Chapter 2
Classification of Electrochemically Active Polymers

Electrochemically active polymers can be classified into several categories based on the mode of charge propagation (note that insulating polymers are not considered here except for those with variable conductivity). The mode of charge propagation is linked to the chemical structure of the polymer. The two main categories are electron-conducting polymers and proton (ion)-conducting polymers. We will focus on electron-conducting polymers here.

We can also distinguish between two main classes of electron-conducting polymers based on the mode of electron transport: redox polymers and electronically conducting polymers.

In this chapter, we provide examples of each type of electron-conducting polymers, listing some of the most typical and widely studied of these polymers, as well as several new and interesting representatives of this class of materials. Some sections are also devoted to combinations, such as electronically conducting polymers containing redox functionalities and copolymers. Composites, which has been developed extensively during the recent years, are discussed too.

2.1 Redox Polymers

Redox polymers contain electrostatically and spatially localized redox sites which can be oxidized or reduced, and the electrons are transported by an electron exchange reaction (electron hopping) between neighboring redox sites if the segmental motions enable this. Redox polymers can be divided into several subclasses:

- Polymers that contain covalently attached redox sites, either built into the chain, or as pendant groups; the redox centers are mostly organic or organometallic molecules
- Ion exchange polymeric systems (polyelectrolytes) where the redox active ions (mostly complex compounds) are held by electrostatic binding
2.1.1 Redox Polymers Where the Redox Group Is Incorporated into the Chain (Condensation Redox Polymers, Organic Redox Polymers)

2.1.1.1 Poly(Tetracyanoquinodimethane) (PTCNQ) [1–22]

Synthesis: 2,5-bis(2-hydroxyethoxy)-7,7′,8,8′-tetracyanoquinodimethane+ adipoyl chloride [2, 11, 14].

\[
\text{Redox reaction:}
\]

\[
\frac{1}{2}\text{TCNQ}_\text{polym} (\text{orange}) + e^- + K^+_{\text{sol}} (\text{blue}) \rightleftharpoons \frac{1}{2}\text{TCNQ}^+K^+_{\text{polym}}, \quad (2.1)
\]

\[
\frac{1}{2}\text{TCNQ}^+K^+_{\text{polym}} + e^- + K^+_{\text{sol}} (\text{colorless}) \rightleftharpoons \text{TCNQ}^-K^2+_{\text{polym}}, \quad (2.2)
\]

The subscripts “polym” and “sol” denote the polymer and solution phases, respectively.

These reaction formulae indicate that the electron transfer taking place at the metal–polymer interface is accompanied by ionic charge transfer at the polymer–solution interface, in order to maintain the electroneutrality within the polymer phase. Counterions usually enter the polymer phase, as shown above. However, less frequently the electroneutrality is established by the movement of co-ions present in the polymer phase, e.g., in so-called self-doped polymers. Oxidation reactions are often accompanied by deprotonation reactions, and H⁺ ions leave the film, removing the excess positive charge from the surface layer. It should also be mentioned that simultaneous electron and ion transfer is also typical of electrochemical insertion reactions; however, this case is somewhat different since the ions do not have lattice places in the conducting polymers, and both cations and anions may be present in the polymer phase without any electrode reaction occurring. The establishment of equilibria and the different reaction and transport mechanisms involved will be discussed in Chaps. 5 and 6, respectively. For the sake of simplicity, only the electron transfer (redox transformation) will be indicated in some cases below.

In the case of the formation of TCNQ dimers, TCNQ₂⁺K⁺ and (TCNQ)₂⁻K₂⁺ (green) and the protonated species TCNQH⁻K⁺ and TCNQH₂ may also occur inside the polymer film [11, 12].
A postfunctionalization by treatment with electron-rich molecules may convert PTCNQ into a strongly colored polymer with low-energy charge transfer bands [22].

### 2.1.1.2 Poly(Viologens) [23–27]

[Poly(N,N'-alkylated bipyridines]

![Poly(xylyliogen)](image)

Synthesis: \(\alpha,\alpha'-\)dibromoxylene + 4,4'-bipyridine [26].

Redox reaction

\[
\text{bipm}^{2+} + e^- \rightleftharpoons \text{bipm}^+; \quad \text{bipm}^+ + e^- \rightleftharpoons \text{bipm} \text{ (bipyridine)} \quad \text{(weak color)}
\]

\[
\text{MV}^{2+} + e^- \rightleftharpoons \text{MV}^+; \quad \text{MV}^+ + e^- \rightleftharpoons \text{MV} \text{ (methylviologen)} \quad \text{(colorless)}
\]

#### 2.1.2 Redox Polymers with Pendant Redox Groups

### 2.1.2.1 Poly(Tetrathiafulvalene) (PTTF) [28–32]
Synthesis: poly(vinylbenzylchloride) + potassium salt of \( p \)-hydroxyphenyl-tetrathiafulvalene or other derivatives [31, 32].

Redox reaction:

\[
[TTF]_{\text{polym}} + [X^-]_{\text{sol}} \rightleftharpoons [TTF^\ddagger X^-]_{\text{polym}} + e^-
\]  

(2.5)

\[
[TTF^\ddagger + X^-]_{\text{polym}} + [X^-]_{\text{sol}} \rightleftharpoons [TTF^\ddagger X_2^-]_{\text{polym}} + e^-
\]  

(2.6)

Also formation of dimers: TTF\( _2^\ddagger \), TTF\( _2^\ddagger \).

### 2.1.2.2 Quinone Polymers [33–39]

[Chemical structures of poly(vinyl-p-benzoquinone) and poly(acryloyl/dopamine)]

Synthesis: radical polymerization of vinylbis(1-ethoxyethyl) hydroquinone [35] or by reaction of acryloyl chloride with dopamine [34].

Redox reactions (in nonaqueous solutions) [33]:

\[
\text{hydroquinone form} \rightarrow \text{quinone form} + 2e^- + 2H^+
\]  

(2.7)

(in aqueous solutions) [34]:

hydroquinone form → quinone form + 2e\(^-\) + 2H\(^+\)

\[
\text{Synthesis: electropolymerization of 5-hydroxy-1,4-naphthoquinone [39].}
\]
2.1 Redox Polymers

Redox reaction:

\[
\text{PNQP} + 2e^- + 2H^+ \rightleftharpoons \text{PNQPH}_2 \quad (2.9)
\]

Synthesis: poly(ethyleneimine) + 2-anthraquinone carbonyl chloride [37, 38].

Redox reaction:

\[
PQ + 2e^- + 2H^+ \rightleftharpoons \text{PQH}_2 \quad (2.10)
\]

2.1.2.3 Poly(Vinylferrocene) (PVF or PVFc) (Organometallic Redox Polymer) [40–81]

Synthesis: polymerization of vinylferrocene [77].

Redox reaction:

\[
[\text{ferrocene}]_{\text{polym}} + [X^-]_{\text{sol}} \rightleftharpoons [\text{ferrocenium}^+X^-]_{\text{polym}} + e^- \quad (2.11)
\]
2.1.2.4 [Ru or Os (2,2′-Bipyridyl)$_2$(4-Vinylpyridine)$_n$Cl]Cl [82–90]

[Ru(bpy)$_2$(PVP)$_n$Cl]Cl, $n = 5$

Also copolymers with styrene or methylmethacrylate; PVP was also replaced by poly(N-vinylimidazole) [83–85, 89, 90].

Redox reaction [82–90]:

$$\begin{align*}
\text{Ru}^{2+} + X^{-}_{\text{polym}} + \frac{1}{2} X^{-}_{\text{sol}} & \rightleftharpoons \text{Ru}^{3+} + e^- \\
\text{Os}^{2+} + X^{-}_{\text{polym}} + \frac{1}{2} X^{-}_{\text{sol}} & \rightleftharpoons \text{Os}^{3+} + e^- 
\end{align*}$$

(2.12) (2.13)

2.1.3 Ion Exchange Polymers Containing Electrostatically Bound Redox Centers

Usually the electrode surface is coated with the ion exchange polymer, and then the redox active ions enter the film as counterions. In the case of a cation exchanger, cations (in anion exchangers, negatively charged species) can be incorporated, which are held by electrostatic binding. The counterions are more or less mobile within the layer. A portion of the low molar mass ions (albeit usually slowly) leave the film and an equilibrium is established between the film and solution phases. Polymeric (polyelectrolyte) counterions are practically fixed in the surface layer.
2.1.3.1 Perfluorinated Sulfonic Acids (Nafion®) [68, 91–110]

\[
\left\{ \begin{array}{c}
(CF_2)_m - CF - CF_2 \\
O \\
CF_2 \\
\end{array} \right\}_n \\
\text{R}_2C - CF - O - (CF_2)_2 - SO_3^\text{+H}
\]

Synthesis: copolymerization of perfluorinated ethylene monomer with SO\textsubscript{2}F containing perfluorinated ether monomer [93, 96]; \( m = 6–12 \). Nafion® 120 (DuPont) means 1,200 g polymer per mole of H\textsuperscript{+}, there are Nafion® 117, 115, 105, etc.

Dow ionomer membranes [94]:

\[
\left\{ \begin{array}{c}
(CF_2)_m - CF - CF_2 \\
O - (CF_2)_2 - SO_3^\text{+H}
\end{array} \right\}_n
\]

Redox active ions that have been extensively investigated by using Nafion-coated electrodes: Co(bpy)\textsubscript{3}\textsuperscript{3+/2+/+} (bpy = 2,2'-bipyridine) [92, 99], Co(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/2+} [92], Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/2+} [92], Ru(bpy)\textsubscript{3}\textsuperscript{3+/2+} [68, 93, 97, 99, 100, 103, 104, 107–110], Os(bpy)\textsubscript{3}\textsuperscript{2+} [91, 97, 105, 106], Eu\textsuperscript{3+} [99], ferrocenes\textsuperscript{3+/0} [104, 106], methylviologen (MV\textsuperscript{2+/+/0}) [95, 98, 103], methylene blue [102], phenosafranin and thionine [101].

2.1.3.2 Poly(Styrene Sulfonate) (PSS) [111–119]

\[
\left\{ \begin{array}{c}
CH - CH_2 \\
\end{array} \right\}_n \\
\text{SO}_3^\text{H}
\]

Redox ions investigated are as follows: Ru(bpy)\textsubscript{3}\textsuperscript{3+/2+}, Os(bpy)\textsubscript{3}\textsuperscript{3+/2+} [111–119], Eu\textsuperscript{3+/2+} [114].
2.1.3.3 Poly(4-Vinylpyridine) (PVP, QPVP) [120–132]

![Poly(4-Vinylpyridine) structure diagram]

In this cationic, anion-exchanger polymer, the following redox anions have typically been incorporated and investigated:

\[ \text{Fe(CN)}_3^{3-} \rightarrow \text{Fe}^{2+} \]

\[ \text{IrCl}_6^{2-/3-} \]

\[ \text{Mo(CN)}_8^{3-/4-} \]

\[ \text{W(CN)}_8^{3-/4-} \]

\[ \text{Ru(CN)}_6^{3-} \]

\[ \text{Co(CN)}_6^{3-} \]

\[ \text{Fe(edta)}^{1-/2-} \]

\[ \text{Ru(edta)}^{1-/2-} \]

2.2 Electronically Conducting Polymers (Intrinsically Conducting Polymers—ICPs)

In the case of conducting polymers, the motion of delocalized electrons occurs through conjugated systems; however, the electron hopping mechanism is likely to be operative, especially between chains (interchain conduction) and defects. Electrochemical transformation usually leads to a reorganization of the bonds of the polymers prepared by oxidative or less frequently reductive polymerization of benzoid or nonbenzoid (mostly amines) and heterocyclic compounds.

2.2.1 Polymers from Aromatic Amines

2.2.1.1 Polyaniline (PANI) and PANI Derivatives [133–413]

Idealized formulae of polyaniline at different oxidation and protonation states:

\( L = \text{leucoemeraldine (closed valence; shell reduced form; benzenoid structure);} \)

\( E = \text{emeraldine (radical cation intermediate form; combination of quinoid and} \)

[129]
benzenoid structures); P = perigraniline form (quinoid structure); LH$_{8x}$, EH$_{8x}^1$, EH$_{8x}^2$ are the respective protonated forms:

Illustration of delocalization (polaron lattice) of the emeraldine state:

Synthesis: oxidative electropolymerization of aniline in acidic media [133, 149, 152, 169, 177, 180, 196, 198, 202, 213, 216, 219, 230, 234, 241, 245, 280, 288, 291, 295, 301, 314, 327, 348, 349, 351, 353, 369, 386] or chemical oxidation by Fe(ClO$_4$)$_3$, K$_2$S$_2$O$_8$, etc. [165, 179, 271, 363, 364].
Redox reactions [150, 151, 154, 182, 216, 236, 249, 267, 310]:

\[
\begin{align*}
L & \iff E & \iff P \\
\text{ } & -4 \times H^+ & -4 \times e^- & -4 \times H^+ & -4 \times e^- \\
\text{ } & +4 \times A^- & -4 \times e^- & +4 \times HA & -4 \times HA \\
\text{ } & -4 \times II^- & -4 \times e^- & -8 \times II^- & -4 \times A^+ & -4 \times e^- \\
LH_{8x} & \iff EH_{8x} \text{ } & \text{ }
\end{align*}
\]

The color change during the redox transformations is as follows: yellow $\iff$ green $\iff$ blue (violet).

It should be mentioned that polymers that behave in a similar way to PANI can also be prepared from compounds other than aniline (e.g., from azobenzene [213]). Substituted anilines—especially the formation and redox behavior of poly(o-toluidine) (POT)—have been studied in detail [388–404].

Polymers such as poly(o-methoxyaniline) [409–411], poly(o-ethoxyaniline) [402], poly(1-pyreneamine) [405], poly(4-aminobenzoic acid) [412], poly (1-aminoanthracene) [406], poly(N-methylaniline) [407], and poly(N-phenyl-2-naphthylamine) [408] have also been synthesized by electropolymerization from the respective monomers. Even monomers of more complicated structure have been polymerized, e.g., \(N\)-(N',N'-diethylthiocarbamoylethylamidoethyl) aniline [243].
Interestingly, the oxidative electropolymerization of 1,8-diaminonaphthelene leads to a polyaniline-like polymer; however, the second amine group of the monomer does not participate in the polymerization reaction [342]:

The redox transformations of poly(1,8-diaminonaphthalene) (PDAN) can be described by the following scheme:

The oxidative polymerizations of other aryl amines yield polymers with ladder structures. We will discuss these polymers later (Sects. 2.2.1.3, 2.2.1.4, 2.2.1.5).

In the case of the electropolymerization of 2-methoxyaniline [162, 410, 411] at high monomer concentrations, a PANI-like conducting polymer was obtained, while at low concentrations a polymer with phenazine rings was formed [411]:
Different “self-doped” polyanilines have been prepared using aniline derivatives containing carboxylate or sulfonate groups, or the acid functionalities were incorporated during a postmodification step using the appropriate chemical or electrochemical reactions [170, 241, 283, 361, 362].

![Poly(aniline-co-N-propanesulfonic acid-aniline)](image)

Copolymers from aniline and another monomer have also been electrosynthesized and characterized (see later).

2.2.1.2 Poly(Diphenylamine) (PDPA) [414–425]

[Specifically, poly(diphenylbenzidine).]

![Poly(diphenylamine)](image)

Redox reactions:

\[
\begin{align*}
\text{DPAH} & \quad \text{DPA}^+ \quad \text{DPA}^+ \\
+H^+ & \quad -e^- & \quad +H^+ & \quad -e^- & \quad -H^+ \\
\text{DPAH}_2^+ & \quad \text{DPAH}^+ \quad \text{DPAH}^2+ \\
2\text{DPA}^+ & \quad \text{irrev.} \quad \text{DPBH}_2 \\
2\text{DPAH}^+ & \quad \text{irrev.} \quad \text{DPBH}_4^{2+} \quad \text{DPBH}_2 + 2\text{H}^+ \\
\text{DPA}^- & \quad \text{irrev.} \quad \text{DPBH}_3^+ \quad \text{DPBH}_2 + \text{H}^+ \\
\text{DPBH}_2 & \quad \text{DPBH}^- \quad \text{DPBH}^+ \quad \text{DPBB} \\
+H^+ & \quad -e^- \quad +H^+ \quad +H^+ \\
\text{DPBH}_3^+ & \quad \text{DPBH}_2^{2+} \quad \text{DPBH}^+ \quad \text{DPBBH}^+ \\
+H^+ & \quad +H^+ \quad +H^+ \\
\text{DPBH}_4^{2+} & \quad \text{DPBH}_3^+ \quad \text{DPBH}_2^{2+} \quad \text{DPBBH}_2^{2+} \\
\text{DPBH}_4^{2+} & \quad \text{DPBB} \quad \text{colored complex}
\end{align*}
\]
where

\[
\begin{align*}
\text{DPAH} & \quad \text{N} \quad \text{H} \\
\text{DPAH}_2^+ & \quad \text{N} \quad \text{H} \\
\text{DPAH}^+ & \quad \text{N} \quad \text{H} \\
\text{DPBH}_2 & \quad \text{N} \quad \text{H} \\
\text{DPBH}_3^+ & \quad \text{N} \quad \text{H} \\
\text{DPBH}_4^{2+} & \quad \text{N} \quad \text{H} \\
\text{DPBB} & \quad \text{N} \quad \text{H} \\
\text{DPBBH}^+ & \quad \text{N} \quad \text{H} \\
\text{DPBBH}_2^{2+} & \quad \text{N} \quad \text{H}
\end{align*}
\]

Color change is colorless (reduced form) \( \Leftrightarrow \) bright blue (violet) (oxidized form) at pH 0.

A polymer with a similar structure and properties can also be obtained by the oxidative electropolymerization of 4-aminobiphenyl [419] or benzidine [416].

The polymeric films including diphenylamine or triphenylamine units and five-member heterocyclic ring moieties have also been synthesized from the respective monomers, whose formulae are seen below [422].
Monomers containing diphenylamine or triphenylamine units and five-member heterocyclic rings.

2.2.1.3 Poly(2-Aminodiphenylamine) (P2ADPA) [426]

P2ADPA contains phenazine and open-ring (PANI-like) units.

Synthesis: oxidative electropolymerization of 2-aminodiphenylamine in acid media. Redox reaction: similar to that of polyphenazine and neutral red (see later).

2.2.1.4 Poly(\(o\)-Phenylenediamine) (PPD) [427–460]

(In fact, PPD is a ladder polymer that contains pyrazine and phenazine rings.)
Preparation: oxidative electropolymerization of \( o \)-phenylenediamine \([427–460]\), less frequently by chemical oxidation. A similar polymer can be prepared by the electropolymerization of 2,3-diaminophenazine \([453]\).

Redox reaction:

\[
\begin{align*}
\text{Color change: colorless (reduced form) } & \iff \text{ red (oxidized form).}
\end{align*}
\]

2.2.1.5 Poly(\( o \)-Aminophenol) (POAP) \([461–474]\)

POAP contains phenoxazine and oxazine rings.

Synthesis: oxidative electropolymerization of \( o \)-aminophenol in acid media \([461, 463, 464, 471]\).

Redox reaction \([461–465, 468, 474]\):

Both the reduced and oxidized forms can be protonated, and then \( H^+ \) exchange can also occur.
2.2.1.6 Polyluminol (PL) [475, 476]

Synthesis: oxidative electropolymerization of luminol (3-aminophthalhydrazide) in acid media [477].
Redox reaction: PANI-like benzenoid $\rightarrow$ quinoid, pH-dependent transformations [477–479].
PL shows similar electrochemiluminescence to the parent compounds in alkaline media.

2.2.2 Polymers from Aromatic Heterocyclic Compounds

2.2.2.1 Polypyrrole (PP) and PP Derivatives [480–634]

Synthesis: oxidative electropolymerization of pyrrole [482, 490–492, 494, 505, 507, 516, 552, 564, 575, 582, 585, 595, 596, 624, 631] in aqueous and nonaqueous media or chemical oxidation by Fe(ClO$_4$)$_3$, K$_2$S$_2$O$_8$, etc. [622].
Redox reaction \[484–493, 501, 503, 517, 518, 522, 536, 537, 565, 587, 607, 613, \]

615, 618, 626, 627]:

\[
\text{Polaron (radical cation associated with a lattice distortion) (PP\(^+\)).} \quad (2.18)
\]

\[
\text{Bipolaron (dication associated with a strong localized lattice distortion).} \quad (2.19)
\]

The color change is yellow \(\rightarrow\) black.

A wide variety of substituted pyrrole and pyrrole comonomers has also been prepared and electropolymerized, e.g., poly(1-pyrrolyl-10-decanephosphonic acid) [625], poly(3,4-ethylenedioxy pyrrole), poly(3,4-propylenedioxy pyrrole), poly(N-sulfonatopropoxy-dioxypyrrole), etc. [497]. The formulae of dioxypyrrole polymers are shown below.

\[
\text{poly(3,4-ethylenedioxy pyrrole) \quad poly(3,4-propylenedioxy pyrrole) \quad poly(N-sulfonatopropoxy-dioxypyrrole)}
\]

\[2.2.2.2\] Polyindole and Derivatives [618, 635–658], Polymelatonin (PM) [659], and Polyindoline [326]

Polyindole (PI)
Synthesis: oxidative electropolymerization in aqueous acidic [653] or in non-aqueous media [642, 643, 656]. Most likely sites of coupling are 1 and 3; however, 2 and 3, and 3 and 3 linkages are also proposed [653, 658]. The positive potential limit is crucial because the overoxidation produces a nonelectroactive polymer.

Redox reaction [641]:

\[
\text{Pln} + n \text{A}^- \rightleftharpoons n \text{e}^- + n \text{H}^+ + n \text{A}^- \\
\text{Pln}^+ \text{A}_n^- \rightleftharpoons n \text{e}^- + 2 n \text{H}^+ + n \text{A}^- 
\]

(2.19)

Dimethylindole [642]

The 3 and 6 linkage has been proposed based on the investigation of a series of substituted indoles [642].

Poly(5-Carboxyindole) (PCI) [639, 648] and Poly(5-Fluorindole) (PFI) [649]

\[
R = -\text{COOH} \text{ (PCI)} \text{ and } -\text{F} \text{ (PFI)}, \text{ respectively.} \\
\text{This formula was suggested in [639], while in [648] } -\text{C–C– bond was assumed.} 
\]
Synthesis: oxidative electropolymerization of 5-carboxyindole at 1.4 V vs. SCE in TEABF$_4$–acetonitrile solution [639], and that of 5-fluorindole by potential cycling between 0 and 1.2 V vs. SCE in diethyl etherate or between 0.6 and 1.4 V vs. SCE in TBAF$_4$–acetonitrile [649].

Redox reaction: two redox processes: indole $\rightarrow$ cation radical $\rightarrow$ quinoid structure or dication [639].

Color change: gray–green (reduced) $\rightleftharpoons$ dark green (oxidized) [649].

The formation of redox active cyclic indole trimer has also been suggested as a result of the electrochemical oxidation of 5-substituted indole monomers, except in the cases of 5-aminoindole and 5-hydroxyindole. This effect was attributed to the strong adsorption of the monomer, which inhibits this reaction. If the platinum had been covered by a layer of predeposited film of 5-cyanoindole or 5-nitroindole, the electropolymerization became possible [644]. Polyindoline has also been prepared by electropolymerization [326].

Polymelatonin (PM) [659]

Synthesis: oxidative electropolymerization of melatonin (N-acetyl-5-methoxytryptamine) in an aqueous solution of LiClO$_4$ (pH 1.5) [659].
Redox reaction:

\[
\text{PM} + 2nA^+ \rightleftharpoons + 2nH^+ + 4ne^- 
\]  

(2.21)

### 2.2.2.3 Polycarbazoles (PCz) [660–687]

Synthesis: anodic polymerization of carbazole [660, 662, 672, 676] or chemical or electrochemical polymerization of N-vinylcarbazole [662, 664, 666, 670]. Other carbazole derivatives have been electropolymerized such as 9-tosyl-9H-carbazole [663], N-hydroxyethylcarbazole [679], 1,8-diaminocarbazole [686], and 3,6-bis (2-thienyl)-N-ethyl carbazole [683].
Redox reaction [669, 672, 676]:

Protonation may also occur.  
Color change: colorless (reduced) ⇋ dark green (oxidized) [677].

2.2.2.4 Polythiophene (PT) and PT Derivatives [477–479, 688–825]

Synthesis: oxidative electropolymerization from thiophene or chemical reduction of halogen-substituted thiophene [781].

Usually substituted thiophenes (e.g., 3-methylthiophene) or bithiophene are used in electropolymerization since the oxidation process leading to the formation of cation radicals and polymerization occurs at less positive potentials [693, 694, 696, 701, 704, 706, 708, 712, 718, 741, 746, 771, 774] (Figs. 2.1 and 2.2).

Redox reactions [600, 689, 694, 695, 698, 705–709, 731, 744, 751, 770, 771]:

\[
\text{PT} + nA^- \rightleftharpoons \left[ \begin{array}{c} \text{PT} \end{array} \right] + n\text{e}^{-} 
\]
Cation radical (polaron), PT\(^+\).

\[
\text{PT}^+ + nA^- \rightleftharpoons \text{PT}^{2+}A_2^- + ne^-
\]  

Dication (bipolaron) state (see PP).

During the redox reaction there is a color change; e.g., in the case of poly(3-methylthiophene), red \(\rightleftharpoons\) blue.

Many thiophene derivatives have been polymerized in order to obtain new materials tailored for different purposes, e.g., to obtain different electrochromatic behavior. Roncali [746] reviewed the enormous amount of literature regarding the synthesis, functionalization, and applications of polythiophenes in 1992. Besides the polymerizations of thiophene and bithiophene, polymers from several thiophene oligomers, substituted thiophenes, thiophenes with fused rings—among others 3-substituted thiophenes with alkyl chains (e.g., methyl-, ethyl-, butyl-, octyl-), fluoralkyl chains, aryl groups, oxyalkyl groups, sulfonate groups, thiophene–methanol, thiophene–acetic acid, alkyl-linked oligothiophenes [739], poly(4-hydroxyphenyl
thiophene-3-carboxylate) [769], thiophenes containing redox functionalities, a series of poly(bis-terthienyl-B) polymers, where \( B = \) ethane, ethylene, acetylene, diacetylene, disulfide [788], etc.—have been prepared and characterized.

Poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives [603, 726, 789–825] have become a very important group of conducting polymers due to their advantageous properties.

Synthesis: electropolymerization of 3,4-ethylenedioxythiophene (EDOT) monomer. Deposition has also been performed by oxidative chemical vapor deposition [726].

Redox processes: similar to PT.
The color change is deep blue $\rightarrow$ transparent blue.
Examples for the functionalized thiophenes [478, 479, 691, 698, 703, 713, 714, 719, 726, 732, 740, 746, 748, 749, 755–759, 762, 776, 777, 788, 797, 811, 818] are shown below:
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poly(5-vinyl-2,2':5',2''-terthiophene)

poly(4,4''-dicyclopenta[2,1-b;3',4'-b']dithiophene)

poly(thionaphthene-indole)

doxyterthiophene)

poly(3,3-dimethyl-3,4-dihydro-2H-thieno-[3,4-b]dioxepine)

poly(thieno[3,4-b]thiophene)
2.2 Electronically Conducting Polymers (Intrinsically Conducting Polymers—ICPs)
Polymers containing different redox active groups, e.g., thiophene or PEDOT and carbazole [497, 759] or pyrrole [691, 783] or furan [711] have been prepared by using comonomers (monomers containing two or more different rings) or by copolymerization, exhibit several distinct redox transformations and consequently, e.g., multicolor electrochromism. Copolymers are versatile systems in this respect, even a change of the relative concentrations of the monomers influences the variation of the specific properties, e.g., the color changes (see Chaps. 2.4, and 7).

2.2.2.5 Polyazines [826–875]

Polyphenazine (PPh) and Poly(1-Hydroxyphenazine) (PPhOH)

Polyphenazine (PPh) [781, 826].

\[
\text{Synthesis: oxidative electropolymerization of phenazine in acid media in the dark [826]. (The photoreduction of phenazine produces 1-hydroxyphenazine, and then poly(1-hydroxyphenazine) is formed.) Dehalogenation polymerization of 2,7-dibromophenazine [781].}
\]

Redox reactions: the polymer exhibits the redox transformations of phenazine (Ph), which take place in two one-electron steps:

\[
\begin{align*}
\text{PhH}^+ + \text{e}^- + \text{H}^+ & \rightleftharpoons \text{PhH}_2^+ + \text{A}^- & \text{pH} \leq 0 \\
\text{PhH}_2^+ + \text{e}^- & \rightleftharpoons \text{PhH}_2^+ + \text{A}^- & \text{pH} \leq 1 - 2 \\
\text{Ph} + \text{e}^- + \text{H}^+ & \rightleftharpoons \text{PhH}^- & \text{pH} \leq 2 - 4 \\
\text{Ph} + \text{e}^- + \text{K}^+ & \rightleftharpoons \text{Ph}^\cdot\text{K}^+ & \text{pH} > 5
\end{align*}
\]
\[
\text{PhH}^+ + e^- + K^+ \rightleftharpoons \text{PhH}^- K^+ \tag{2.30}
\]
\[
\text{PhH}^+ K^+ + e^- + K^+ \rightleftharpoons \text{PhH}^- K^+ \tag{2.31}
\]
\[
\text{Ph}^- K^+ + e^- + K^+ \rightleftharpoons \text{Ph}^2^- (K^+)_2 \tag{2.32}
\]

where

Poly(1-Hydroxyphenazine) (PPhOH) [827–830].
Synthesis: oxidative electropolymerization of 1-hydroxyphenazine in acid media [829, 830].
Redox reaction: see polyphenazine.

Poly(Acridine Red) (PAR) [831]

(The exact position of the linkage has not yet been determined.)
Synthesis: oxidative electropolymerization of acridine red in aqueous solution at pH 7.4 [831].
The redox transformations of PAR have not been studied thus far. However, it has been demonstrated that the carmine polymer film has catalytic activity and can be used in the determination of dopamine [831].

Poly(Neutral Red) (PNR) [832–846]

Synthesis: oxidative electropolymerization of neutral red [838–840, 845, 846].
Redox reaction [833–846]: 
This is a pH-dependent process.

Poly(Phenosafranin) (PPhS) [847–850]

Synthesis: oxidative electropolymerization of phenosafranin in acid media [847]. Redox reaction [847]:

\[
PPhS^{+}A^{-} + 2n e^{-} + 2n H^{+} \rightleftharpoons \text{polymer} \tag{2.34}
\]

Poly(Methylene Blue) (PMB) and Other Polythiazines [832, 841, 851–872]

(The exact position of the linkage has not yet been determined.)
Synthesis: oxidative electropolymerization of methylene blue at pH 8.2 [841, 859, 860, 863, 868] or in ionic liquid [872].

Redox reaction: PMB shows similar electrochemistry to the parent compound [841, 860–864, 868].

At low pH values:

\[
\begin{align*}
\text{(2.35)}
\end{align*}
\]

At higher pH values:

\[
\begin{align*}
\text{(2.36)}
\end{align*}
\]

In a similar way, other phenothiazines such as methylene green [871] azure A [851, 852, 856], toluidine blue [870], and thionine [854, 855, 858, 860, 868] have also been electropolymerized and characterized.
Polyflavin (PFl) [873]

Synthesis: oxidative electropolymerization of riboflavin, flavin mononucleotide, and flavin adenine dinucleotide (FAD) in acid media [873].

Redox reactions: monomer-type, pH-dependent redox activity. This indicates that polymerization occurs without the destruction of the corresponding monomer. The structure of the electronically conducting, redox active polymer is similar to that of polyazines, with the monomers bound to each other via ring-to-ring coupling [873].

Poly(New Fuchsin) (PnF) [874, 875]
Synthesis: oxidative electropolymerization of new fuchsin [874, 875].
Redox reaction:

\[
\begin{align*}
\text{C} & \quad \text{N} \\
\text{H} & \quad \text{A}^{+} \\
\text{CH}_{3} & \quad \text{A}^{-}
\end{align*}
\]

(2.37)

2.2.3 Polymers from Nonheterocyclic Aromatic Compounds

2.2.3.1 Polyfluorene (PF), Poly(9-Fluorenone) (PFO) [876–881], and Poly (9,10-Dihydrophenanthrene) [882]

Synthesis: oxidative electropolymerization in boron trifluoride diethyl etherate (BFEE) or BFEE + CHCl₃ solvents [880, 882] as well as in dichloromethane and acetonitrile [878].

Redox reaction: the polymer films show good redox behavior. The mechanism has not yet been clarified.
Color change is blue ⇔ deep brown (PF) and dark brown ⇔ red (doped state) (PFO). The polymer, like the monomer, exhibits photoluminescence.

2.2.3.2 Poly(p-Phenylene) (PPP) and Poly(Phenylenevinylene) (PPPV) [883–891]

Poly(p-Phenylene) (PPP) [883–887]

![Poly(p-Phenylene) (PPP) structure]

Synthesis: reductive coupling of dihalogenophenyl compounds in the presence of Ni\(^0\) complexes [883–885] or oxidative coupling of cation radicals originating from either benzene or biphenyl species in weakly nucleophilic media [887]. Highly crystalline PPP films have been prepared by electrochemical oxidation from benzene/96% H\(_2\)SO\(_4\) solution [885, 886].

Redox reaction:

\[
\text{PPP} + z\cdot e^- \rightleftharpoons \left[ \begin{array}{c} \text{PPP} \\ \text{PPP} \end{array} \right]_{n}^{+} + z\cdot e^- \tag{2.38}
\]

\[
\text{PPP} + z\cdot Li^+ + z\cdot e^- \rightleftharpoons \left[ \begin{array}{c} \text{PPP} \\ \text{PPP} \end{array} \right]_{n}^{+} + z\cdot e^- \tag{2.39}
\]

Poly(Phenylenevinylene) (PPPV) [888–891]
Synthesis: electrochemical reduction of $\alpha,\alpha',\alpha''$-tetrabromo-$p$-xylene TEABF$_4$/DMF + 0.2% H$_2$O at $-2.3$ V [888]. Poly(1-methoxy-4-(2-ethyl-hexyloxy)-$p$-phenylenevinylene) (MEH-PPV) was prepared by chemical synthesis [890].

### 2.2.3.3 Polytriphenylamine (PTPA) and Poly(4-Vinyl-Triphenylamine) (PVTPA) [892, 893]

Synthesis: PVTPA was produced by free radical polymerization of 4-vinyltriphenylamine; the electrode was then coated with this polymer using an evaporation technique, and finally the electrooxidation results in the dimer form shown above [892]. PTPA was synthesized by the electrooxidative polymerization of triphenylamine in acetonitrile/TBAPF$_6$ [892].

Redox reaction:

$$\text{PTPA} + 2e^- \rightarrow \text{PVTPA}$$
2.2.4 Other Polymers

Several other molecules, which cannot be fitted to the categories discussed above, have been electropolymerized. Two of those are mentioned below for illustration.

2.2.4.1 Polyrhodanine (PRh) [894]

![Chemical structure of Polyrhodanine (PRh)](image)

Synthesis: oxidative electropolymerization of rhodanine in ammonium oxalate solution [894].

Redox reaction:

\[
PRh \rightleftharpoons \left[ \begin{array}{c}
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
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\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\text{N}^+ \\
\text{S} \\
\end{array} \right] + 4n e^- + 4n H^+ \]

Color change: colorless $\rightleftharpoons$ transparent yellow $\rightleftharpoons$ dark purple.

2.2.4.2 Poly (Eriochrome Black T) [895]

![Chemical structure of Poly (Eriochrome Black T)](image)

Synthesis: oxidative electropolymerization of Eriochrome black T in alkaline solution [895].
2.3 Electronically Conducting Polymers with Built-In or Pendant Redox Functionalities

2.3.1 Poly(5-Amino-1,4-Naphthoquinone) (PANQ) [896]

(Polyaniline-type polymer involving one quinone group per ANQ moiety.)

Synthesis: electrooxidation of 5-amino-1,4-naphthoquinone resulting in electropolymerization via head-to-tail coupling [896].

Redox reactions: the polymer shows both quinone and PANI electrochemistry [896]:
2.3.2 Poly(5-Amino-1-Naphthol) [897, 898]

Synthesis: oxidative electropolymerization from 5-amino-1-naphthol in acid media. In basic media, the polymerization proceeds through the oxidation of the –OH group and yields the poly(naphthalene oxide) structure [897].
Redox reaction: polyaniline-like behavior in acid media.

2.3.3 Poly(4-Ferrocenylmethylidene-4H-Cyclopenta-[2,1-b;3,4-b’]-Dithiophene) [899]

Synthesis: oxidative electropolymerization of the respective cyclopenta-dithiophene monomers via the coupling of the thiophene units [899].
Redox reactions: this polymer exhibits the redox transitions of both the ferrocene unit and the polythiophene backbone.
2.3.4 Fullerene-Functionalized Poly(Terthiophenes) (PTTh–BB) [900]

Synthesis: electropolymerization of \(N\)-methyl-2-(2,2',5',2''-terthiophene-3'-yl)ethenyl)fullero-[3,4]-pyrrolidine [900].

Redox reaction: the polymer shows the redox reactions of fullerene and polythiophene.

2.3.5 Poly[Iron(4-(2-Pyrrol-1-Ylethyl)-4'-Methyl-2,2'-Bipyridine)\textsubscript{3}\textsuperscript{2+}] [901, 902]
Synthesis: electrochemical polymerization of the parent compound [901]. Redox reactions: it exhibits the redox behaviors of both the complex and the polypyrrole [902].

### 2.3.6 Polypyrrole Functionalized by Ru(bpy)(CO)$_2$ [903]

![Polypyrrole Functionalized by Ru(bpy)(CO)$_2$](image)

Synthesis: two-electron reduction of $[\text{Ru(bpy)(CO)$_2$(CH}_3\text{CN)}]^{2+}$, resulting in redox polymeric Ru–Ru bonded films $[\text{Ru(bpy)(CO)$_2$}]_n$, and the anodic oxidation of the complexes leads to the formation of functionalized polypyrrole films [903].

### 2.3.7 Poly(Tetra-Substituted Porphyrins) [904] and Poly(Tetra-Substituted Phthalocyanines) [905–907]

![Poly(Tetra-Substituted Porphyrins) and Poly(Tetra-Substituted Phthalocyanines)](image)

$\text{Ar} = $

- 9,9'-Spirofluorene-2-yl
- fluorene-2-yl
- phenyl

$\text{H}_2\text{TPP}$

$\text{MTTP}$
Synthesis: oxidative electropolymerization of the respective free or metallated tetraphenyl—or fluorenyl or spirobifluorenyl—porphyrin [904].

Redox reactions: four redox waves in the potential region between 0.1 and 2 V vs. Fc/Fc⁺ in CH₂Cl₂/TBAPF₆ (p-doping) and two pairs of waves between −1 and −2 V (n-doping).

Iron tetra (o-aminophenyl) porphyrin was also electropolymerized; in this case, the oxidation of amino groups is the key step; therefore, the mechanism of electropolymerization is similar to that of polyaniline and its analogs [905].

Metal-phthalocyanines have also been electropolymerized starting from the respective tetraamino and other derivatives [905–907].

2.3.8 Poly[4,4'-(5')-Bis(3,4-Ethyleneoxy)Thien-2-Yl] Tetrathiafulvalene (PEDOT–TTF) and Poly [3-7-Oxa-8-(4-Tetrathiafulvalenyl) Octyl]-2,2'-Bithiophene] (PT–TTF) [908]
Synthesis: oxidative electropolymerization of the respective monomers [908].

Redox reaction:

Both polymers show the characteristic redox responses of tetrathiafulvalene; however, the behavior of PEDOT–TTF, where TTF is incorporated into the polymer chain, differs from that of the other polymer, where TTF moieties are pendant groups. In the latter polymer, the oxidation of polythiophene occurs more quickly due to a mediated mechanism between TTF moieties and the polymer chains.

Many other conducting polymers containing redox groups have been synthesized; e.g., polyflourenylidene containing ferrocene units was prepared by means of anodic oxidation of the monomer in dichloromethane and acetonitrile [909]. Polypyrrole functionalized with titanocene dichloride [910], 1,3,5 triazine core with flourene arms [911] have also been investigated.

2.4 Copolymers [356, 865, 912–945]

The polymers described in Sects. 2.2.2.4 and 2.3 can be considered to be copolymers, and in many cases they are actually called copolymers. However, those polymers have been synthesized from monomers with polymerizable groups (e.g., thiophene), and the monomer already contains the redox functionality. For instance, poly[bis(3,4-ethylenedioxythiophene)-(4,4'-dinonyl-2,2'-bithiazole)] (PENBTE) [919] synthesized by oxidative electropolymerization of bis(3,4-ethylenedioxythiophene)-4,4'-dinonyl-2,2'-bithiazole) in dichloromethane/TBAPF$_6$ or TEABF$_4$ [919] is a typical representative of this class of copolymers.
It shows two reversible redox processes in which the thiazole units participate during oxidation (p-doping), and one reversible redox process involving both the thiazole and EDOT units at high negative potentials (n-doping), while the respective color change is blue (reduced) ⇔ red (oxidized).

The copolymers that will now be discussed have been prepared from two or more different monomers, which can also be electropolymerized separately, and the usual strategy is to mix the monomers and execute the electropolymerization of this mixed system. It should be mentioned that the structures of the copolymers have not been clarified unambiguously in many cases. Usually the cyclic voltammetric responses detected show the characteristics of both polymers, and so it is difficult to establish whether the surface layer consists of a copolymer or whether it is a composite material of the two polymers. However, several copolymers exhibit electrochemical behaviors that differ from the polymers prepared from the respective monomers. The properties of the copolymer depends on the molar ratio of the monomers (feed rate) and can be altered by other experimental conditions such as scan rate and pH, since generally the electrooxidation of one of the comonomers is much faster than that of the other one (a typical example is the comonomer aniline, whose rate of electropolymerization is high even at relatively low positive potentials). In many cases, the new materials have new and advantageous properties, and it is the aim of these studies to discover and explore these properties. We present a few examples below.

2.4.1 Poly(Aniline-co-Diaminodiphenyl Sulfone) [929, 930]
2.4 Copolymers

Synthesis: chemical oxidation of aniline and 4,4’-diaminodiphenyl sulfone mixture by \( \text{K}_2\text{S}_2\text{O}_8 \) in acid media \([929]\) or by electropolymerization \([930]\).

Redox reactions: two oxidation waves, formation of cation radical (polaronic form), and bipolarons.

Color change: yellow (reduced) \(\rightleftharpoons\) green (half-oxidized) \(\rightleftharpoons\) blue (fully oxidized).

2.4.2 Poly(Aniline-co-2/3-Amino or 2,5-Diamino Benzenesulfonic Acid) \([920, 935, 937]\)

Synthesis: electropolymerization of a mixture of aniline and 2-amino- or 3-amino or 2,5-diamino benzenesulfonic acid \([920, 935, 937]\).

Redox reaction: see polyaniline.

(Soluble in alkaline media and the copolymer is still electrochemically active at pH 7.2.)

2.4.3 Poly(Aniline-co-o-Aminophenol) \([925, 938]\)

Synthesis: co-electropolymerization of aniline and \(o\)-aminophenol \([938]\).

Redox reaction: benzoid \(\rightleftharpoons\) quinoid, PANI-type transformations \([925]\).

2.4.4 Poly(m-Toluidine-co-o-Phenylenediamine) \([916, 927]\)

The copolymer contains \(m\)-toluidine and \(o\)-phenylenediamine units in the polymer backbone. The exact structure has not been clarified thus far.

Synthesis: co-electropolymerization of \(m\)-toluidine and \(o\)-phenylenediamine \([916]\). Similar copolymerization has been carried out by using \(o\)-toluidine and \(o\)-phenylenediamine \([917, 918]\).

Redox reaction: superposition of the constituents.
2.4.5 Poly (Luminol-Aniline) [923]

Synthesis: co-electropolymerization of aniline and luminol [923].
Redox reaction: benzoid ⇔ quinoid, PANI-type transformations.
Copolymers prepared from acid solutions with different monomer concentration ratios display electroactivity even at pH 8 due to the self-doping role assured by luminol moiety in the copolymer.
2.4.6 Other Copolymers

Finally, we mention some other attempts that have been directed toward the preparation of copolymers: poly(aniline-co-o/m-toluidine) [939, 941], poly(aniline-co-thiophene) [933], poly(aniline-co-aniline with sulfonate, alkylsulfonate, sulfopropyl, carboxylate, methoxy, chloro and fluoro groups) [912, 928, 936], poly(aniline-co-o-phenylenediamine [945], poly(aniline-co-p-phenylene diamine) [356], poly(aniline-co-m-phenylenediamine) [922, 926], poly(aniline-co-diphenylamine) [921, 943], poly (aniline-co-dithioaniline [942], poly[(o-chloroaniline)-co-(4,4'-diaminodiphenylsulfone) [932] as well as copolymers of diphenylamine and anthranilic acid [944] or benzidine [915], carbazole and N-p-tolysulfonfyl pyrrole [913, 914], and aniline with pyrrole [934] or aminonaphthalenesulfonates [931]. Random copolymer of 3,4-propylenedioxythiophene and N-phenylsulfonfyl pyrrole was synthesized electrochemically [924]. The copolymer of 3,4-ethylenedioxythiophene and N-phenylsulfonfyl pyrrole was also prepared and characterized [940]. Copolymerization of phenothiazine with thiophene or furan has been reported [865]. Several other works that describe the preparation and properties of both the homopolymers and copolymers can be found among the references given for the parent compounds.

2.5 Composite Materials [156, 157, 270, 330, 340, 367, 381, 498, 578, 602, 786, 790, 806, 946–1061]

In the last decade, the researchers have started to apply novel approaches. The new trend is the fabrication and utilization of composites including nanocomposites of conducting polymers and other materials such as carbon nanotubes, graphene or inorganic compounds having special structure and properties.

In the literature various, rather different, systems are called composites. In some cases the word “composite” or “hybrid” is used to describe systems where the monomer is polymerized in the presence of polymeric counterions (e.g., poly-anions), and the resulting material contains practically equal amounts of the polymers (by mass). Even in these cases, it has been found that special interactions exist between the components, so the composite film cannot be viewed as simple mixtures of the two components, as has been demonstrated for the composite of PEDOT with partially polymerized 4-(pyrrole-1-yl) benzoic acid [999]. The deposition of conducting polymers by chemical or electrochemical polymerization onto high-surface-area inorganic materials (e.g., carbon including carbon nanotubes, metal hexacyanoferrates, silica, and metal oxides) also leads to composites. Nano-composites are also formed when a small polymerizable molecule can be incorporated into the layered structure of an inorganic crystal, and the host material acts as an oxidizer that induces the polymerization.

The incorporation of different components (e.g., catalytically active metals, enzymes, photochemically active compounds, silicomolybdate, Keggin-type
2.5.1 Composites of Polymers with Carbon Nanotubes and Other Carbon Systems

A composite of poly(methylene blue) and multiwalled carbon nanotubes showed a good stability, high reproducibility, and catalytic activity on different biochemical compounds [1060]. Polypyrrole–carbon nanotubes composites were prepared, which are of interest for supercapacitor applications [1037]. Poly(diphenylamine)–single-walled carbon nanotube (PDPA/SWNT) composites were synthesized electrochemically and tested as active electrode materials for rechargeable lithium batteries [951]. Poly(diphenylamine)–multiwalled carbon nanotube (MWCNT) showed enhanced electrocatalytic properties toward the reduction of hydrogen peroxide [1030]. Polyaniline–porous carbon composite was fabricated for supercapacitor application [965]. Platinum nanoparticles were deposited onto the composite supports from platinum salts by formaldehyde reduction. 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. The durability of MC-PEDOT-supported catalysts in PEFCs was attributed to enhanced corrosion resistance of MC [1048]. The polymerization of 3,4-ethylenedioxythiophene with sol–gel-derived mesoporous carbon leading to a new composite and its subsequent impregnation with Pt nanoparticles for application in PEFCs was reported. The composite exhibited good dispersion and utilization of platinum nanoparticles akin to other commonly used microporous carbon materials, such as carbon black. This composite exhibited promising electrocatalytic activity toward oxygen reduction reaction, which is central to PEFCs [1047]. Polyaniline deposited on carbonic substrates [1026] and carbon nanotubes [1014] were applied as hydrogen mediator and catalyst in fuel cells [1026] as well as for supercapacitor application [1014]. Poly(m-toluidine) [1022] and poly(o-toluidine) [1023] were 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 [1022] and nickel ions [1023], respectively. Both systems enhanced the oxidation of methanol [1022, 1023]. MWCNTs–poly (neutral red) composites were prepared, and it was found that the type of the nanotubes strongly influenced the efficiency of the electrocatalytic effect [962].
2.5.2 Composites of Polymers with Metal Hexacyanoferrates

Poly(N-acetylaniline) and Prussian blue composite film was prepared electrochemically and showed high electrocatalytic activity toward the reduction of H$_2$O$_2$ [367]. Controlled fabrication of multilayered 4-(pyrrole-1-yl) benzoate supported poly(3,4-ethylenedioxythiophene)-linked hybrid films of nickel hexacyanoferrate (NiHCF) was executed. The ability of 4-(pyrrole-1-yl) benzoic acid (PBA) to form monolayer-type carboxylate-derivatized ultrathin organic films on solid electrode surfaces was explored to attract and immobilize Ni$^{2+}$ ions. In the next step, the system was exposed to Fe(CN)$_6^{3-}$ or Fe(CN)$_6^{4-}$ solution to form a robust NiHCF layer. By repeated and alternate treatments in solutions of PBA, Ni$^{2+}$ cations, and hexacyanoferrate anions, the amount of the material could be increased systematically in a controlled fashion to form three-dimensional multilayered NiHCF-based assemblies. The layer-by-layer method was also extended to the growth of hybrid-conducting polymer-stabilized NiHCF films in which the initial PBA-anchored NiHCF layer was subsequently exposed through alternate immersions to 3,4-ethylenedioxythiophene, Ni$^{2+}$, and hexacyanoferrate solutions. During electropolymerization PEDOT-linked NiHCF-based multilayered films were produced. They showed good stability and high dynamics of charge transport [1011]. PEDOT–NiHCF composite was used for the detection of ascorbic acid [1051]. Hybrid composed of poly(2-(4-aminophenyl)-6-methylbenzothiazole) and NiHCF was investigated; a good electrocatalytic activity was found toward the oxidation of methanol and oxalic acid [811]. Composite materials based on poly(2-[(E)-2-azulene-1-yl)vinyl] thiophene) (PAVT) and Prussian blue were prepared for phenol detection [1003].

2.5.3 Conducting Polymer Composites with Metals

Several nanocomposites have been prepared by using conducting polymers and metals. For instance, gold–polyaniline core/shell nanocomposite particles with controlled size were fabricated on the highly oriented pyrolytic graphite (HOPG). The HOPG surface was modified by covalent bonding of a two-dimensional 4-aminophenyl monolayer employing diazonium chemistry. AuCl$_4^-$ ions were attached to the Ar-NH$_2$ termination and reduced electrochemically. This results in the formation of Au nuclei that could be further grown into gold nanoparticles. The formation of polyaniline as the shell wrap of Au nanoparticle was established by localized electropolymerization. The AFM results showed that the gold–polyaniline core–shell composites had a mean particle size of 100 nm in diameter and the polyaniline shell thickness is about 15 nm [1005]. Au nanoparticle–polyaniline nanocomposite layers obtained through layer-by-layer adsorption were applied for the simultaneous determination of dopamine and uric acid [1040]. PANI–Ag nanocomposite was prepared in water-in-ionic liquid and ionic
liquid-in-water microemulsions, respectively [381]. 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 electro-oxidation of methanol, formic acid, and borohydride [1036]. Metal nanoparticles have been deposited on polyaniline nanofibers and used in memory devices and for electrocatalysis [270]. The advantages of incorporation of metallic particles into porous matrixes of conducting polymers for fuel cell applications have been emphasized, recently [948]. PtRu particles were deposited in PANI–polysulfone composite films, and the catalytic activity has been studied [976]. A photopolymerization process has been elaborated that simultaneously deposits conducting polymer, e.g., polypyrrole films and incorporates nanophase silver grains within the films [981, 982]. Poly(3,4-ethylenedioxy)pyrrole) (PEDOP)–Ag and PEDOP–Au nanocomposites were synthesized by electropolymerization in a waterproof ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, followed by Ag/Au nanoparticle incorporation, for the utilization in electrochromic devices [993]. The current state and prospects of the use of electrodes modified with noble metals, polymer films, and their composites in organic voltammetry have been surveyed [1033].

2.5.4 Conducting Polymer and Metal Oxides Composites

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 [1019]. 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 [1021]. Bulk iridium metal and thin films of Ir nanoparticles, subsequently converted to Ir oxide, were used as a template for PANI formation within the porous structure. These hybrid films exhibit an enhanced internal porosity, high charge densities, unusual electrochromic behavior, and very rapid charge transfer kinetics. The formation of this composite also resulted in a widening of the potential window over which pseudocapacitive and electrochromic responses are seen [973]. Polyaniline–RuO2 composite electrodes were prepared by spontaneous oxidative polymerization of aniline and were tested for supercapacitor application [1039]. Hydrous RuO2 on PANI–Nafion matrix was deposited, which also showed high capacitance [1038]. Fine particles of RuO2 were successfully deposited on polypyrrole nanorods, and the system showed good capacitor characteristics [1002]. Composite electroactive films consisting of poly(3,4-ethylenedioxythiophene) and amorphous tungsten oxide, WO3/Hx(WO3), 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 which cannot be considered as a simple mixture of the organic and inorganic components. The hybrid films exhibit good mediating capabilities toward electron transfers and accumulate effectively charge, which may be of importance to electrocatalysis and supercapacitors [1041]. PEDOT–polyoxometallate hybrid layers were also characterized [790]. Polythiophene–magnetite composite layers have been prepared by the electropolymerization of 3-thiophene-acetic-acid in the presence of Fe₃O₄ 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 Fe₃O₄, may be used in magnetic electrocatalysis [988]. A facile and scalable approach for the fabrication of vertically aligned arrays of Fe₂O₃/polypyrrrole core–shell nanostructures and polypyrrrole nanotubes has been reported. It was based on the fabrication of α-Fe₂O₃ nanowire arrays by the simple heat treatment of commodity low carbon steel substrates, followed by electropolymerization of conformal polypyrrrole sheaths around the nanowires. Subsequently, electrochemical etching of the nanowires yields large-area vertically aligned polypyrrrole nanotube arrays on the steel substrate. The developed methodology is generalizable to functionalized pyrrole monomers and represents a significant practical advance of relevance to the technological implementation of conjugated polymer nanostructures in electrochromics, electrochemical energy storage, and sensing [1054]. Polycarbazole was prepared by electropolymerization in TiOₓ by using layer-by-layer and surface sol–gel techniques. TiOₓ acted as dielectric spacer, which limited electron transfer rate and attenuated energy transfer in fluorescence. These hybrid ultrathin films were applied in photovoltaic devices [977]. Polyaniline–TiO₂ [946] and poly(3-methylthiophene)–composite TiO₂ [786] were also tested [946]. Poly(o-toluidine)–CdO nanoparticle composite was prepared for the corrosion protection of mild steel [963].

2.5.5 Conducting Polymer–Inorganic Compounds Composites

Nanocomposites are also formed when small polymerizable molecules can be incorporated into the layered structure of an inorganic crystal, and the host material acts as an oxidizer that induces the polymerization; e.g., the intercalation of aniline [986] and pyrrole [987] into RuCl₃ crystals. A positively charged ruthenium metal complex ([Ru(bpy)₃]²⁺) was immobilized by ion paring 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 [788]. The incorporation of \([\text{Os(bpy)}_3]^{2+}\) in polyaniline and polypyrrole results in a faster electron transport rate between metal centers and enhanced ECL efficiency [968]. 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 [1010]. Titanocene dichloride centers were immobilized inside a polypyrrole matrix, and the redox transformation of polypyrrole matrix and titanocene centers immobilized in the film were investigated [602]. Composite films of polypyrrole with a sulfonated organically modified silica (ormosil) have been prepared on electrodes by the electrochemical oxidation of pyrrole in a liquid sol–gel electrolyte. The ormosil is incorporated into the polypyrrole matrix as an immobile polymeric counterion in addition to mobile Cl\(^-\) counterions from the sol–gel electrolyte [950]. Perovskite \((\text{La}_{1-x}\text{SrMnO}_3)\) was embedded into a polypyrrole layer, sandwiched between two pure PP films, electrodeposited on a graphite support, and the composite was investigated for electrocatalysis of the oxygen reduction reaction [1035]. Polypyrrole (PP) with incorporated CoFe\(_2\)O\(_4\) nanoparticles was investigated for the same purpose [1034]. Polypyrrole–iron oxalate system exhibited photoelectrochemical activity. In the same paper, the catalytic properties of PP-vitamin B12 composite have also been highlighted [956]. Poly(3-octyl-thiophene) and polypyrrole iron oxalate composites were synthesized through a postpolymerization oxidative treatment [1055]. 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 [971]. Polyaniline was synthesized within the pores of sol–gel silica. The template synthesis resulted in more ordered PANI structure with improved charge transport rate and capacity [1015]. Co-condensation of \((\text{ferrocenylmethyl})\text{dimethyl}(\omega\text{-trimethoxysilyl})\) alkylammonium hexafluorophosphate with tetramethysilane resulted in a hybrid film, and the catalysis the oxidation of catechol and catechol violet [1056].

### 2.5.6 Polymer–Polymer Composites

Several efforts have been made in order to utilize the different properties (color change, catalytic activity, etc.) of two different conducting polymers. Polyaniline–poly(o-phenylenediamine) [972] or polyaniline–poly(methylene blue) composites [1006] can be mentioned in this respect. Composites of a conducting polymer with a nonconducting one also have been tested, e.g., poly(aniline) and poly(styrene sulfonate) composite was found to affect the morphology of the polymer film [970, 1004], and the pH dependence of the redox transformations and the conductivity [156, 157], as well as to improve the permeability of the resulting membrane [1020]. The temperature dependence of the doping process has been measured
This composite was also applied in a microelectrochemical enzyme switch responsive to glucose [156]. Polyaniline and poly(methylmetacrylate-co-acrylic acid) offer a better corrosion protection to the aluminum alloy than the epoxy resin films [1017]. The incorporation of β-cyclodextrin in the polyaniline layer results in “comb-like formations” within the layer while the incorporation of sulfated β-cyclodextrin in the polyaniline layer leads to more irregular morphologies and to the layers with the increased ohmic resistance [330]. Polyaniline–Nafion or other perfluorinated sulfocationic composite membranes were prepared for different possible applications such as electrocatalysis or to improve the electron transport [954, 957, 958, 974]. Poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) 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 [960]. Li+ ion transport in the same composite has been studied [806]. Polyaniline was synthesized within the pores of poly (vinylidene flouride). The template synthesis resulted in more ordered PANI structure with improved charge transport rate and capacity [1015]. Nanostructured films of hollow polyaniline and PANI–polystyrene core shells were prepared by template synthesis [990]. Poly(2-acrylamido-2-methyl-1-propanesulfonate)-doped thin polyaniline layers have been also prepared and characterized [1008]. Polypyrrole–poly(styrene sulfonate) electrodeposited on porous carbon was prepared for water softening by removal of Ca2+ ions [1029]. The charge transport in this composite has also been investigated [997]. Composites of polypyrrole and Cladophora cellulose have been investigated in order to use those for desalting, for extraction of proteins and DNA from biological samples [978], as well as for battery application [578]. Polypyrrole–flavin composite film was prepared where flavin molecules act as dopant anions with strong interactions with the PP matrix [498].

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 glucose oxidase 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 [1013].

The synthesis and electrochemical characterization of ferrocene (Fc) functional polymethacrylate (MA) brushes on indium tin oxide electrodes using surface-initiated atom transfer radical polymerization have also been reported. The preparation of block copolymer brushes with varying sequences of FcMA segments was conducted and the effects of spacing from the ITO electrode surface were investigated [994]. Composite fabricated from poly(brilliant cresyl blue) and poly(5-amino-2-naphtalenesulfonic acid) showed pH-dependent catalytic activity [952].

Another class of polymer–polymer composites is that when multilayers are formed by layer-by-layer technique. A detailed experimental work and theoretical analysis can be found in the papers of Calvo and coworkers. They studied a cationic osmium pyridine–bipyridine derivatized poly(allylamine) and poly(vinylsulfonate) polyanion model system in different electrolytes [1042, 1043].
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