

FORMATION, GROWTH AND PROPERTIES OF THIN POLYPYRROLE FILMS

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Abstract

The different steps involved in the formation and growth of polypyrrole films on electrode surfaces are described, as well as the molecular structures present in neutral and positively charged polypyrrole. A discussion is given of the kinetics and energetics of charge carrier generation during oxidation and doping, and the role of ions in charge transport and the insulator-conductor transition.

I. INTRODUCTION

Polypyrrole has been one of the most studied conducting polymers during the past decade, due to the stability of its electrical properties under normal ambient conditions as compared to other similar materials, e.g., polyacetylene. Evidence for the synthesis of polypyrrole date back to at least 60 years ago [1,2], but it was only after the work of Macneil et al. in 1963 [3] that the nature of this polymer began to elucidate. They reported the synthesis of polypyrrole by heating tetraiodopyrrole in an inert atmosphere, obtaining a black powder which expelled iodine upon cathodic reduction, increasing its resistivity from 200 to $5.3 \times 10^8 \Omega \text{ cm}$ [4]. The first electrochemical synthesis of polypyrrole was reported by Dall'Olio et al. [5], where the deposition of a black film during anodic oxidation of pyrrole in sulphuric acid was accomplished. These were early attempts before the work of Shirakawa et al. [6] and Ito et al. [7] with crystalline films of polyacetylene. Modern work on polypyrrole starts from the work of Diaz et al. [8] who reported the synthesis of polypyrrole films in acetonitrile with excellent conductivity.

Most publications on the synthesis of polypyrrole have focused on the characterization of the mechanical and electric properties of the materials obtained under diverse experimental conditions, and thus the fundamental aspects of the mechanisms of deposition of the films and their transformations at diverse oxidation states have remained most often unclarified. In this paper we describe the several steps involved in the formation and growth of the polymeric phase on electrodes, and the distinct molecular structures present in neutral and positively charged polypyrrole. We then discuss the generation of charge carriers during oxidation and doping, giving rise to the insulator-conductor transition and, in some cases, to overoxidation.

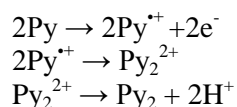
II. ELECTROCHEMICAL DEPOSITION OF POLYPYRROLE FILMS

The process of electropolymerization is affected by several variables. In order to identify the salient features of the mechanisms involved we will examine briefly the basic results and describe the anodic formation of polymer films in terms of two distinct stages: (i) oxidation of pyrrole, and (ii) formation and growth of the polymer phase.

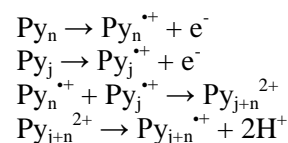
Anodic oxidation of the monomer.

It is generally accepted that oligomeric species of different chain length accumulate in the vicinity of the electrode during anodic oxidation of pyrrole [9-17]. Baker and Reynolds [12], using an in situ micro gravimetric technique, found faradaic efficiencies lower than 100% during the electropolymerization of pyrrole from different media. Raymond and Harrison [13] detected the presence of bipyrrrole during oxidation of pyrrole with ring-disc electrodes. Recent spectrophotometric studies [18] reveal that several absorption bands arise in solution during anodic oxidation of pyrrole in aqueous solution, chromatographic analysis suggest the presence of oligomers with up to nine monomers. It has been postulated that the oligomerization process occurs through couplings of radical cations generated during oxidation of the monomer at the electrode, resulting first in a dicationic adduct which doubly deprotonates to form the neutral dimer, as indicated by the following scheme [9,12,15,16,19-21]:

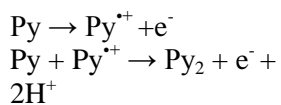
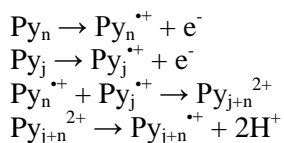
Initiation:



Propagation:



A second mechanism which has been also postulated considers couplings between cation radicals and neutral molecules at the surface of the electrode [14,22-24]:

Initiation:**Propagation:**

These mechanisms differ in that the first considers oxidation of monomers and coupling of cations radicals in solution, whereas the latter contemplates the coupling of monomers to cation radicals at the electrode during their oxidation. The mechanism according to scheme (1) has been largely discussed in the literature. Molecular orbitals calculations [25] indicate that the coupling of radical cations to neutral molecules is impeded by symmetry and thus that couplings between radicals would be favoured. Baker and Reynolds [12] monitored the amount of polymer deposited during oxidation of pyrrole and determined second order kinetics with respect to pyrrole concentration, concluding that the rate determining step for oligomerization in solution was the coupling of radical cations. Lowen and Van Dike [19] have also suggested (1) as the appropriate mechanism for oligomerization, on the basis of isotopic effects and radical trapping studies. Mechanism (2), however, overcomes the electrostatic repulsion between two radical cations during coupling and avoids the existence of a doubly charged intermediate. Further kinetic evidence for mechanism (2) is provided by a reaction order of one with respect to pyrrole during oligomerization [14,23], which suggests that the rate determining step is the formation of the radical cation, followed by oxidative coupling with monomer on the electrode surface. Fermin and Scharifker [18] reported that accumulation of oligomeric species during oxidation of pyrrole in aqueous neutral solutions is strongly inhibited by stirring. During oxidation of pyrrole at rotating disk electrodes, only very low concentrations of short oligomers (up to three monomeric units) are found, in contrast with oxidation at stationary electrodes, as discussed above. Similarly, it has been found [26] that the rate of pyrrole oxidation decreases sharply with electrode rotation. Mechanism (2) also

accounts for the autocatalytic oxidation of pyrrole indicated by these results, as it requires the presence of intermediates reacting on the electrode surface throughout the oligomerization process.

Either through couplings between radical cations in solution or by way of oxidative coupling monomers to radical cations on the electrode surface, oligomeric species are generated during the electrochemical oxidation of pyrrole. We will next turn to discuss how these oligomers are involved in the formation of the polymer phase and through which mechanisms the films grow.

Birth and growth of polypyrrole films on electrodes.

The initial stages of growth of polypyrrole films on electrodes are characterized by ascending currents in potentiostatic experiments [22,27], potential maxima under galvanostatic conditions [28] or current loops during voltammetric deposition [15]. This has been associated to nucleation and growth of the polymer, in analogy with the corresponding results observed during the electrodeposition of metallic phases [29]. John and Wallace [15] studied the deposition of polypyrrole using microelectrodes and electrodes of conventional size and their results suggested that the process of formation and growth of polymer films occurs by the continuous precipitation of oligomers accumulated in solution during oxidation. Other studies indicated that the birth of the polymer on the electrode surface occurs after saturation of the solution in its vicinity with oligomers, while growth follows through the successive addition of monomers to already deposited polymer chains [9-14,16-18,26]. The experimental evidence indicates that ascending currents during potentiostatic experiments do not constitute unambiguous evidence for nuclear growth during the electrodeposition of conducting polymer films. Fig. 1 shows that the ascending transient currents vanish and the stationary currents decrease as the rotation speed of the electrode is increased and, likewise, fig. 2 shows that the potentiodynamic current loops disappear and the anodic currents decrease at increasing rotation rates. These results reflect the role of oligomers in the birth of the polymer on the electrode surface. Through either mechanism (1) or (2) oligomeric species are generated near the surface, which are more readily oxidized than the original monomer [10] giving rise to an autocatalytic process. Upon stirring, the rate of

accumulation of oligomers near the electrode decreases, in turn diminishing the current.

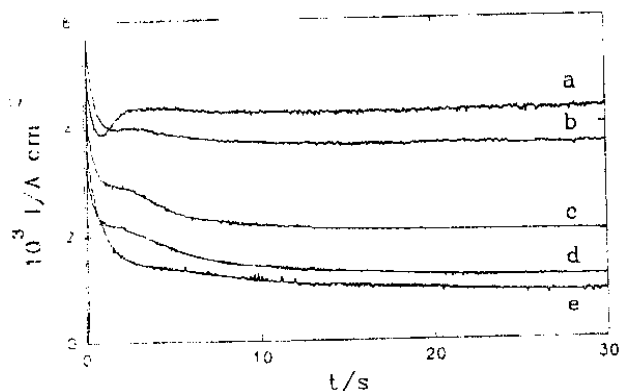


Figure 1. Oxidation of pyrrole on rotating vitreous carbon disc electrode at 0.700 V and 100 (a), 200 (b), 500 (c), 1000 (d) and 2000 (e) rpm [26].

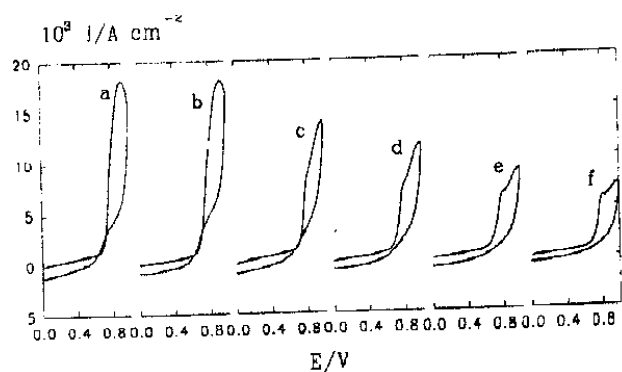


Figure 2. Cyclic voltammograms of rotating vitreous carbon disc electrode in 36 mM pyrrole and 1M KN03 aqueous solution at 100 mV/s and 0 (a), 100 (b), 500 (c), 1000 (d), 2000 (e) and 3000 (f) rpm.

Thus the birth of the film takes place by accumulation of oligomers in the solution adjacent to the electrode surface, from which they precipitate after reaching saturation. However, the same path does not explain film growth. The rate of growth of polypyrrole is not controlled by mass transfer [27], a result which has been repeatedly confirmed [30]. Scharifker et al. [14] found that the rate of expansion of the polymer phase was controlled by its ohmic resistance during growth, of expansion of the polymer phase was controlled by its ohmic resistance during growth, suggesting that growth occurred through the slow oxidation of the deposited polymer, yielding polarons, followed by their fast elimination by addition of monomers, a process during which the polymer remains essentially neutral. The resistivity of polypyrrole in the

direction perpendicular to the electrode surface during growth is then several orders of magnitude higher than that of already grown films at the same potential. This potential drop is associated with the effective potential for the interfacial reaction, in contrast with the in situ measurements of Kankare and Kupila [31] yielding 106 higher conductivities along the plane of the electrode surface.

Fig. 3 shows the effect of electrode rotation rate on growth current at different potentials [26]. In contrast with fig. 1, the current does not depend on rotation rate for already formed films, and the linear dependence between current and potential confirms the resistive control of the kinetics of growth [14]. Further evidence of resistive control during polypyrrole growth from aqueous solution is discussed by Higgins and Hamnett [32] on the basis of differential ellipsometry data.

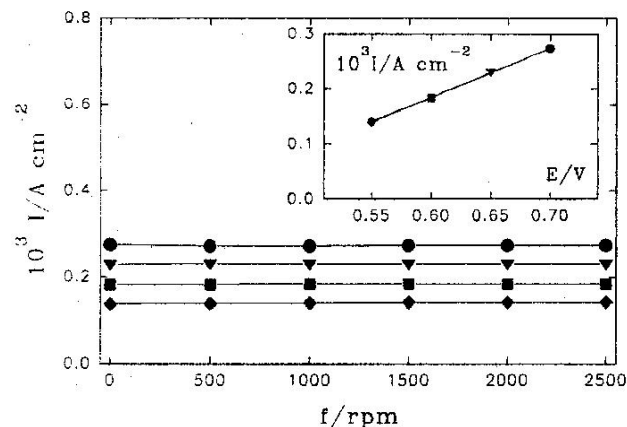


Figura 3. Current density as a function of rotation rate during growth of electrodeposited polypyrrole film at 0.55 (Δ), 0.60 (◻), 0.65 (×) and 0.70 (◉) V.

Given the complexities involved in the of generation and growth of polypyrrole on electrodes and the assortment of variables that affect these processes, a number of different models have been developed to describe particular phenomena [20,21,33-36]. Nevertheless, it seems that the most salient features of the electrogeneration of polypyrrole from aqueous neutral solutions may be described in terms of: (i) anodic oxidation of the monomer and generation of oligomers; (ii) accumulation of oligomers in solution and their precipitation on the surface of the electrode, and (iii) growth of polymers by oxidative attachment of monomers.

III. STRUCTURE OF ELECTRODEPOSITED FILMS

The structural characterization of chemically or electrochemically generated polypyrrole meets two fundamental difficulties: (i) it is insoluble, thus studies are limited to solid state spectroscopy, additionally complicated by (ii) its poor crystallinity. Thus information about the average length of polymer chains, their conformation, distance between rings, crosslinking, and so on, are not available from direct measurement but mainly through interpretation of spectroscopic data, assisted by models and theoretical calculation.

NMR [37,38], IR [39,40] and XPS [41] studies suggest that polypyrrole is constituted by chains joined fundamentally through α carbons with contributions from α - β' bonds for a certain degree of crosslinking. X-ray diffraction [42] and electron scattering [43] have established that the polymer structure is macroscopically amorphous, slight ordering along the plane of the electrode surface has been interpreted as evidence for coplanar orientation of pyrrole rings along the electrode. Structural disorder has been associated to two types of defects: (i) random loss of ring orientation, and (ii) crosslinking and opening of rings, giving rise to non-aromatic segments with loss of coplanarity and conjugation, generating "isolated" segments. The occurrence and density of these defects is associated with the temperature and rate of growth of the polymer phase, and hence the electrodeposition potential [42]. Recent studies [44] show evidence for the formation, during the initial stages of polymer growth, of microislands 20 to 50 Å wide, as well as strands with helical structure, some of them extending up to 100 nm.

The distribution of chain lengths is an important aspect which has not been appropriately elucidated. From elemental analyses [45] and XPS spectra [46] it seems that polypyrrole is made up by chains of few monomers in length. Fermin and Scharifker [18] compared uv-visible spectra of the polymer with those of products accumulated in solution during its electrodeposition and suggested that polypyrrole is composed of short chains no longer than 10 monomer units, in agreement with earlier *ex situ* measurements [47] and comparisons of UPS and optical absorption spectra of pyrrole and polypyrrole with CNDO calculations [48], concluding that polypyrrole chains were about four

units long. Although some interpretations are contrary to supposing that the polymer is made up of short chains [49-51], it is generally accepted that the polymer is a conglomerate of segments with few monomer units in length.

A detailed analysis of chain structure of polypyrrole reveals that, beside σ linkages between carbons, it is necessary to consider the quinoid isomer in which rings are linked by double carbon-carbon bonds. Unlike polyacetylene, polypyrrole has a non-degenerate ground-state structure, and thus the aromatic and quinoid structures are energetically non-equivalent. This quinoid isomer of polypyrrole has hitherto been described only by theoretical studies that have established its energy as slightly higher (by ca. 0.5 eV) than that of the aromatic form [52,53]. Yet we have recently interpreted the dominant features of the uv-visible spectra of polypyrrole films at different oxidation states considering two valence levels, associated with the neutral aromatic and quinoid structures, and a single conduction band [54], avoiding thereby shifting the valence band level upon oxidation [47,52,55]. Further evidence for the presence of both quinoid and aromatic structures in neutral polypyrrole is also obtained from recently reported deconvoluted solid-state ¹⁵N NMR spectra [56].

The polymer structure is still one of the most controversial aspects of polypyrrole. Its nearly amorphous nature, electronic transitions which suggest the coexistence of domains with different types of bonds, as well as the morphological differences between nascent and bulk polymer [44], are all consistent with the deposition of oligomers from solution and their slow growth by oxidative addition of monomers, as discussed in the previous section.

IV. ELECTROOXIDATION OF POLYPYRROLE

Several processes are involved in the anodic oxidation of polypyrrole. The generation of positively charged defects during oxidation is accompanied with changes in the polymer chains, ingress of counteranions and reordering of charges at the polymer/electrolyte interface. In the first part of this section we will concentrate on the generation of charge carriers. This constitutes the first stage in the oxidation of the polymer and it is also the only faradaic process in the absence of overoxidation. This will lead us to the other non-faradaic processes

associated with the oxidation-reduction of the polymer, and to a brief discussion of overoxidation that occurs even at moderate potentials in appropriate environments.

Charge carriers.

Transport of charges in conducting polymers is assisted by electronic defects. Polypyrrole, being a non-degenerate ground-state polymer [51], supports polarons (with spin) and spinless bipolarons as the charge-carrying self-localized states. Polarons are radical cations generated by primary oxidation, whereas bipolarons are dicationic species arising from further oxidation of polarons as well as polaron recombination. Besides structural changes [41,50,57,58], generation of polarons and bipolarons induce changes in the space charge layer at the polymer/solution interface, due to entrance of anions to compensate the positive charge carriers [21,50,59,60]. This affects electronic conduction and may induce chemical changes, as discussed below. The concentration of paramagnetic species increases with polymer oxidation, but then decreases at higher oxidation states, without an accompanying decline in conductivity [61-64]. Polarons are in fact intermediates in the process of switching the film from its neutral to fully oxidized state [64]. Generation of charge carriers results in new energy levels between the valence and conduction bands of the polymer [52,62,65-67]. Spectra of polypyrrole films at various potentials [54,65,66], such as those in fig. 4, show that the electronic transitions that arise due to charge carriers are located at wavelengths longer than the isosbestic (480 nm), where the absorbance increases with potential, approaching a limiting value below 600 nm, in the region of absorption by polarons, but increasing indefinitely at longer wavelengths due to the presence of bipolarons. The region below 480 nm corresponds to the interband transition of the neutral polymer, and its intensity decreases with potential. Genies and Pernaut [65] describe the oxidation of the film in terms of the following reactions:

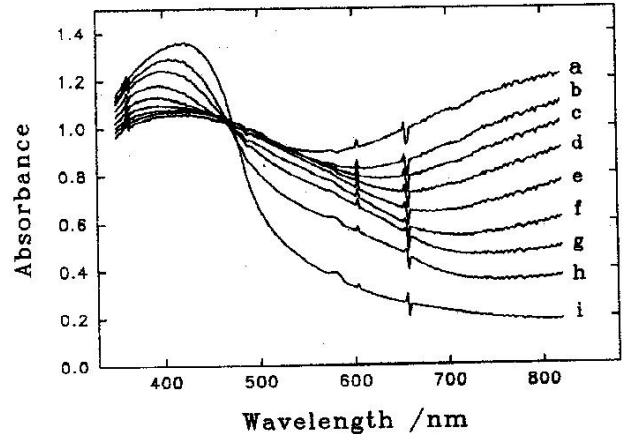
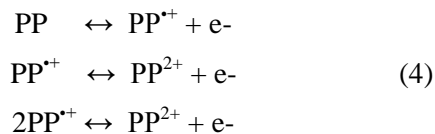


Figure 4. Transmission absorption spectra of 0.41 μm width polypyrrole film at 0.4 (a), 0.2 (b), 0.1 (c), 0.0 (d), -0.1 (e), -0.2 (f), 0.3 (g), -0.4 (h) and -1.1 (i) V vs SeE.

where the third reaction corresponds to polaron recombination and accounts for the decay of their concentration at high oxidation. However, the changes in absorbance at the absorption maxima are not Nernstian, as required by the equilibria in (4). A variant of this polaron/bipolaron model, proposed by Amemiya et al. [66], also fails to rationalize the absorption spectra. Both studies neglect overlap of the absorption bands, which, given their width, turns out to be a less than satisfactory oversimplification.

It is relevant to consider the kinetics of generation of charge carriers, since this is closely related to the kinetics of polymer oxidation. Early measurements [62] found that polaron recombination took hours to complete, but later it was established [63] that the kinetics of this process was two to three orders of magnitude faster, and further that at low oxidation the generation of two polarons was favoured with respect to formation of a bipolaron. Oudard et al. [64] followed the EPR signal during redox switching of the polymer, from which estimated the equilibrium constant of polaron recombination (third reaction in 4) and separated the current associated with the transition in its faradaic and non-faradaic components. From the comparison of the faradaic component to the voltammetric response, it follows that the formation of polarons from neutral polymer is faster than their disappearance upon further oxidation to form bipolarons. Recently we [54] have analyzed uv-visible spectra of polypyrrole, describing the changes corresponding to the aromatic and quinoid forms of neutral polymer segments. The absorbance due to the aromatic isomer decays with a first order rate law throughout

the potential range of film stability, but the first order law breaks down at high oxidation for the quinoid form, a result that suggests that polaron recombination yields bipolarons and quinoid neutral segments. Thus charge carriers, polarons and bipolarons, are generated during electrochemical oxidation of polypyrrole, through a series of consecutive first order reactions coupled through equilibria in which polarons, bipolarons and quinoid neutral segments are involved.

The energetics of charge carrier generation processes is an important aspect of the insulator-conductor transition. It has received theoretical consideration, but direct experimental studies have been rare and limited to measurements of the temperature dependence of the electromotive force of solid-state galvanic cells in which one of the conducting polymer constitutes one of the electrodes [68]. Such measurements yield through the Gibbs-Helmholtz equation the total enthalpy changes of the overall galvanic reactions, but do not provide direct information on the half-cell processes occurring at each of the electrodes. The latter is obtained from direct microcalorimetry of the conducting polymer during charge carrier generation [69]. On account of the disruption of π bonds in the polymer backbone that entails the formation of polarons, molar enthalpies of charge carrier generation processes upon oxidation of polypyrrole are endothermic and large (40-90 kJ mol⁻¹) at moderate doping, but diminish at higher oxidation states to ca. 10 kJ mol⁻¹, due to recombination of polarons or further oxidation leading to formation of bipolarons. The latter are thermodynamically favourable processes [70] since, according to theoretical estimates, the energy of the bipolaronic state is 0.4 eV (38 kJ mol⁻¹) lower than that of two adjacent polaronic states [71,72]. Thus, given the weak nature of dopant-polymer interactions, the most significant contribution to the insulator-conductor transition heat relates to the generation of charge carriers. But in addition to charge carrier generation, other chemical processes, some of which are briefly discussed below, occur during the redox switching of the polymer.

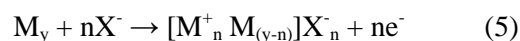
Overoxidation.

At sufficiently positive potentials and with the assistance of nucleophiles, oxidation of polypyrrole leads to the irreversible modification of its structure and properties known as overoxidation [73-75].

With in situ infrared [76] and ESCA [77] spectroscopies, it has been determined that the irreversible degradation of the polymer is associated with formation of hydroxyl (-OH) and carbonyl (=O) groups in the β , β' positions of the pentacycle, arising from reactions of the aqueous solvent with charge carrying species. Overoxidation readily occurs at high positive potentials in alkaline solutions [78] by nucleophilic attack of OH⁻ [74], but we have recently shown that the same process takes place also at lower pH and moderate potential, e.g., in the presence of fluoride [69], albeit at slower rates.

Ionic contribution to charge transport.

Motion of counterions is related to redox processes within the film. Its detailed knowledge is essential for applications such as batteries [79], electromagnetic interference shielding [80], sensors [81], electrochromic devices [82], molecular clamps [83] and controlled drug release [84]. The insulator-conductor transition may be expressed as:



where M represents the polymer backbone repeating units and X⁻ the anions initially present in the contacting solution phase. The neutral polymer M_y represents the insulating form, whereas the polycation at the rhs of (5) is the conductive form of the film. The redox transition thus involves the removal of electrons from the polymer backbone as well as transport of charges throughout the polymer phase. Non-faradaic currents invariably present in the oxidized state interfere with the faradaic currents of the redox processes [85,86], as recently reviewed by Heinze [87]. Cai and Martin [28] studied the redox processes of polypyrrole at high doping levels and determined that these are purely capacitive at this condition and that the ionic conductivity is determined by the concentration of electrolyte in excess within the film, not by the chargebalancing ions. Notwithstanding, Heinze et al. [88], from voltammetric studies of the discharge process, concluded that faradaic processes are dominant throughout. Given the disparity of results obtained, it appears that the identification of faradaic and capacity currents in such a complex process may not be realistic. Measurement of non-electrochemical quantities associated with charge/discharge provide valuable information for the understanding of the redox processes. The close relationship between the electrical and optical ac response [89-

91] identifies the ac capacitance with faradaic processes, while other techniques, such as in situ probe beam deflection [92], confirm that ion exchange occurs throughout the potential range of the conducting regime.

It has been established that oxidized polypyrrole films are permeable to both the solvent and the electrolyte [93] and that their behaviour correspond to that of a porous electrode with a large area/volume ratio and double-layer capacitance proportional to the amount of oxidized polymer. Several groups have studied ionic transport within the film. Pickup and Osteryoung [94] have used the porous electrode model to analyze potential step experiments extending over both insulating and conducting regimes of the polymer, concluding that migration of ions within the pores is the predominant transport mechanism. This was later confirmed with further detail for oxidized polypyrrole [95]. Cai and Martin [28] analyzed chronopotentiometric charging curves of oxidized polypyrrole films and concluded that the boundaries between polymer and electrolyte within the pores is the most relevant interface determining its electrochemical behaviour. Further generalizations [96,97] have considered the hydrated polymer as two superimposed phases, one (the polymer) transporting electronic defects and contributing a resistance R_e , and the other (the electrolyte) transporting ions with resistance R_i . Whilst a truly metallic porous electrode the accumulation of charges at the double-layer is represented by a distributed capacitance along a transmission line, in a conducting polymer the capacitance arises from redox processes in the backbone. A general theory of conductive-polymers behaviour in electrolyte solutions is still unavailable and many effects remain still to be accounted for more elaborate models [98] will be needed before gaining a truly comprehensive view.

V. CONCLUSION

The description of the anodic synthesis of polypyrrole as deposition of oligomers of relatively low molecular weight growing by the successive addition of monomers correlates with the poor crystallinity of the films, the morphologic differences between nascent and bulk polymer, and the energies of the interband transition as compared with absorption spectra of pyrrole oligomers in solution. This leads naturally to mechanisms of

transport of charge carriers localized in short segments, i.e., hopping of polarons and bipolarons [99,100,101]. Some of the still unresolved aspects of the redox processes in polypyrrole may be affected by insufficient knowledge of its structure and how it is affected by, e.g, electrode potential, requiring studies using diverse complementary techniques. Spectroscopic [54] and microcalorimetric [69] information reflect the chemical changes occurring in the polymer that are closely related to generation of charge carriers. Gravimetric techniques allow the precise determination of the amounts of ions involved in such changes [21]. Electrochemical methods are useful for the elucidation of the charge transport processes [95,102]. A combined approach is thus needed to fully appreciate the complex faradaic and non-faradaic processes involved, including expansion of the conducting phase through the insulating polymer during oxidation [103]. Also needed is an electronic and ionic model germane to polypyrrole and other conducting polymers [104], possibly incorporating the role of the solvent [105], as conventional band theory does not provide an adequate description of the conduction mechanism [101].

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