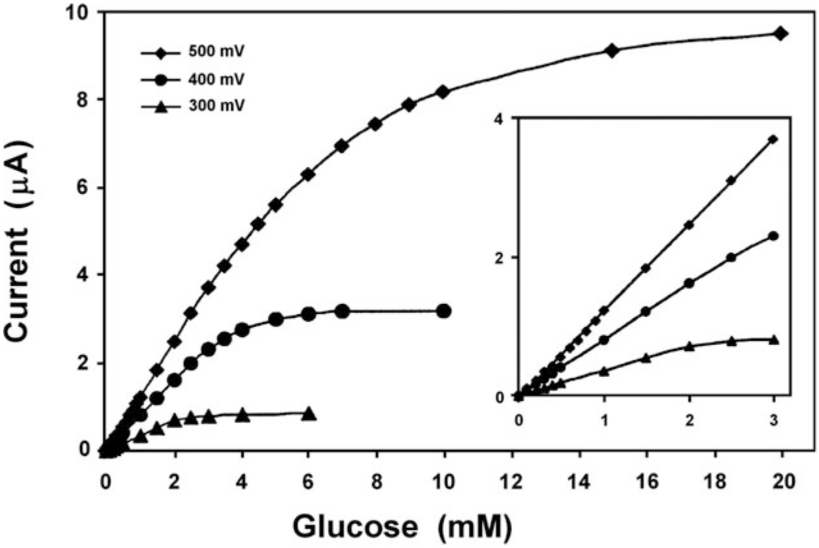

Fig. 7.19 Calibration plots for glucose determination using a ferrocene-containing siloxane-based copolymer (see Fig. 7.17) and GOD enzyme. Solution: air-saturated 0.1 mol dm^{-3} pH 7 phosphate buffer (Reproduced from [194] with the permission of Elsevier Ltd.)

In contrast to GOD, HRP can undergo direct electron transfer; i.e., no mediator is required, since this process is very fast [198]. The application of GOD and HRP together has been proven to be a successful strategy [268, 290]. Bienzymatic systems such as glutamate oxidase + HRP/PANI and lactate oxidase + HRP/PANI have also been used to detect glutamic acid and lactate, respectively [268]. Conducting polymer films can also possess advantageous permselective properties which improve selectivity toward the target molecules.

Urea biosensors containing urease are based on the detection of NH_4^+ and HCO_3^- [8, 229, 272]. Lactate dehydrogenase immobilized in PANI was used for lactate measurements [8]. Cholesterol sensors have been fabricated using cholesterol oxidase absorbed in PP, in which ferrocene carboxylate [238] or hexacyanoferrate (III) [250] was applied as mediators. Electroplated conducting polymers were also used as antibody receptors in immunosensors [276].

DNA recognition has been achieved, for example, by the sorption of DNA in PP [295] or by PP functionalized with a covalently linked oligonucleotide [259]. Poly (vinylferrocenium) (PVF^+)-modified electrode was developed for the improved electrochemical sensing of DNA based on the oxidation signals of polymer and guanine. Experimental parameters, such as the polymeric film thickness, the DNA immobilization time, the concentration of buffer solution, pH, and DNA concentration, were examined in order to obtain more sensitive and selective electrochemical signals. DNA hybridization was also investigated [252]. A simple and label-free electrochemical sensor for recognition of the DNA was prepared by electrochemical polymerization of 4-hydroxyphenyl thiophene-3-carboxylate. The detection limit of the sensor was 1.49 nmol, and it had a good selectivity [293]. Polyfluorenylidene containing ferrocene units was applied for catechol oxidation [277]. Polymerized eriochrome black T exhibited electrocatalytic activity toward the oxidation of dopamine and ascorbic acid [222].

The effect of mediator distance from the polymer backbone on the redox behavior, electron transport, electrochemical stability, and electrical communication with redox enzymes was studied with novel linear poly(ethylenimine) redox polymers. Increasing the spacer length to either three or six carbons resulted in a single peak redox behavior over the entire pH range and also resulted in a sixfold increase in the electrochemical stability of cross-linked redox polymer films. Electron transport increased with spacer length, and no correlation between mediator spacing and electron transport or electrical communication with the enzyme GOD was observed. It was found that the complexation between the polymer and the enzyme was important and concluded that small changes in the redox polymer structure could substantially affect its properties [265]. Electrocatalytic activity toward the oxygen reduction of fungal laccase entrapped in poly (*o*-phenylenediamine) matrix was tested [271].

Deoxyguanosine-triphosphate and 5′-phosphate-modified deoxyguanosine oligonucleotide (an oligomer containing 20 monomer units) were immobilized in polythionine [219].

In [218], the use of Nafion-coated electrodes for the in vivo measurement of neurotransmitters was discussed. These polymers may have electrocatalytic properties. It has been reported that PP and PANI catalyze the oxidation of ascorbic acid [209], dopamine [283], and quinines [236]. Poly(acridine red) can promote the oxidation of dopamine, and a detection limit of 1×10^{-9} mol dm^{-3} can be reached using differential-pulse voltammetry, even in the presence of ascorbic acid [307]. The electrocatalytic activity of poly(3-methylthiophene) can be utilized for detecting catecholamines [246].

Poly(methylene blue), in which methylene blue entities are preserved [203, 241–243, 247, 248, 284, 289], is a very good catalyst for the oxidation of hemoglobin. This property has been utilized in an amperometric sensor [203] (see Figs. 7.20 and 7.21). A good correlation was found between the results of the electrochemical

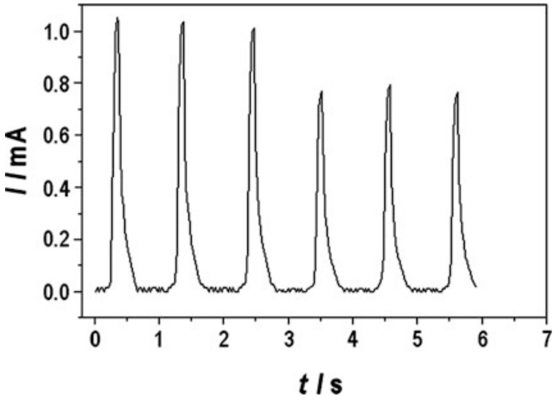

Fig. 7.20 Chronoamperometric responses for consecutive injections into a flow cell of samples of whole blood diluted 1:10 in phosphate buffer (pH 6.24) and 0.5 mol dm^{-3} NaCl on a poly (methylene blue) electrode at $E = 0.4$ V vs. SCE. Flow rate: 4 ml min^{-1}. The *tall* and *short waves* are the responses to 6 and 4 cm^3 dilute solutions, respectively

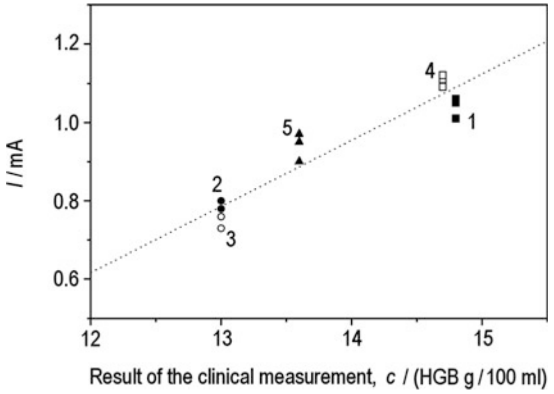

Fig. 7.21 Comparison between electrochemical and cyanidation methods for the analysis of blood samples provided by five donors. Blood samples *2* and *3* were from females, while *1* and *4* were from male patients. Patients *1–4* were healthy, while patient *5* was a potentially ill donor. Experimental conditions were the same as for Fig. 7.20

method and those of the spectrophotometric cyanidation analysis method, which is used in clinical practice as a standardized protocol. Poly(methylene blue) was also used for the electrocatalytic oxidation of pyridoxine hydrochloride (vitamin B6), which results in the formation of pyridoxal. A linear dependence was found between the electrocatalytic current and the concentration of vitamin B6 [289]. A composite of poly(methylene blue) and multiwalled carbon nanotubes (MWCNTs) has been developed, which showed a good stability, high reproducibility, and catalytic activity on different biochemical compounds such as vitamin C, epinephrine, dopamine [305]. Methylene blue electropolymerized on an ionic-liquid-modified carbon paste electrode showed excellent catalytic response to 3,4-dihydroxybenzoic acid [308]. Au nanoparticle–polyaniline nanocomposite layers are obtained through layer-by-layer adsorption for the simultaneous determination of dopamine and uric acid [288]. Poly(1-aminoanthracene) has also been proposed for the determination of dopamine [291]. Electrodes covered with redox active polymer derived from Direct Blue 71 azo dye have also been suggested for the determination of ascorbic acid [251]. Poly(4-aminobenzoic acid) [232] and poly(methyl red) [232] were successfully employed to determine tryptophan in pharmaceutical samples. The relationship between the structure of different polyazines and their ability for NADH oxidation both for sensors and biofuel cell applications has been investigated in detail [278].

Poly(toluidine blue) electrode was used as a nitrite amperometric sensor [303]. Because this compound also exhibits good electrocatalytic activity toward NO, such a sensor was also developed [296]. Poly(copper-tetraaminophthalocyanine), deposited on porous alumina by electropolymerization, was also proposed as amperometric sensor for NO [223]. The product of the electroreduction of NAD^+ was identified as enzymatically active NADH at poly(neutral red) electrodes, which is a very important recognition regarding the application of PNR electrodes in the study, and the electrochemical regeneration of nicotinamide adenine dinucleotide [240].

However, conducting polymers that do not have special catalytic groups are usually not very good catalysts. Therefore, their performances can be improved by using substituted polymers or, more frequently, catalytic moieties such as metallic particles [200, 253], oxometalates [245, 282], ferrocene [221], etc., that have been immobilized in the polymer films. The hybrid of polypyrrole and nickel hexacyanoferrate was synthesized in order to enhance the reduction of H_2O_2. It was also used in an oxalate biosensor after immobilization of oxalate oxidize enzyme [220]. PEDOT doped with hexacyanoferrate was applied in Cu^{2+}-selective electrodes [269]. Poly(*N*-acetylaniline) or Prussian blue composite film was prepared electrochemically and showed high electrocatalytic activity toward the reduction of H_2O_2 [300]. Poly(2-[(ε-2-azulene-1-yl)vinyl] thiophene) (PAVT) and Prussian blue (PB) were combined in order to obtain new composite materials with peculiar properties in phenol detection. Under the optimal experimental conditions, the peak currents were proportional to the concentrations of phenol in the range from 30 to 100 nM [255]. Polyaniline was encapsulated in interconnected pore channels of mesoporous silica, and the resistance of the composite linearly changed with the relative humidity of the environment [216]. Polyaniline doped with poly (vinylsulfonate), containing in situ deposited tyrosinase enzyme was prepared and served both as an efficient mediator and biocompatible enzyme immobilization platform [261]. Two types of biosensors were designed by immobilizing tyrosinase on polypyrrole and PEDOT with regard to the synthesis of 1-3, 4-dihydroxi phenylalanine (L-dopa) [217]. Poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) composite in combination with graphite–poly(dimethylsiloxane) was fabricated and applied as flexible microelectrode arrays for the capture of cardiac and neuronal signals in vivo [201]. Impedimetric immunosensor using a membrane of poly(*o*-phenylenediamine) with antibodies was developed for the high-throughput screening of liver fibrosis [230]. The effects of β and γ irradiation on conducting polymers for sensor application were also studied. It has been concluded that chain scission and the formation of free radicals as well as chain cross-linking were responsible for the degradation of conductivity [239]. Molecular imprinting, i.e., a synthetic approach to mimicking molecular recognition properties of natural systems, has been developed in the last decades. It is achieved by inducing the substrate-selective recognition in an artificial matrix by using a template. Conducting polymers, for example, polypyrrole, are suitable systems for this purpose. The first step is prearrangement of the functional monomers around the template by using some kind of interactions between them. It is followed by the formation of cross-linked polymer, and then the template can be removed. Now, there will remain an imprinted site, which can rebind the template molecules or species similar to the template in the spaces vacated by the templating species via combination of steric exclusion and specific interactions [298].

7.2.6 Materials for Energy Technologies [309–375]

The ability to reversibly switch conducting polymers between two redox states initiated their application to rechargeable batteries [313, 315, 317, 319, 320, 322, 326, 329–331, 336–338, 340, 341, 343, 344, 346, 348–350, 353, 367, 371, 373]. The first prototypes of commercial batteries with conductive polymers used Li/polypyrrole [337] (Varta-BASF) or Li/polyaniline [340, 341, 353]. It was demonstrated that high charge densities can only be achieved in Li–PANI–propylene carbonate-based batteries when PANI is dried thoroughly. The presence of traces of sorbed water in PANI results in significant degradation during the first oxidation. A significant increase in the energy densities of rechargeable, polymer-based Li batteries to values of >100 Wh kg^{-1} and >150 Wh L^{-1} can be expected only if Li^{+} plays the role of the charge-compensating ion, i.e., by modifying conducting polymers with negatively charged groups [320]. Currently, development is focused on new cathode materials for lithium batteries. Even exotic systems such as the fullerene-functionalized poly(terthiophenes) (see Sect. 2.3.4) have been proposed as cathode materials for Li batteries [317]. Good results were obtained with substituted polythiophenes and poly(1,2-di(2-thienyl)ethylene). A flexible fiber battery has been constructed consisting of a PP/PF_6 cathode and a PP/PSS anode [374]. Unresolved problems include the insufficient cycle stability of the system compared with inorganic systems and its high discharge rate. A detailed review is given in [346].

Conducting polymers have been shown to be highly effective when used as protective layers on anodes in fuel cells [345, 357, 360]. It was demonstrated that platinum electrocatalysts covered with PANI [360] or fluorinated polyaniline [345] are effective anodes in microbial fuel cells, in which living microbial cultures are used as biocatalysts for the degradation of organic fuels. In particular, 2,3,5,6-tetrafluoroaniline is well suited for use in these batteries due to its high stability toward microbial and chemical degradation [345]. For instance, in cultures of *Chlamydomonas reinhardtii*, a green algae, photosynthetically produced hydrogen was oxidized in situ in a fuel cell compartment containing such anodes [357]. A biofuel cell electrode based on poly(vinylferrocene-*co*-acrylamide)-grafted carbon was developed to obtain high current density. This electrode was employed as a glucose-oxidizing anode, using GOD as an enzyme [367]. All polymer battery has been developed where styryl-substituted dialkoxyterthiophene polymer cathode and polypyrrole anode were applied [373]. An ultrafast polypyrrole-based battery has been developed where the nanostructured high-surface area electrode material for energy storage applications composed of cellulose fibers of algal origin individually coated with a 50 nm thin layer of PP. This aqueous batteries can be charged with currents as high as 0.6 A cm^{-2}; the charge capacity is 25–50 mAh g^{-1}. These lightweight energy storage systems are environmentally friendly and cheap [349].

Another field of application is provided by the excellent ionic conductivities of conducting polymers, which permit high discharge rates. Their use as electrode materials in supercapacitors [73, 311, 312, 314, 318, 321, 324, 328, 333, 335, 339, 342, 363, 365, 366, 375] is a good example. Supercapacitors require high capacitance and quick charge/discharge electrode materials. Compared with classical used carbon materials, conducting polymers show promising characteristics [312]. Further, ICPs are now used as electrode materials in capacitors [73, 328]. They show enlarged stability against breakdown phenomena because of the loss of conductivity at higher field strength. The preparation of composites, for example, PANI/porous carbon, further widens their range of applications [165, 333, 335, 351, 362, 365, 366]. Fuzzy nanofibrous network of polyaniline electrode is successfully electrosynthesized for supercapacitor application. Network of polyaniline is highly porous with interconnected fuzzy nanofibers having diameter typically between 120 and 125 nm. The highest specific capacitance of 839 F g^{-1} was reported [321]. Polyaniline and self-doped polyaniline nanofibers were also proposed for application in electrochemical redox capacitors [324]. Polypyrrole–carbon nanotubes composites were prepared, which are of interest for supercapacitor applications [363]. Incorporation of metallic particles into porous polymeric matrixes increases the specific surface area and thereby improves the catalytic efficiency. The development of metal–polymer composite as electrode materials for low-temperature fuel cells has been reviewed recently [309]. An asymmetric supercapacitor was fabricated which consists of polyaniline nanofibers and graphene nanosheets [327].

Lithium ion polymer batteries and laminated solid-state redox supercapacitors have also been fabricated [310]. In these plastic power sources, a highly conducting gel-type membrane electrolyte is placed between a PP–PANI electrode combination. The Li ion manganite prototypes reached densities of up to 120 Wh kg^{-1}, and specific powers of up to 1,000 W kg^{-1} were obtained when PP was used. The PANI–PP system yielded a specific power of 120 W kg^{-1} and a specific energy of 4 Wh kg^{-1}. Poly(diphenylamine)-single-walled carbon nanotube (PDPA/SWNT) composites were synthesized electrochemically and tested as active electrode materials for rechargeable lithium batteries [313]. Polyaniline and vanadium pentoxide composite films were prepared for their application in lithium batteries. The cell exhibited excellent cycle stability with a high charge storage capacity [351]. A set of two-component guest–host hybrid nanocomposites composed of conducting polymers and vanadium oxide was prepared via a single-step, solvent-free, mechanochemical synthesis. The nanocomposites have a guest–host structure, with the conducting polymer located in the interlayer space of the inorganic nanoparticles. The nanocomposites are capable of reversible cycling as the positive electrode in a lithium ion cell and retain their capacity over 100 full charge–discharge cycles [352]. Polyaniline–RuO_2 composite electrodes were prepared by spontaneous oxidative polymerization of aniline and were tested for supercapacitor application [365]. Hydrous RuO_2 on PANI–Nafion matrix was deposited, which also showed high capacitance [364]. Fine particles of RuO_x were successfully deposited on polypyrrole nanorods, and the system's maximum specific capacitance was 419 mF cm^{-2} or 681 F g^{-1} [333]. Composite electroactive films consisting of poly(3,4-ethylenedioxythiophene) and amorphous tungsten oxide, $WO_3/H_{(x)}$ $WO_{3,}$ were fabricated on carbon electrodes through electrodeposition by voltammetric potential cycling in acid solution containing EDOT monomer and sodium tungstate. Electrostatic interactions between the negatively charged tungstic units and the oxidized positively charged conductive polymer sites create a robust hybrid structure. The hybrid films exhibit good mediating capabilities toward electron transfers and accumulate effectively charge, which may be of importance to electrocatalysis and supercapacitors [366].

The use of organic semiconductors is of special interest because of the possibilities of depositing them over large areas at low cost and synthesizing materials tailored to special goals. A first device using a bilayer structure of copper phthalocyanine and a perylene derivative is described in [364].

Conducting polymers have also been utilized in photovoltaic devices [25, 53, 273–277, 325, 332, 336, 356, 359, 370]. Due to their conducting properties, polythiophenes can only be used in photovoltaic devices in their reduced state. The reduction must take place electrochemically before vapor deposition of the top electrode. Different layer structures and combinations of PT with PPPV or C_{60} were studied [356, 359]. Al/C_{60}-modified PT/ITO devices exhibit a conversion efficiency of 15% with zero bias and 60% with a bias of 2 V (for $\lambda = 500$ nm, 1.5 mW cm^2).

A device with an active layer of poly(3-methylthiophene) (PMT) and an intermediate layer of sulfonated polyaniline (SPAN) in the following arrangement was created:

$$\text{TO(tin oxide)} - \text{SPAN} - \text{PMT} - \text{Al}.$$

This device gave an incident-photon-to-collected-electron efficiency of 12.1% and a power conversion efficiency of 0.8% under monochromatic irradiation [332]. Single-polymer-layer photovoltaic devices using polybithiophene (PBT) thin films and fluorine-doped tin oxide substrate have also been constructed (Fig. 7.22). As well as the difference in the work functions of the electrodes, the high organization of the molecular dipoles in PBT yielded an open-circuit potential of 2 V when an aluminum top contact was used [332].

The PBT–FTO–Al devices were characterized by measuring the current–voltage characteristics when they were irradiated with the air mass 1.5 (AM 1.5) spectral distribution, with the devices being illuminated through the glass substrate (Fig. 7.23) [332].

The power conversion efficiency (η) of such a device can be given as follows:

$$\eta = \frac{U_{\text{oc}} \times J_{\text{sc}} \times \text{FF}}{E_{\text{AM1.5}}}, \tag{7.4}$$

where U_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, FF is the fill factor, and $E_{\text{AM1.5}}$ is the total irradiance at the AM1.5 spectral distribution.

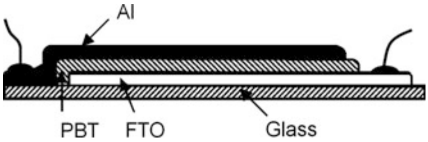

Fig. 7.22 Schematic structure of the photovoltaic device. PBT polybithiophene, FTO fluorine-doped tin oxide [332] (Reproduced with the permission of Springer-Verlag.)

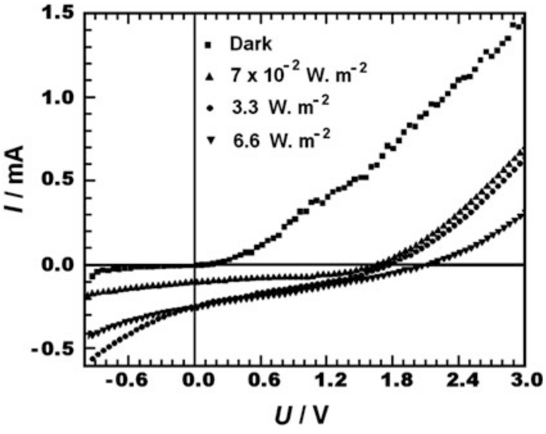

Fig. 7.23 Current–voltage characteristics of an FTO (PBT) (160 nm)–Al device in the dark and under different irradiances [332] (Reproduced with the permission of Springer-Verlag.)

The fill factor is given by

$$\mathrm{FF} = \frac{U_\mathrm{p} \times I_\mathrm{p}}{U_\mathrm{oc} \times I_\mathrm{sc}}, \tag{7.5}$$

where U_p and I_p represent the maximum-power-rectangle U and I values, respectively.

Polycarbazole was prepared by electropolymerization in TiO_x by using layer-by-layer and surface sol–gel techniques. TiO_x acted as dielectric spacer, which limited electron transfer rate and attenuated energy transfer in fluorescence. These hybrid ultrathin films were applied in photovoltaic devices [323]. Polypyrrole with embedded semiconductor (CdS) quantum dots was obtained by electropolymerization of pyrrole in the presence of CdS nanoparticles dispersed in the electrolytic aqueous solution. The illumination effects were also observed in the reduced form of the polymer. The presence of CdS nanoparticles in the polypyrrole film improves the optical properties of PP, and these films can be used in photovoltaic cells [336]. Nanoporous layers of poly(3,4-propylenedioxythiophene) were deposited on transparent conductive oxide substrates by electropolymerization employing different ionic liquids. In this way, catalytically effective, platinum-free, stable, and flexible counter electrodes can be fabricated for dye-sensitized solar cells [376].

Mesoporous carbon (MC)–poly(3,4-ethylenedioxythiophene) composites were synthesized using structure-directing agents and explored as catalyst supports for polymer electrolyte fuel cell (PEFC) electrodes. Platinum nanoparticles were deposited onto the composite supports from platinum salts by formaldehyde reduction. The durability of MC-PEDOT-supported catalysts in PEFCs was attributed to enhanced corrosion resistance of MC [369]. Polyaniline deposited on carbonic substrates was applied as hydrogen mediator and catalyst in fuel cells [355]. Poly(*m*-toluidine) was prepared in the presence of nonionic surfactant at the surface of MWCNTs, and this substrate served as a porous matrix for dispersion of platinum particles. This system enhanced the oxidation of methanol [354]. Perovskite ($\mathrm{La}_{1-x}\mathrm{SrMnO}_3$) was embedded into a polypyrrole layer, sandwiched between two pure PP films, electrodeposited on a graphite support, and the composite were investigated for electrocatalysis of the oxygen reduction reaction [362]. Polypyrrole with incorporated $\mathrm{CoFe}_2\mathrm{O}_4$ nanoparticles was investigated for the same purpose [361]. Failure and stabilization mechanisms in multiply cycled conducting polymers for energy storage devices have been analyzed [334].

7.2.7 Artificial Muscles [377–396]

Conducting polymers swell with increasing oxidation (doping) [55, 67, 377–396]. The ingress of counteranions into the polymer leads to a structural change in the polymer backbone and to an increase in volume of up to 30% [383]. These electromechanical properties are used in actuators, like polymer-based artificial

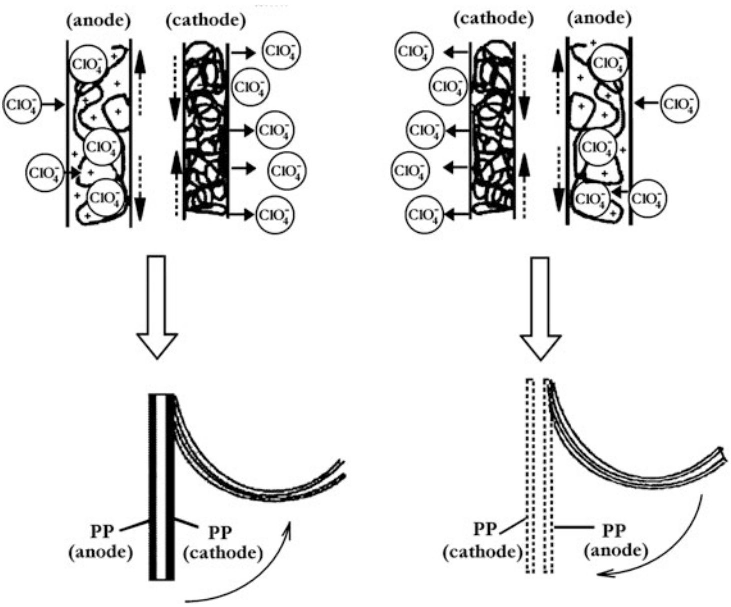

Fig. 7.24 A schematic drawing of an electrochemical triple-layer actuator (polypyrrole$^+$$ClO_4^-$–nonconducting, double-sided plastic-tape polypyrrole) immersed in aqueous $LiClO_4$ solution, and the macroscopic movement of the actuator produced due to a volume change in the PP films (Reproduced from [388] with the permission of Elsevier Ltd.)

muscles. Bilayer structures based on PP [67, 392] have been described. Triple-layer actuators consisting of two layers of conducting polymers separated by a flexible insulating foil have been developed by Otero and coworkers to avoid the need to use a separate metallic counter electrode [388] (Fig. 7.24).

The PP film used as the anode is swollen by the entry of hydrated ClO_4^- counterions, while the other PP layer, which acts as the cathode, shrinks because of the expulsion of counterions and water molecules. These volume changes and the constant length of the nonconducting film promote the movement of the triple layer toward the PP film that is contracted. Upon changing the direction of the current, the movement takes place in the opposite direction. The effect depends on the concentration of the $LiClO_4$ and the temperature [388].

The linear actuation of PP was also studied by electrochemical deformation measurements during cyclic voltammetry and potential step experiments [384]. It was found that in $TBACF_3SO_3$–propylene carbonate electrolyte, the shortest length of the PP strip investigated presents itself at 0 V vs. Ag wire quasireference electrode, while 6.6% expansion was achieved at +1 V and ca. 4% at -1 V. The potential-dependent shrinkage and expansion phenomena show long-term stability. Polypyrrole–dodecylbenzenesulfonic acid system, which responds to the surrounding conditions during actuation, was studied in detail. Artificial muscles can be fabricated by using this material [378]. An in situ electrochemical strain gauge method was applied to monitor the mechanical properties of conducting and redox polymers such as PP, poly(3,4-ethylenedioxypyrrole), and poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-carbazole) during their redox transformations [377]. Biological–medical application of microelectromechanical systems including conducting polymer has been reviewed recently [382]. Chemically induced actuation of a polypyrrole artificial muscle was controlled by biocatalytic reactions, resulting in changes in the redox state of the polymer film mediated by soluble redox species. The biocatalytic process triggered by diaphorase in the presence of NADH resulted in the reduction of the PP film. Conversely, the biocatalytic process driven by laccase in the presence of oxygen resulted in the oxidation of the PP film. Both reactions produced opposite bending of the PP flexible strip, allowing reversible actuation controlled by the biocatalytic processes. The biocatalytic reactions governing the chemical actuator can be extended to multistep cascades, processing various patterns of biochemical signals and mimicking logic networks. The present chemical actuator exemplifies the first mechanochemical device controlled by biochemical means with the possibility to scale up the complexity of the biochemical signal-processing system [396]. A dynamic electromechanical model for electrochemically driven conducting polymer actuators has been developed, recently, which can be effectively used for designing devices based on the actuation response [393].

7.2.8 Electrocatalysis [397–490]

Electrocatalysis has already been mentioned in Sect. 7.2.5, in connection with amperometric chemical and biological sensors. Of course, the electrocatalytic properties of conducting polymers can be utilized not only to sense substances but also for electrochemical synthesis or in power sources. Indeed, there are endless ways to design tailor-made electrodes for specific catalytic purposes, which makes this approach highly attractive. Many conducting polymers act as electrocatalysts [10, 26, 324, 400, 404, 406, 411, 416, 420, 430, 431, 436–439, 443, 452, 454, 457, 458, 460–467, 470, 474, 482] toward different reactions; however, the polymers that mediate the electron transfer can also be further modified by catalytic centers built into the polymer [403, 405, 406, 411, 416, 417, 422, 423, 425, 427, 431, 432, 438, 439, 443–446, 466, 473, 474, 477, 482–485]. This can be achieved in different ways. Derivatives of the monomer are used; i.e., the monomer species are chemically modified by the appropriate functional groups before polymerization. Another technique is the incorporation of catalytic centers into the polymer matrix. Metal nanoparticles or oxide clusters can be produced inside the film by chemical or electrochemical reduction and oxidation, respectively [423, 427, 443]. Such a process is exemplified by the deposition of Ag onto poly(1-hydroxyphenazine) (PPhOH). Due to the narrow potential interval over which PPhOH films are conductive, silver can be only deposited cathodically into the film or at the film surface within this narrow interval (from ca. 0.1 to −0.2 V vs. SCE), and the implanted Ag cannot be redissolved anodically due to the low conductivity of the surrounding or underlying PPhOH matrix at positive potentials [423] (see Figs. 7.25 and 7.26).

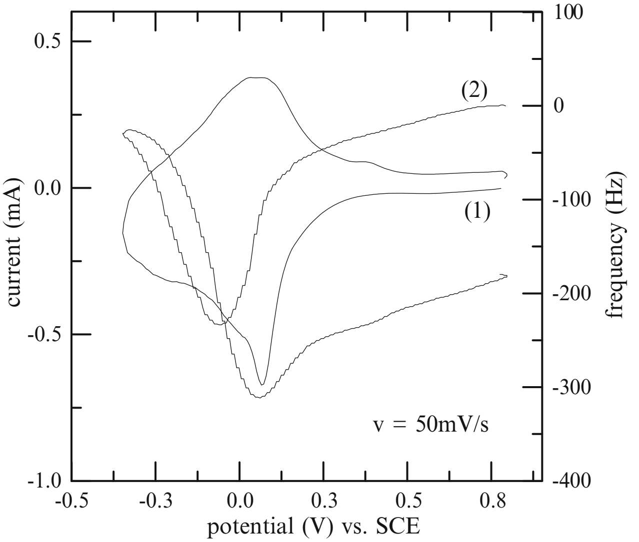

Fig. 7.25 Cyclic voltammogram (*1*) and the simultaneous EQCM frequency changes (*2*) during the cyclic polarization of poly(1-hydroxyphenazine) film in the presence of Ag^+ ions in 1 mol dm^{-3} $HClO_4$ + 10^{-3} mol dm^{-3} $AgClO_4$ [423]

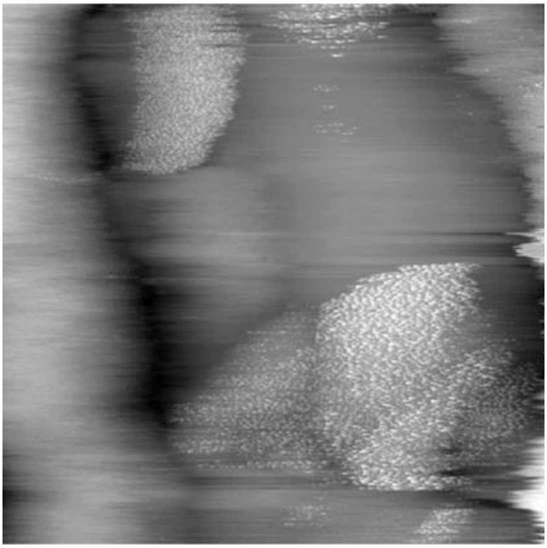

Fig. 7.26 In situ STM image of poly(1-hydroxyphenazine) film on HOPG after subsequent Ag deposition. Electrolyte: 0.1 mol dm^{-3} $HClO_4$. Scan size: 1.2 × 1.2 μm, Δz: 60 nm. Substrate potential: −0.4 V vs. MSE. *E*: 5 mV, *I* = 5 nA [423]

A good scattering of metallic particles on Au–PANI films was achieved by using a repetitive square-wave potential signal. Codeposition of Ru and Pt from suitable combinations of H_2PtCl_6 and $RuCl_3$ onto PANI films produces PANI–Pt–Ru electrodes, which exhibit catalytic properties toward CO and methanol oxidation [439].

Ionic species can be immobilized by electrostatic interactions, specifically as counterions; however, these systems can be sensitive to the redox transformations of the polymer, i.e., "counterion" desorption is expected when the film becomes neutral or oppositely charged. Other interactions (e.g., complex formation) can also be exploited.

It should be mentioned that in some cases, the higher current observed is not due to the catalytic enhancement of the reaction but is instead a consequence of the increased surface area. Nevertheless, this effect is also important, especially when precious metal particles are dispersed in the polymer matrix. Although the conducting polymers are rather stable chemically, there are often problems with the long-term physical stability when gas evolution occurs or intense mechanical stirring is applied.

In order to design effective electrocatalytic systems, the fundamental mechanism of how the deposited polymer layer mediates the oxidation or reduction of the substrates of interest must be understood. The two main questions to be clarified are the relationship between the conductivity of the polymer and the electrocatalytic activity, and the location of the reaction.

It was initially assumed that polymer films in their insulating state should inhibit the reaction at the polymer–electrolyte interface, such that kinetic measurements could be used to test the film's conductivity [383]. In accordance with this concept, the oxidations of species with formal redox potentials in the insulating potential range of the polymer are usually shifted to the interval of the onset of film conductivity, while the reduction reactions are suppressed (at least for polymers without n-doping).

For example, for several polymers [480], the Fe^{2+} oxidation reaction does not take place at either negative (insulating film) or high positive (fully oxidized polymer) potentials, while it occurs in the intermediate potential range. Of course, size exclusion and electrostatic repulsion effects should be considered [458, 459].

There are numerous examples of reaction catalysis by polymer films in their conductive states rather than the bare electrode; for example, reduction of oxygen [404, 406, 472] and HNO_3 [465]; oxidation of Fe^{2+} [441, 462, 490], I^-, Br^-, $Fe(CN)_6^{4-}$, $W(CN)_8^{4-}$, $Ru(CN)_6^{4-}$ [340], hydrazine [322], formic acid [434], and hydroquinone [453, 462, 490] at PANI; as well as oxygen [399] and bromine [453] reduction at PPP. Nanostructured films of hollow polyaniline and PANI–polystyrene core shells prepared by template synthesis were applied for the electrocatalytic reduction of nitrite [436]. Poly(neutral red) can electrocatalyze the reduction of IO_3^-, BrO_3^-, and O_2, as well as the oxidation of I^- [413]. It was found that the rate of hydroquinone oxidation at PANI electrodes increases by two orders of magnitude; however, this electrocatalytic activity of PANI films deteriorates somewhat upon aging [409].

On the other hand, the rates of some other reactions are even diminished by films in their conducting states; for example, ferrocene oxidation at polythiophene [44]. Composites of poly(diphenylamine)-MWCNT [476] as well as that of poly (brilliant cresyl blue) and poly(5-amino-2-naphtalenesulfonic acid) [401] showed enhanced electrocatalytic properties toward the reduction of hydrogen peroxide. Hybrid composed of poly(2-(4-aminophenyl)-6-methylbenzothiazole) and nickel hexacyanoferrate was investigated, a good electrocatalytic activity was found toward the oxidation of methanol and oxalic acid [426]. PtRu particles were deposited in PANI–polysulfone composite films, and the catalytic activity toward methanol oxidation has been studied [421]. Polyaniline–thiol composite [481] and PEDOT–NiHCF composites [484] were used for the detection of ascorbic acid. MWCNTs–poly(neutral red) composites were used for the oxidative determination of ascorbate, and it was found that the type of the nanotubes strongly influences the efficiency of the electrocatalytic effect [208].

Cocondensation of (ferrocenylmethyl)dimethyl(ω-trimethoxysilyl) alkylammonium hexafluorophosphate with tetramethylsilane resulted in a hybrid film, and it showed a catalytic effect toward the oxidation of catechol and catechol violet [489]. Poly (3,4-ethylenedioxythiophene) was used to immobilize metal particles and borohydride reagent, and the composite was applied for hydrogenation of nitrophenol as well as for electrooxidation of methanol, formic acid, and borohydride [478]. Metal nanoparticles have been deposited on polyaniline nanofibers and used in memory devices and for electrocatalysis [454]. Iron tetra(*o*-aminophenyl) porphyrin was electropolymerized and utilized for oxygen reduction as well as for the determination of organohalides [412].

Polythiophene–magnetite composite layers have been prepared by the electropolymerization of 3-thiophene acetic acid in the presence of Fe_3O_4 nanoparticles in nitrobenzene. Stabilization of magnetite in this organic medium could be achieved by the reaction between surface –OH groups of the nanoparticles and the –COOH function of the monomers. This new modified electrode, incorporating a large amount of Fe_3O_4 may be used in magnetic electrocatalysis [431].

Exceptions to the simple relationship between polymer conductivity and its effect on the reaction kinetics have been found. Iodine reduction on PT [452] as well as viologens at PANI [460] take place within the conducting range but continue at more negative potentials. These observations testify in favor of the generation of positively charged electronic species at the polymer matrix by those reagents, similar to dark hole injection at insulator or semiconductor electrodes [452, 460].

Exceptionally high hydrogen sorption, 6 and 8 wt% at room temperature and under 9.3 MPa, was observed in polyaniline and polypyrrole treated with HCl. It is believed that both molecular sieving and a stabilization effect due to the conducting electronic environment are responsible for this unusual hydrogen sorption [414].

In most cases, the interpretation of these kinetic data assumes (usually without a detailed analysis) that the reaction is localized at the film–solution interface. For qualitative considerations, films with sufficiently high electronic conductivities are identified with the metal electrode, which means that the whole potential drop, i.e., its varying part, is attributed to the film–solution interface. Quite the opposite view (i.e., that the latter interfacial potential is practically constant [89, 419]) means a close analogy to the case of redox polymer films [462, 467].

Thermodynamic analysis of the charging process, taking into account both electron exchange with the metal and ion exchange with the solution [486–488] (see also Chap. 5), provides evidence in favor of an intermediate variant: both interfaces are markedly polarizable. In this case, the relations for the rate coefficients or the reaction rate have a more complicated form at high charging levels, and some features similar to inorganic semiconductor electrodes at lower potentials. Experimental attempts to verify this hypothesis [450, 488] have not supplied sufficient information for a definitive conclusion, especially in view of the currently inadequate description of the charging process.

The establishment of the location (reaction zone) of the electrocatalytic redox reaction is a rather complex issue. In principle, the reaction can take place at the polymer–electrolyte interface, within the polymer matrix at the interfaces of the macropores, nanopores, channels, and pinholes, and/or at the metal–polymer interface when the reacting species can diffuse to the metal surface through the channels or pinholes. There are some simple observations which may indicate the location of the reaction. For instance, it was observed that the respective reactions of H_2 and O_2 take place at greater overpotentials when the polymers are in their insulating state, compared to the bare metal electrode, and the kinetics were strongly dependent on the nature of the metal substrate [480]. This indicates that these reactions take place at the metal–polymer interface or at the bare metal surface that is not covered by the polymer, due to the porous or the brush-like structure [447–449] of the deposited polymer.

The rate of the transport of the reacting species through the polymer layer may also depend on the charging state of the polymer; positively charged species are repelled by the positive charges of the polymers, or the sizes of the solvent-filled cavities in the pores are greater due to the extensive swelling of the charged films. As discussed in Chap. 6, the film morphology depends on other factors, such as the electrolyte concentration, the temperature, and the nature of ions used during the electropolymerization and in the kinetic experiments. Besides electrostatic interactions, specific interactions (e.g., complex formation) may also affect the rate of the transport process inside the film, which also influences the rate of the catalytic current.

The dependence of the reaction rate on the film thickness suggests that the reaction takes place within the polymer layer; however, the depth of penetration into the layer depends on several parameters, including (among others) the time scale of the experiment, the charge state, the morphology, and the relative rate of consecutive transport and charge transfer steps. It is important to account for the fact that thick films are usually less dense than thin ones [400, 410, 424, 430, 433, 469, 475] (see also Chaps. 4–6).

The situation is not significantly different when the polymer films are modified by catalytic centers, such as clusters of transition metals [411, 415, 422, 425, 442, 485], polyoxometallates [406, 432, 457], porphyrins, phthalocyanines and their analogs [412, 432, 472], other transition metal complexes [473, 474], biomolecules [407], arenas and rotaxane [408, 438], etc.; see [7, 15, 397, 417, 428, 429, 446, 456, 482] for reviews.

The theoretical description of electrocatalysis that takes into account electron and ion transfer and the transport process, the permeations of the substrates, and their combined involvement in the control over the overall kinetics has been elaborated by Albery and Hillman [397, 428, 429] and by Andrieux and Savéant [398], and a good summary can be found in [456]. Practically all of the possible cases have been considered, including Michaelis–Menten kinetics for enzyme catalysis. Inhibition, saturation, complex mediation, etc., have also been treated. The different situations have also been represented in diagrams. Based on the theoretical models, the respective forms of the Koutecký–Levich equation have been obtained, which make analyzing the results of voltammetry on stationary and rotating disk electrodes a straightforward task.

From the dependences of the limiting current density (j_L) on the rotation rate (ω), the concentration of the substrate species (c_S), the thickness (d), and the potential, it is possible to derive not only kinetic parameters but also the location of the catalytic reaction and the rate-determining step. In a relatively simple case, we can write

$$\begin{aligned} j_\mathrm{L}^{-1} &= (nFk_\mathrm{e}\Gamma c_\mathrm{S})^{-1} + \left(nFD_\mathrm{S}^\mathrm{pol}Pc_\mathrm{S}d^{-1} + nFD_\mathrm{ct}\Gamma_\mathrm{T}d^{-2}\right)^{-1} \\ &\quad + \left(0.62nFD_\mathrm{S}^{2/3}\nu^{-1/6}\omega^{1/2}c_\mathrm{S}\right)^{-1}, \end{aligned} \tag{7.6}$$

where $D_\mathrm{S}^\mathrm{pol}$ and D_ct are the diffusion coefficients of the substrate and the charge transport inside the polymer layer, respectively, k_e is the rate of electron transfer (or electron exchange reaction) in the polymer, Γ and Γ_T are the surface concentration and the total concentration of redox centers available for the catalytic reaction at a given potential, and P is the distribution coefficient of the substrate between the polymer and the electrolyte phases. The first term is related to the electron transfer, the two terms in the second set of parentheses express the diffusional transport through the polymer matrix, and the third term stands for the Levich diffusion current in the solution; i.e., regarding the Koutecký–Levich equation, ${j_\mathrm{L}}^{-1} = {j_\mathrm{k}}^{-1} + {j_\mathrm{D}}^{-1}$, the first two terms are related to the kinetics of the reaction, while the third term is related to diffusion in the solution phase (stirring has no effect inside the polymer layer).

When charge transfer is very easy (e.g., at limiting current potentials), the first term of (7.6) can be neglected. If j_L is independent of the layer thickness, the charge transport in the polymer layer is not rate determining. If these two conditions prevail, only the first term in the second set of parentheses and the third term remain. It follows that ${j_\mathrm{L}}^{-1}$ vs. $\omega^{-1/2}$ gives a straight line and, knowing d and $D_\mathrm{S}^\mathrm{pol}$ P or knowing d and P from separate experiments, $D_\mathrm{S}^\mathrm{pol}$ can be calculated from the intercept. When the catalytic reaction takes place within the polymer layer, d can be replaced by the penetration depth, $\mu = \mathrm{P}D_\mathrm{S}^\mathrm{pol}/k_\mathrm{F}$ where k_F is the reaction rate coefficient at the limiting current potentials [459, 462]. In this case, the plot of

$j_L{}^{-1}$ vs. $\omega^{-1/2}$ gives a straight line with an intercept. Upon plotting these intercepts ($j_k{}^{-1}$) as a function of $c_S{}^{-1}$, a straight line with an intercept of zero is obtained, and $\mu/nFD_S^{\mathrm{pol}}P$ can be derived from the slope. This situation has been analyzed by Mandic and Duic for the electrocatalytic reaction of Fe^{2+} and hydroquinone at PANI electrodes [462]. It was found that the slope of the $j_k{}^{-1}$ vs. $c_S{}^{-1}$ plot increases as d decreases, which indicates that there is a change in the film's morphology which affects the penetration depth. It was also demonstrated that PANI in its protonated emeraldine form behaves as a metal electrode, while at more positive potentials, where polyaniline exists in pernigraniline form, the behavior of PANI resembles a redox polymer.

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