Account

Recent Advances in Electrochemical Studies of π-Conjugated Polymers

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We review the evolution of electrochemical studies of conducting polymers into the current state-of-the-art based primarily on our work. While conventional electrochemical experiments sufficed for the needs in the phase of studies of both electrochemical synthesis and characterization of conducting polymers, developments of various new experimental techniques have led to their introduction to this field for more refined information. As a result, the conventional electrochemical, spectroelectrochemical, electrochemical quartz crystal microbalance, impedance, and morphological as well as electrical characterization studies all made important contributions to a better understanding of the polymerization mechanisms and the conductive properties of these classes of polymers. From this review, we hereby expect that the electrochemical techniques will continue to play important roles in bringing this field to the practical applications such as nanoscale electronic devices.

Key Words : Conducting polymers, Electrochemical synthesis and characterization, Electrical properties, Current-sensing AFM, Nanoscale characterization

Introduction

Since the very first paper on polyacetylene,[1] which eventually led to the authors' Novel prize winning in 2000, was published in 1977, π-conjugated (conducting) polymers have been studied extensively from both fundamental and practical points of view. As a result, thousands of papers have been published on various aspects of conducting polymers and a few monographs have also been published on the subject.[2]

Electrical properties of π-conjugated polymers and their controllability by a doping/dedoping process have been one of the most important issues in this filed.[2] For this reason, electrochemical techniques emerged first as a major tool for studying conducting polymers and their electrical, as well as electrochemical, properties.[3] In fact, electrochemical experiments have been employed for studies on aniline oxidation well before its oxidation product, polyaniline, received spot lights as a conducting polymer.[4] Also, results of various spectroscopic and electrical measurements have been used in describing both their electrical and physical properties. While techniques such as scanning electron microscopy (SEM) and tunneling electron microscopy (TEM) have initially been employed as a tool for studies of morphologies of conducting polymers prepared on flat surfaces, these techniques provided little information on their electrical properties and chemical functionalities. In the meantime, other related techniques including electrochemical quartz crystal microbalance and impedance measurements have also been introduced to the field.

While results obtained from these techniques have been used for directly or indirectly describing bulk electrical properties, almost no detailed information has been available on nanoscale although the STM technique has been used in very restricted occasions.[5] Had one been able to measure the electrical properties of conducting polymer films and map them on the nanometer scale, it would help investigators better understand and control them. The newly developed current-sensing atomic force microscopy (CS-AFM) technique meets these requirements in studying the electrical properties of π-conjugated polymer films because it provides topographic and conductance images simultaneously.[6] In this article, we briefly review various experiments that have been used to probe electrochemical, spectroscopic, morphological, electrical, and other properties of conducting polymers and describe how the CS-AFM technique would

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become a major tool for investigating various electronic states of π-conjugated polymers for their future applications to nanoscale electronic devices.

A Brief Review on Conducting Polymers

In 1977, Shirakawa et al. reported that the conductivity of polyacetylene could be increased by more than several orders of magnitudes when it was chemically doped.[1] This large change in conductivity of an organic polymer corresponds to that from an insulator to a metallic conductor. This finding was a very important breakthrough, which opened up a whole new field. Following the study on polyacetylene, other polymers such as polypyrrole, polythiophene, polyaniline, poly(*p*-phenylenevinylene), and poly(*p*-phenylene), as well as their derivatives, have been reported as π-conjugated conducting polymers (Figure 1).

There are two main ways of preparing conducting polymers[2]: chemical and electrochemical polymerization. The principal advantage of the chemical methods of synthesis is that they offer possibilities of mass production at low cost. On the other hand, electrochemical methods offer materials with better conducting properties in a form of thin film for some designated applications. Electrochemical experiments also offer a great deal of controllability during the preparation of these polymers. By controlling the potential or the current at the working electrode, the thermodynamics of the system or the kinetics of the reaction is controlled for some specific purposes. These features of electrochemistry give a number of ways to control the quality of polymerized products.

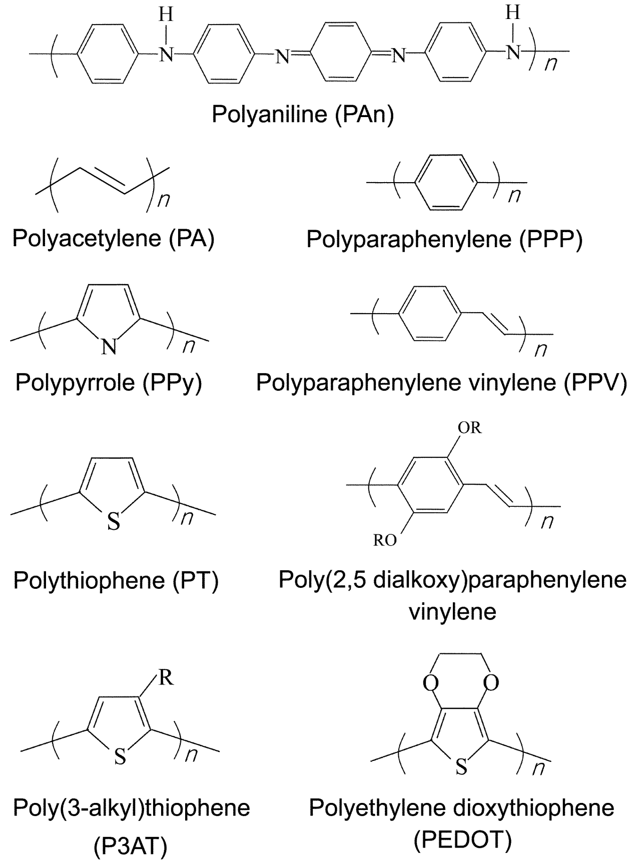

Polyaniline (PAn)
Polyacetylene (PA)
Polyparaphenylene (PPP)
Polypyrrole (PPy)
Polyparaphenylene vinylene (PPV)
Polythiophene (PT)
Poly(2,5 dialkoxy)paraphenylene vinylene
Poly(3-alkyl)thiophene (P3AT)
Polyethylene dioxythiophene (PEDOT)

Figure 1. Structures of a few conducting polymers.

Charge injection into conjugated semiconducting macromolecular chains, *i.e.*, "doping", leads to a wide variety of interesting and important phenomena. These reversible charge injections can be accomplished by either chemical or electrochemical doping:

Chemical doping by charge transfer. The initial discovery of the ability to dope conjugated polymers involved charge-transfer chemistry: oxidation (p-type doping) or reduction (n-type doping) with proper electron donors or accepters as illustrated by the following chemical reactions.[7]

p-type doping: $(\pi\text{-polymer})_n + 3/2\ ny(I_2)$
$\rightarrow [(\pi\text{-polymer})^{+y}(I_3^-)_y]_n$
n-type doping: $(\pi\text{-polymer})_n + [Na^+(C_{10}H_8)^{-\bullet}]_y$
$\rightarrow [(Na^+)_y(\pi\text{-polymer})^{-y}]_n + (C_{10}H_8)^0$

Electrochemical doping. Although chemical doping (charge transfer reaction) is an efficient and straightforward process, it is difficult to control the degree of doping. Complete doping to achieve the highest charge concentrations yields reasonably high-quality materials. However, attempts to obtain intermediate doping levels often result in electrically inhomogeneous materials. Electrochemical doping was explored to solve this particular problem.[8] In the electrochemical doping, the electrode supplies the charges to the polymer *via* electron transfer reactions, in which ions diffuse into (or out of) the polymer matrix from the nearby electrolyte to compensate the electronic charge introduced. The doping level is determined by the voltage between the polymer film and the counter electrode. Electrochemical doping is illustrated by the following reactions:

p-type doping: $(\pi\text{-polymer})_n + ny\cdot[Li^+(BF_4^-)]_{soln}$
$\rightarrow [(\pi\text{-polymer})^{+y}(BF_4^-)_y]_n - nye^-$

n-type doping: $(\pi\text{-polymer})_n + ny\cdot[Li^+(BF_4^-)]_{soln} + nye^-$
$\rightarrow [(Li^+)_y(\pi\text{-polymer})^{-y}]_n$

By adjusting the doping level, a change in conductivity between that of the undoped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained.

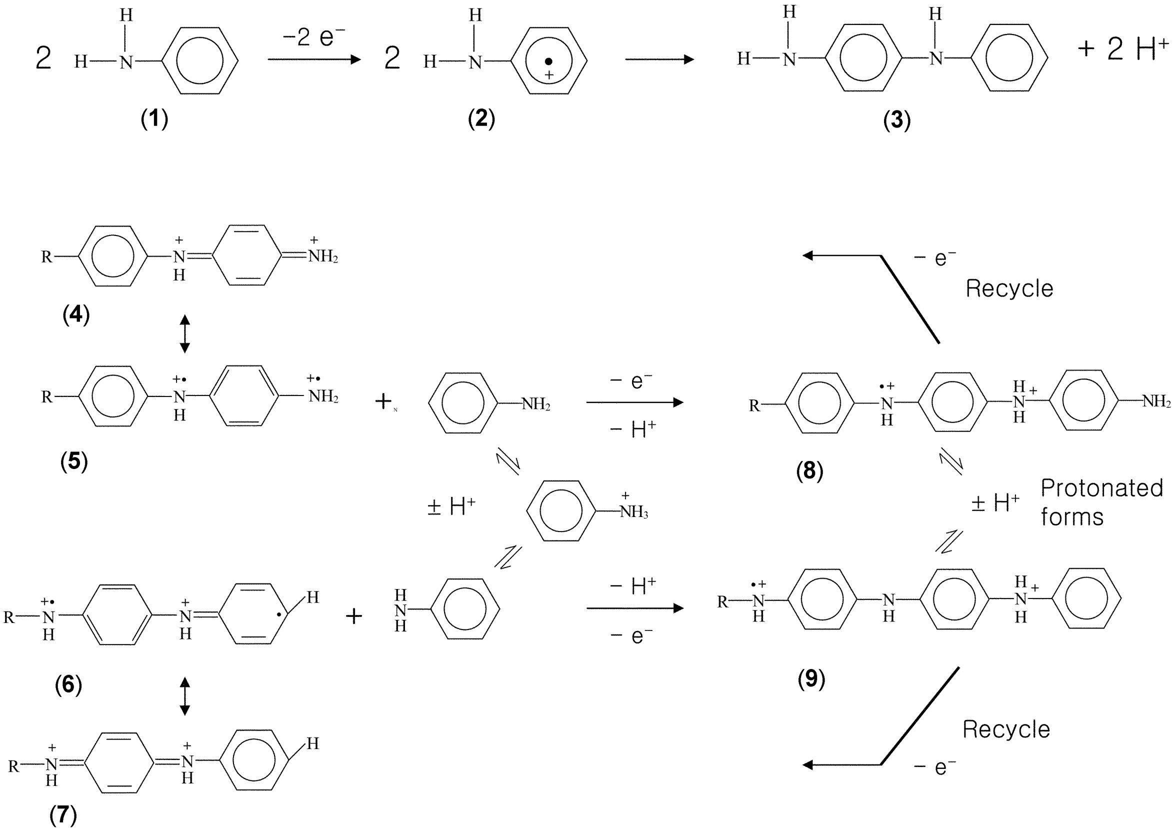
In this article, we demonstrate how various electrochemical studies led to a better understanding of conducting polymers as well as better qualities. In doing so, we start out with the classical electrochemical studies followed by a few other nontraditional experiments.

Classical Electrochemical Studies

Since electronically conducting polymers are also electroactive materials, their electrochemical characterization would be a first step in describing their electrical properties. For this reason, the polymer films have been characterized by either electrochemical or electrical measurements either on the electrode surface in electrolyte solutions or in solid states. Thus, the earlier measurements were just to establish the electrochemical activity of the polymer films[9] or to determine conductivity using a four-probe method.[10] Another reason for the popularity of the classical electrochemical technique in the conducting polymer community is that the doping reaction is merely electrochemical oxidation or reduction, and the amount of charge used up in the reaction determines the degree of doping.[3]

As already pointed out, the classical techniques have been employed to study aniline oxidation and the product formed thereof, polyaniline (PAn), long before it has been recognized as a conducting polymer. Adams and his group reported a series of papers on the electrochemical oxidation of aniline, in which they used primarily classical electrochemical techniques.[4] Employing these experiments, they worked out the oxidation mechanism of aniline oxidation. The mechanism of electropolymerization of various other monomers has been addressed in many studies[3]; the principal difficulties encountered in the study of the mechanism are the rapidity of the polymerization reactions in comparison to the time resolving capability of the classical electrochemical experiments and the insolubility of the resulting films. However, it will be a good starting point to take a look at a well known and accepted process about electropolymerzation of aniline[11] for understanding the mechanism of various oxidative electropolymerization.

This mechanism can be described by following stepwise reactions as shown in Figure 2; the first step is the oxidation of monomer R, **1**, at the surface of the electrode to form a radical cation $R^{+\bullet}$ (**2**). These monomer radical cations can undergo different reactions depending on their reactivity. When $R^{+\bullet}$ is relatively stable, it would diffuse into the solution and react to form soluble products of low molecular weights. When $R^{+\bullet}$ is very unstable, it can react rapidly near the electrode with the solvent or the anion, forming soluble products of low molecular weights. Between these two extremes, $R^{+\bullet}$ can also undergo dimerization reactions. This radical cation, $R^{+\bullet}$, having greater unpaired electron densities at either the *para-* or *ortho-* position dimerizes mostly *via p*-position. Of various possible dimers identified, we here show only the head-to-tail dimer, **3**, obtained from the dimerization reaction at the *p*-position in Figure 2. The dimer thus obtained undergoes a two electron reaction to



$$x\mathrm{C_6H_5\text{-}NH_2} \rightarrow (\mathrm{C_6H_4\text{-}NH})x + 2x\mathrm{H^+} + 2x\mathrm{e^-}$$

$$(\mathrm{An})_x^{sem} \rightarrow (\mathrm{An})_x^{ox} + x\mathrm{e^-}$$

$$(\mathrm{An})_x^{ox} + \mathrm{An} \rightarrow\rightarrow\rightarrow (\mathrm{An})_{x-1}^{ox}\,(\mathrm{An})_2^{red}$$

Figure 2. A proposed mechanism for electrochemical polymerization of aniline.

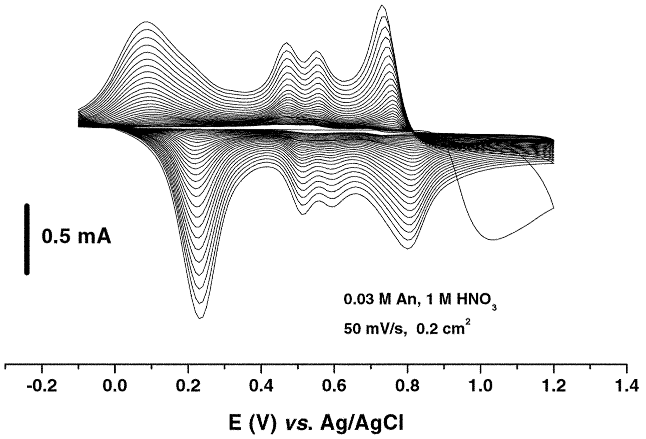


Figure 3. Cyclic voltammograms recorded during potentiodynamic growth of polyaniline in an aqueous solution containing 30 mM aniline and 1.0 M nitric acid. The electrode had an area of 0.20 cm^2 and the scan rate was 50 mV/s.

produce dication diradical, **5**, whose resonance structures are shown as structures **4**, **6**, and **7**. The oxidation product, dication, picks up a neutral aniline to produce a molecule, whose chain length becomes one unit longer than its precursor, while it becomes a slightly reduced form, **8** or **9**. This reduced form is reoxidized back to the dication at the electrode and the whole process is repeated again. This process is termed the autocatalytic growth, which is shown in the bottom of Figure 2 as a series of chemical reactions. The electropolymerization reaction usually results in an oxidized, conducting (doped) form. Actually, the final polymer chain carries a positive charge for every 3 to 4 aniline units, which is counter-balanced by an anion. The structure of the doped polymer is represented by structure **8**.

These types of experiments would have been conducted regardless of whether the final products are conductive polymers or not, because electrochemists have been trying to work out reaction mechanisms for oxidation of many organic compounds. The true utility of electrochemical experiments has been demonstrated in studying conducting polymer growth thanks to their quantitative aspects. It is from these works[11,12] that the autocatalytic mechanism of PAn growth has been established. From a visual inspection alone, a typical electrochemist can recognize that the cyclic voltammograms (Figure 3) obtained during consecutive potential scans are rather unusual in that the oxidation wave for aniline is observed only during the first scan but not the following cycles. Nevertheless, the PAn film is shown to grow as can be seen from the increasing current waves corresponding to oxidations and reductions of the film. Not only from the visual inspection but also from a variety of other quantitative analyses, a conclusion that the fully oxidized or doped form of PAn catalyzes the polymer growth was reached.[11]

More quantitative evaluation of the growth kinetics has been made by counting the charge spent on the polymer growth. From the amount of cathodic charges, which record the amount of electric charge required for reducing the polymer produced on the electrode during the potentiodynamic growth of PAn, the following empirical equation has been obtained from the data,[11]

$$\text{Growth (mC)} \cong k\cdot[\text{An}]^2(\text{Cycle Number})^2.$$

This expression leads to a new equation,

$$\text{Growth Rate (mC/cycle)} = k'[\text{An}][\text{charge}]^{1/2},$$

after a few mathematical operations. This equation has two important significances. One is that the monomer concentration and the amount of polymer, *i.e.*, charge, are both involved in polymer growth. In other words, this equation states quantitatively that the reaction is autocatalytic. The other is that the polymer grows in one or two dimensions because the power dependency of the charge is 1/2; a full power dependency would indicate a three dimensional growth. The growth rate law, however, depends on the medium used and it has been demonstrated that the morphology of the polymer depends much on the medium used.[13] Under an appropriate growth condition, one can also simulate one-dimensional growth of polypyrrole.[14] The same technique of analyzing the growth kinetics from the potentiodynamic (cyclic voltammetric) data has been applied to many other polymers as well.[15] While the experiments as simple as cyclic voltammetry have been quite useful, more involved experiments such as those using a rotating ring-disk electrode can also offer information on the growth mechanism,[16] which may be difficult, if not impossible, when other experiments are used.

The electrochemical experiments have also been used to quantitatively follow the degradation reactions as well. A comprehensive study has been carried out first on the degradation of electrochemically prepared PAn films.[17] In the study, the authors clearly demonstrated by employing rotating ring disk electrode (RRDE) experiments that the degradation product is detected at the ring electrode when the potential goes beyond a certain value at the disk, which is covered by a PAn film. Of course, other experiments have been carried out to positively identify the product, which turned out to be *p*-benzoquinone. Further detailed analysis of the rotating ring disk data has been made and the results led to a detailed understanding of its degradation mechanism.[17b]

Classical electrochemical techniques offer a powerful tool for studying not only degradation chemistry but also other properties of conducting polymers.[18] In a way, this is similar to the position of electrochemistry in studying corrosion of metals and alloys,[19] in which the electrode is harshly treated and the time for making the desired reactions occur is saved significantly. Similar strategies have been employed for studying the degradation chemistry of conducting polymers, and degradation products such as *p*-benzoquinone and fumaric acid have been identified during the electrochemical degradation reaction of PAn and PPy, respectively.[18c]

Spectroelectrochemical Studies

Spectroscopy is a powerful technique for determining energy levels, and conducting polymers offer no exception in proving its power in characterizing their fundamental properties such as their conductivities. However, most of conducting polymers electrochemically prepared form films on the opaque electrode surfaces, and recording their spectra is not always straightforward. For this reason, electrochemists began to use transparent electrodes such as the one made of indium-tin oxide (ITO), on which polymers were electrochemically grown and their spectra recorded.[20] While this approach gets around the problem that opaque electrodes present, the growth properties of the polymers are not always the same at all electrodes. This could be an important parameter because hardly any polymers are grown on the ITO electrodes except during the afore-mentioned spectroelectrochemical studies. Further, the ITO electrodes absorb photons in the ultraviolet region and no spectra whose peak absorbance appears below about 350 nm can be recorded. For this reason, a reflectance mode, in which a branch of a bifurcated optical fiber brings in the light beam and another branch guides the light reflected from the electrode surface to the detector,[21] has been used in later studies.

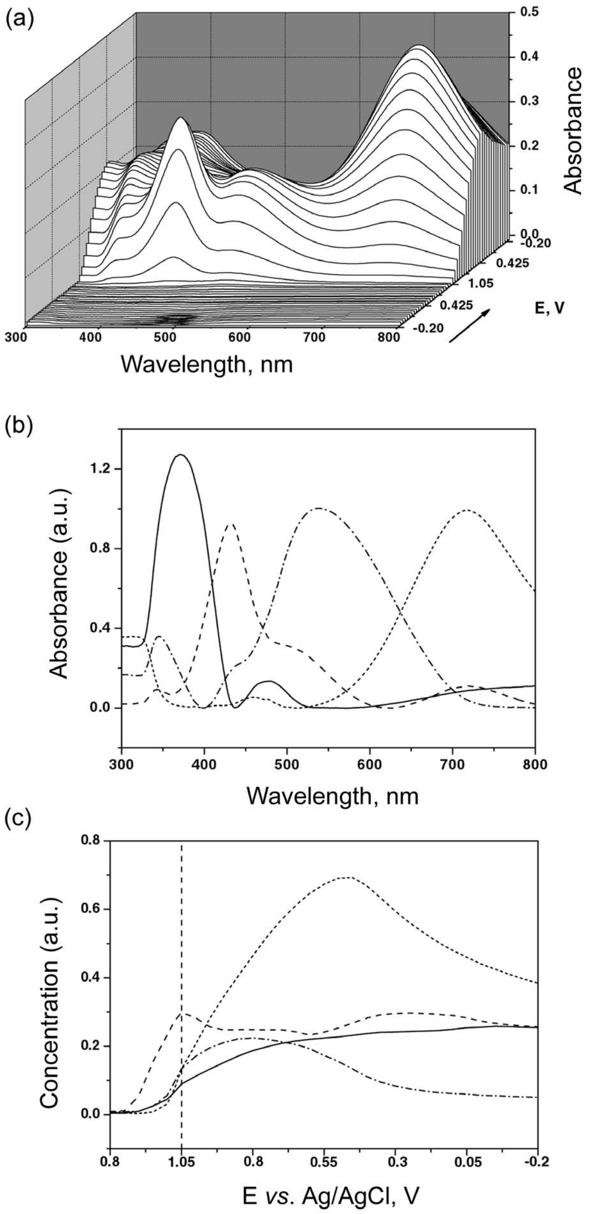


Figure 4. (a) A series of absorption spectra recorded concurrently with scanning the potential at a scan rate of 50 mV/s, (b) supposedly “pure” spectra extracted from the spectra shown in (a), and (c) the concentration profiles of each species represented by the absorption spectra shown in (b). [From Ref. 22 with permission of the American Chemical Society].

Spectroelectrochemistry is a powerful technique in following the spectral changes of conducting polymer films during their electrochemical growth and doping processes. Many studies have addressed the formation and growth mechanisms of the polymers. For example, details of aniline oxidation have been studied using spectroelectrochemical experiments until very recently.[22] An early study identified intermediate species including oxidized states of head-to-head, head-to-tail, and tail-to-tail dimers and other oligomers during oxidation of aniline.[23] These spectral assignments have later been confirmed by another spectroelectrochemical studies.[22] In interpreting the spectral data, the so called derivative cyclic voltabsorptometric (DCVA) curves[21b,c] played important roles because the DCVA signals are supposed to match straightforwardly the cyclic voltammetric currents, provided that the peaks are resolved reasonably well. This is very important because a current represents a convoluted form of various signals originating from more than one source, whereas the DCVA curves would provide a behavior of a specific species if the spectral band is well separated from others. However, the ideal cases, in which spectral bands are well separated, are rare because absorption bands are very broad for most conducting polymers. Nevertheless, this technique has been very useful in sorting out the signals.

Recent evolution of spectroelectrochemical techniques allowed complete resolution of spectral bands to be possible and their concentration profiles to be extracted from a complex set of spectra.[22] As a result, four “pure” spectra as shown in Figure 4b have been extracted from a series of spectra (Figure 4a) that appeared impossible to resolve. This was accomplished by using two-dimensional correlation spectral analysis, followed by what is called the alternating least squares based self-modeling curve resolution method. As can be seen, the resolved spectra shown in Figure 4b allow positive identification of intermediate species to be possible. Further, relative concentration profiles of the species represented by the four spectral bands resolved have also been extracted (Figure 4c) from the data, which allows one to see clearly how the four species change their concentrations as a function of the potential scanned.

Spectroelectrochemical techniques have been quite useful also in monitoring the changes taking place while doping-dedoping processes are taking place.[24] When polymers are electrochemically prepared, the as-prepared films are usually in a doped state as already pointed out. The undoped polymer, which usually has a single absorption peak corresponding to the band gap transition, can then be doped

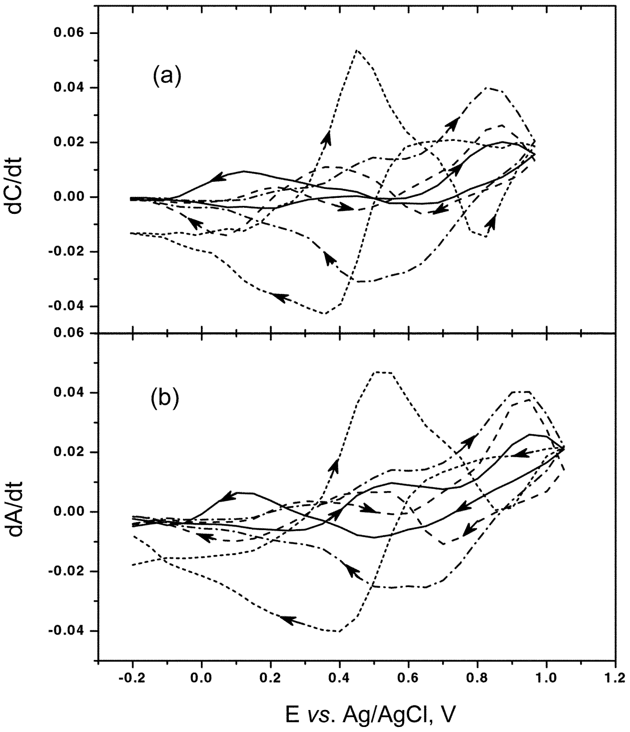


Figure 5. (a) dC/dt curves for the species shown in Figure 4b, which was obtained from the data shown in Figure 4c, and (b) dA/dt curves for the same species obtained from the data shown in Figure 4a. Both were obtained during doping and dedoping of PAn. [From Ref. 22 with permission of the American Chemical Society].

by oxidizing it. Upon doping, a new broad absorption band develops at a much longer wavelength than that for the band gap transition at its expense. The longer wavelength peaks arise from the absorption of the free carriers such as polarons and/or bipolarons, which usually have larger extinction coefficients than the absorption peaks due to the band gap transition.[24a,b] The absorption bands are also very broad because they represent electronic transitions from the polaronic/bipolaronic bands, located between the valence and conduction bands of the polymer, to the conduction band. Because absorption bands are broad and, therefore, they overlap heavily with each other, it is often difficult to resolve the peaks. For this reason, the DCVA technique[21b,c] played a very important role in sorting out the complex spectroelectrochemical data. Figure 4a shows an example for a set of complex spectra recorded during the first potential cycle for aniline oxidation, Figure 4b shows the resolved absorption bands, Figure 4c shows the change in the concentration of each species generated during the first potential scan, Figure 5a shows the first derivative of the concentration with respect to time (d*C*/d*t*) for the second potential scan, and Figure 5b shows the DCVA curves also for the second scan, which trace how each absorption peak behaves as a function of scanned potential. Ideally, the d*C*/d*t* and DCVA signals should have identical shapes if peaks are well resolved; these should represent the faradaic currents due to the specific species and, thus, might be termed as species selective currents. The two signals generally agree with each other, although they are not exactly the same.

One can see clearly in Figure 5b recorded during the second potential scan that the absorption peaks at 430, 600, and 800 nm assigned to the localized radical cations, delocalized diradical dications, and delocalized polarons (radical cations) of PAn, respectively, are all generated at its first oxidation peak (~0.2 V). However, the rate of generation of the bipolaron becomes maximal at the second oxidation peak (~0.4 V) at the expense of both the localized and delocalized radical cations, indicating that the conductivity of the polymer film becomes less conductive. Note that there was a small amount of PAn deposited on the electrode surface by the time when the data shown in Figure 5 were recorded. Thus, one can expect that the conductivity would become maximal beyond about 0.25 V through about 0.5 V, which would then taper off beyond about 0.7 V. This has been confirmed recently by nanoscopic conductivity measurements.[25]

Electrochemical Quartz Crystal Microbalance Studies

Because conducting polymers are readily produced as an insoluble film on the electrode surface upon anodic or cathodic electrolysis of a monomer, electrochemical quartz crystal microbalance (EQCM) experiments would provide valuable information about the change in weight taking place during the experiments with the polymer coated electrode. This technique, which allows the measurements of changes in weight to be made *in situ* during an electrochemical technique, was first introduced by Orata and Buttry[26] in their studies of doping-dedoping behavior of PAn. Since it was introduced to this community, it has been offering an independent tool for studying the deposition mechanism, the doping-dedoping mechanism, and other behaviors involving weight changes accompanying electrochemical experiments.

Perhaps the best illustration of the utility of the EQCM experiments might be the evaluation of the current efficiencies during the electrochemical deposition of conducting polymers.[13,27] This can be done when the number of electrons transferred ($n_{app.}$) obtained from the electrical charge spent is compared with the amount of polymer deposited on the electrode. During the PAn deposition, for example, the $n_{app.}$-value was found to be much larger than 2.0, which is a number derived from the stoichiometry for an ideal polymerization reaction. The $n_{app.}$-value was first reduced to a little larger than 2.0 in a few subsequent cycles but increased back to about 3.0 in later stages.[13,27] This indicates that the dimers and other small oligomers produced during the first cycle are more soluble than their longer chain counterparts, but the deposition efficiency gets deteriorated as the film thickness increases.

Also noted from these studies was that the anion insertion and de-insertion reactions become increasingly important in determining the current efficiencies. For example, the doping/de-doping process was not reversible for a thick film in sulfuric acid solutions[13]; small positive ions were found to be inserted and de-inserted instead of anions. This is particularly true when the dopant anions are bulky.[27c] At times, ion pair clusters as large as $(TBA)_4(BF_4)^-$ were found to be exchanged during doping and de-doping processes for polyfluorene in a non-polar solvent such as CH_2Cl_2.[28] Conclusions like these would not have been possible without EQCM measurements. Often, hyphenated techniques combining more than two experiments such as spectroelectrochemistry and EQCM could provide complementary information about the system of interest.[29]

Impedance Studies

When a conducting polymer is either synthesized or characterized by an electrochemical method, one uses an electrochemical cell with an appropriate electrolyte and necessary electrodes. This system is represented by an electrical circuit and the reactions taking place across the electrode/electrolyte interfaces are often interpreted in terms of an equivalent circuit. Indeed, an electrode/electrolyte interface cannot be fully described without making impedance measurements.[30]

Unfortunately, earlier attempts on impedance measurements might not have provided an accurate picture of what is going on, particularly for polymerization reactions, because it takes more than half an hour to record a complete electrochemical impedance spectrum for a full range of frequencies, because the electrode/electrolyte interface continuously changes its electrical characteristics during the measurements. Electrical characterization of conducting polymer films on the electrode surface in an electrolyte solution alone, however, could be more straightforward as the system does not undergo changes during the measurements after it reaches a steady state. For this reason, impedance measurements have been utilized for evaluating the transport properties of ions during doping-dedoping processes.[31]

As pointed out, early attempts have been made to study the polymerization reactions by impedance measurements although it is not very straightforward.[32] However, these efforts did not lead to reliable, interpretable results due to the continuous changes in electrochemical interface during the reaction until a fast impedance technique was worked out. Two approaches were taken for faster impedance measurements. One was to mix ac voltage signals of various frequencies and apply the mixed wave to the system of interest, which was followed by Fourier transform to single out the ac currents of the premixed frequencies.[33] This approach, while significantly reducing the measurement time, is still limited by the time taken by the slowest ac signal. The second approach was to use a small step signal, which is an integrated form of the Dirac δ function, as a source of excitation, and the resulting current is Fourier transformed into the frequency domain after its derivative is taken.[34] For a fast electrochemical reaction, this technique allows the impedance to be measured for the whole frequency range in as short a period as a few ms. Both methods have recently been employed for studies on the polymerization reaction of aniline.[33c,34b] The second method provides greater insights into the electrical properties of the electrode/electrolyte interface during the aniline polymerization reaction by providing snap shots of the interface while the reaction goes on.[34b] This technique is still in a very early stage of development and expected to solve numerous problems encountered during all sorts of electrochemical reactions.

Morphological and Electrical Characterization

From an early phase of studies of conducting polymers, scientists have had curiosities about what the polymer surfaces would look like. When the studies of conducting polymers were first initiated, the only tools for surface characterization available were scanning electron microscopy (SEM) and transmission electron microscopy (TEM). While the former was readily available for studies of conducting polymers, the needs for the latter were rather scarce because it was more for higher resolution studies. Thus, many studies on the morphology of conducting polymer surfaces have been conducted using SEM.

Early attempts at the elucidation of relations of the structures of conducting polymers with growth kinetics, with their conductivity, and with the medium of polymer growth have laid grounds on a better understanding of the polymers. A rudimentary study on the relation between the growth kinetics and the electrolyte, as well as that between the structure and the growth kinetics, was reported by Zotti *et al.*,[35] which in turn is determined by the anions present in the case of the PAn growth. A similar study on the growth mechanism of PPy and the resulting morphology as well as conductivity has been reported.[36] Zotti *et al.*'s suggestion that the structure would be related with the type of electrolyte has been confirmed later.[13]

More recently, various scanning probe microscopic (SPM) techniques have been used for studies on the morphology of the conducting polymer films. Of these, the scanning tunneling microscopy (STM) can be used only for the conductive substrates and, thus, is not very useful for studying conducting polymers due to the inhomogeneous nature of the conducting polymer surface in terms of conductivities. When the conductivity of the surface varies from spot to spot, the STM imaging experiments may lead to the observation of experimental artifacts, in which the less conductive area may be regarded by the instrument as the topographically low area in the image. When probing the insulating area, there is a good chance that the STM tip would damage the film as well as the tip itself. For this reason, atomic force microscopy (AFM) offers more power in characterizing the conducting polymer surfaces because it can precisely image the surface by maintaining a constant load force of the tip with respect to the substrate. However, its spatial resolution depends much on how sharp the tip is and the technique usually does not provide as sharp images as high resolution SEM technique does. Thus, just as the

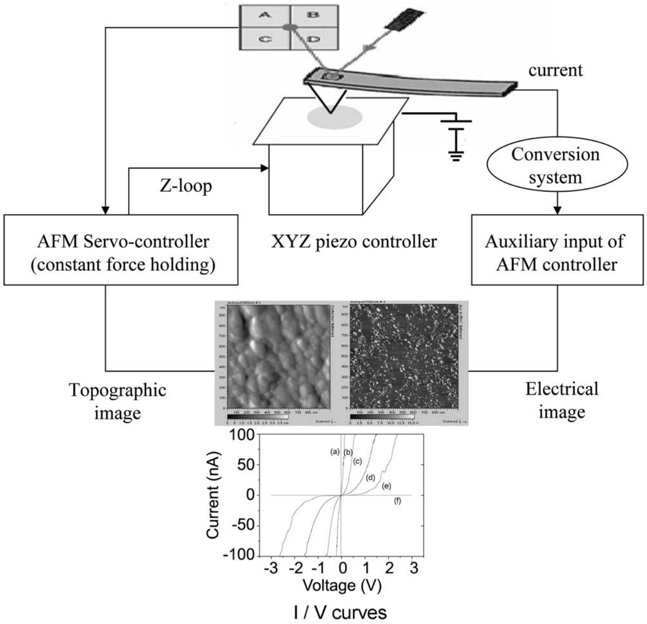


Figure 6. A diagram showing the principle for the CS-AFM along with results that can be obtained. These are the topographical image, current image, and the I/V curves.

SEM, the AFM did not distinguish spots of a chemically different nature, although AFMs currently available offer various ways of distinguishing the chemical functionalities. Since we are preparing another review on this subject in more detail,[37] we are not going to elaborate it too much in this account; we briefly introduce the new technique that has been developed recently for imaging both the topographic and electrical properties.[38]

A diagram showing the new type of AFM, which is capable of recording both topographic and electrical current images, is shown in Figure 6. In this technique, a tip coated with a metal such as gold or platinum is used to image the surface while the current is measured between the tip and the substrate at a given bias voltage. An advantage of this technique is that the contact can be made reliably and reproducibly between the tip and the substrate by applying a known load force. This feature is not available in any other comparable techniques. Thus, both the topographic and the current image at a given bias potential are recorded simultaneously. The technique has been used for studies of self-assembled monolayers,[39] single molecules,[40] carbon nanotubes,[41] and quantum dots.[42] We have also applied the technique for characterizing the Schottky contacts of zinc oxide nanorods with gold.[43] By tracing the current-voltage (I/V) curves, one can study electron transport properties of these substrates on nanometer scales, which would have been impossible otherwise.

After the first work on nanoscale measurements of doping distributions and the I/V curves of electrochemically prepared PPy films,[44] we have examined vertical conductivities of the electrochemically prepared PAn film doped at various potentials,[45] a correlation between the electrical and optical properties of poly(3-methylthiophene),[46] effects of electrolytes on conductivities of the resulting PPy films in aqueous media,[47] and the effects of pH on conductivities of PAn films.[48] While the "two-probe" I/V measurements may contain contact resistances between the conductive tip and the substrate, the conductivities calculated from the tip contact area and the thickness (length) of the film provide valuable information regarding the conducting polymer films. The thickness of the film is obtained independently from the cross sectional view of the SEM image of the film. More difficult is the calculation of the contact area of the tip with the substrate film, which would depend on the load force and how soft or hard the substrate would be. The contact radius, *a*, is calculated using what is called the Hertz theory,[49] which is expressed as

$$a^3(F) = \frac{3}{4}\frac{R^*(F + F_{ad})}{E^*} \qquad (1)$$

where F is the external loading force; F_{ad} is the adhesion force, R^* is an effective radius of curvature of the tip-sample system with $1/R^* = (1/R_{tip}) + (1/R_{sample})$, where R_{sample} is the radius of the sample; and E^* is effective Young's modulus with $1/E^* = (1-\sigma_t^2)/E_t + (1-\sigma_s^2)/E_s$, where E_t and E_s are Young's modulus of the tip (E_t = 168 GPa for gold) and the sample, and σ_t and σ_s are the corresponding Poisson's ratios. Here we need some assumptions for Young's modulus and Poisson's ratios. Again, the conductivity thus obtained may contain a contact resistance between the tip and the film.

Employing the technique, the homogeneity of the PPy film was first examined on nanoscale in terms of doping distributions.[44] The as-prepared PPy film was found to be rather homogeneously doped across the whole area within the sensitivity of the instrument. It was also found that the top of the mountainous area was doped and dedoped preferentially. Well defined I/V curves obtained at various doping levels of poly(3-methylthiophene) indicate that the film could be made to be metallic through insulating, and the band gap obtained from an I/V curve of a film with a semiconducting behavior was in good agreement with those obtained from spectroscopic studies.[46] Also, the morphological and electrical properties of PPy films were found to be heavily affected by the electrolytes used in aqueous media.[47] A similar technique was used to characterize the electrical and morphological properties of a PAn film doped at different potentials; its inhomogeneity was much more serious in its conductivity in comparison to that of the PPy film.[45] As many as three orders of magnitudes of differences were detected in conductivity on a film thoroughly doped at a potential, which is supposed to lead to the highest conductivity.

Since the CS-AFM method reports the conductivity at each spot where the tip contacts the polymer surface, it is also possible to obtain an average conductivity across the whole surface. The average conductivities thus obtained were generally larger than those obtained from the bulk measurements although smaller values would be expected because the method uses two probes instead of four probes, which compensate the contact resistance. Nevertheless, conductivities obtained from the two methods correlate well with each other. The average conductivities were also studied along with spectroscopic measurements in efforts to see how the relative intensities of the spectral bands corresponding to free carrier absorption are related to those of the band gap transitions.[46] Here, the absorbance is an integrated quantity suggesting that it is a bulk property related to the free carrier concentration. Thus, we found that the doping density is directly proportional to the absorbance of the bipolaron band of P3MT and the conductivity was an exponential function of the doping density or the absorbance.

Recent Advances in Studies on Nanostructures of Conducting Polymers

Just as in other areas, investigators in this area have recently turned their interest to the preparation and characterization of nanostructured conducting polymers. The important motives are twofold: 1) the nanostructures are expected to have greater conductivities than their bulk counterparts, and 2) the nanostructures may find applications in the nanoscale electronics.

The first attempts to prepare nanostructures of conducting polymers were made by using well-defined templates such as those made of alumina or polycarbonate templates with hollows of diameters of a few hundred nm[50] as well as zeolites with well defined hollows.[51] The conducting polymers synthesized within these hollows were obtained in the form of nanotubes because the polymers grew along the wall of the templates. More recently, investigators began to use molecular templates made by forming a mixed self-assembled monolayer (SAM) of thiolated cyclodextrins in the forests of the insulating alkylthiol molecular SAM on gold electrodes.[52] After functional molecules such as 4-aminothiophenol are anchored inside the cyclodextrin cavities, aniline is polymerized on the electrode by oxidizing it in a solution containing appropriate amounts of aniline and an electrolyte. The third approach is to control the speed of the addition of the reagents or to polymerize at an interface of two immiscible solvents.[53] Because it was practically impossible to directly characterize electrical properties of these nanotubes, the authors reported optical conductivities,[50,51] which were obtained from the intensity of a certain band in the infrared spectrum. No matter which method is used to prepare the nanostructures of conducting polymers, direct characterization of their electrical properties would require a better defined technique.

Conclusions

We have reviewed briefly how the electrochemical studies on conducting polymers have evolved into the current state-of-the-art based primarily on our own work. While the conventional electrochemical experiments will continue to play important roles in electrochemical synthesis and characterization of conducting polymers, evolution of new experimental techniques and interpretation methods should contribute to a better understanding of the polymer growth and their properties. Those include a new technique of interpreting spectral data such as two-dimensional correlation analysis and CS-AFM for characterizing the electrical properties of conducting polymer nanostructures when combined with the electrochemical preparation of the nanostructures. Currently, there are no better ways of establishing contacts of the nanostructures with electrical leads than their electrochemical preparation.[50,52] Once the contact is established, CS-AFM would serve as a tool for characterizing their electrical properties. Thus, only when these structures are prepared electrochemically, they make solid contacts with the electrode and their electrical properties can be characterized on nanoscale. This is an essential step leading to the future applications of these polymers to the practical devices in nanoscale.

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