

A Perspective on Electrochemical Impedance Analysis of Polyaniline Films on Electrodes

by Vadim F. Lvovich

During the past two decades, extensive studies of conductive polymers have been driven by their special properties such as flexible solution and melt processability manufacturing, blendability with commodity polymers, good ambient stability, and unconventional electrical and optical properties. The most valuable property of these materials is their unique ability to dramatically and reversibly change electrical conductivity over a full range—from insulators to metallic conductors—upon partial electrochemical oxidation or reduction, a process commonly referred to as “doping.”

Among the family of conducting polymers, polyaniline (PANI) is unique because of its ease of synthesis, environmental stability, and simple doping/de-doping chemistry. Because of its rich chemistry and high electrical conductivity, PANI has been

changes at low electrooxidation potentials from nonconductive leucoemeraldine (LE) to highly conducting emeraldine (EM), and at very high oxidation potentials it further changes to insulating pernigraniline (PE) (Fig. 1).¹

Electrochemical Impedance Spectroscopy of PANI Films

Electrochemical impedance spectroscopy (EIS) allows investigation of charge and mass transport kinetics and charging processes taking place within the analyzed material and at the active interfaces of the system. This technique has high experimental efficiency as it contains all necessary electrochemical information, the data quality and the system's

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Electrochemical Impedance Analysis of Polyaniline Films on Electrodes

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ABSTRACT

The ac response of polyaniline films on Pt electrodes in 2.0M HCl was measured at different applied dc potentials, varied in the positive and negative directions. Experimental complex capacitance plots were reproduced using a computer simulation program based upon the equivalent circuit approach. With 150 nm films the complex capacitance plots at +0.55V (vs. SCE) comprise a single capacitive element, which develops at more negative potentials into a parallel combination of two discrete elements C_1 (a capacitor) and Z_0 (a finite transmission line) in series with a polymer resistance R_p . C_1 and Z_0 are interpreted as double-layer and faradaic (diffusion-controlled) components. The hysteresis observed in the volt-ammetric behavior of polyaniline is evident in the potential-dependence of R_p , C_1 , and Z_0 , obtained under constant-potential conditions.

one of the most studied conducting polymers by various optical and electrochemical techniques. PANI can be synthesized and characterized by electrochemical means as a stand-alone polymer film between two solutions or two metal conductors, or as a surface film deposited on a conductive substrate. The electrochemical synthesis of PANI allows counter-anions, from the growth electrolyte, to become incorporated into the film in order to balance the net charge build-up in the film during oxidative polymerization. This doping process modifies the electrical properties of the polymer such that either electrochemical oxidation or reduction will result in a dramatic change in conductivity. In the case of PANI there is an additional protonation doping mechanism, a result of the ingress/egress of protons into/out of the polymer. Thus, PANI conductivity is sensitive to a change in both counter-anions and pH, and a sharp transformation of conductivity is exhibited at the onset of oxidation or reduction. PANI has more than one oxidation state, each with an associated level of conductivity. Thus it

stability can be checked by Kramers-Kronig transformation, and the results can be interpreted and modeled as equivalent circuits (EC). In the recent years, the ac impedance technique has become a primary method of investigation of chemically modified electrodes and it has proven to be a powerful tool for the characterization of conducting films.

Modeling an electrochemical interface by the EC representation approach has been exceptionally popular in studies of PANI-modified electrodes, although an analytical approach based on transport equations derived from the irreversible thermodynamics was also attempted.²⁻³ ECs are typically composed of numerous electrical elements, taking into account the redox electrochemistry of the polymer itself, its highly developed morphology, the interpenetration of the electrolyte solution and the polymer matrix, and the extended electrochemical double layer established between the solution and the polymer with variable localized properties (degree of oxidation, porosity, conductivity etc.).

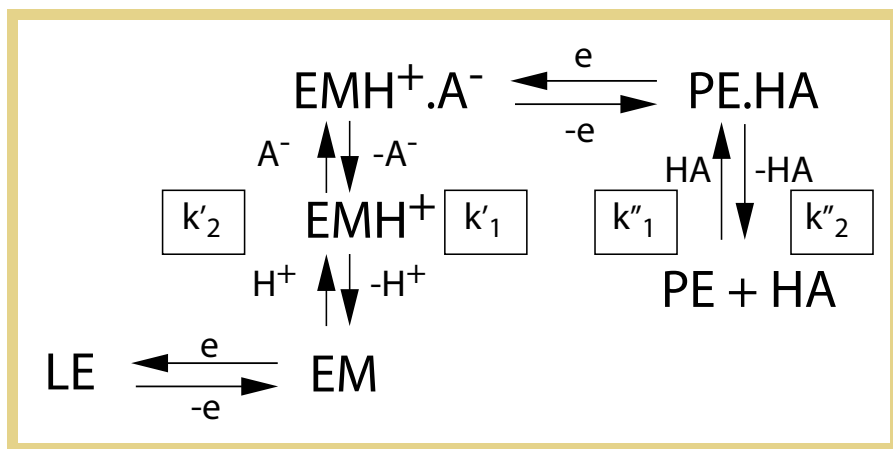


Fig. 1. Coupled chemical and electrochemical steps in polyaniline redox states.¹

The elucidation of the nature of charge transfer processes in electrochemically active polymer films may be the most interesting theoretical problem of the field and a question of great practical importance. A polymer film electrode can be defined as an electrochemical system in which at least three phases are contacted successively in such a way that between an electronic conductor (usually a metal) and an ionic conductor (usually an electrolyte solution) is an electrochemically active polymer layer. The fundamental processes of insertion and transport of charged and non-charged species through this type of electrochemical system are described below and illustrated in Fig. 2.⁴

1. Charge (electron) transfer at the electrode/film interface with associated potential difference ΔE_1 . Ions and solvent cannot move through this interface.
2. Transport of species through the film with associated potential difference ΔE_2 .
 - 2.1. Transport of electrons between the electrode / film and film / solution interfaces.
 - 2.2. Transport of ions and water (solvent) through the film.
3. Insertion or expulsion of ions and water at the film/solution interface with associated potential difference ΔE_3 . Electrons do not move through this interface.
4. Transport of ions and water in the solution.

One of the most challenging aspects of conducting polymers is the occurrence of electron transfer reaction due to the existence of different oxidation states, and simultaneous exchange of solution counterions to compensate for the excess (or the lack) of charge, thus maintaining the film electroneutrality.⁵ The electrical neutrality is maintained by exchange of protons at low pH and insertion of anions into the film at higher pH. These systems must therefore be considered as possessing a mixed ionic-electronic conduction where the migration of both electronic and ionic charge carriers contribute to the total charge transport.²⁻⁶

The electrochemical oxidation or reduction of the conductive polymers and related charge transport occurs either via an electron exchange reaction (long-distance "electron hopping") between neighboring redox sites if the segmental motions of the polymer chains make it possible, or through delocalized electrons that can move through the conjugated systems ("electronic conduction"). PANI is an electrochemically active organic macromolecule with a conjugated system of π -bonds that undergo oxidation and/or reduction in the doping/undoping processes:

charges, "holes," and unpaired electrons are delocalized over a large number of monomer units. The doping process in conjugated polymers is, essentially, a charge transfer reaction, resulting in the partial oxidation or reduction of the polymer, which depends primarily on the electrochemical potential and effects of solution ions—both protons and counterions. Electrochemical transformation of the non-conducting form of these polymers leads to a reorganization of the bonds of the macromolecule and the development of an extensively conjugated system, resulting in very fast electron transfer processes with unusually high capacitive current and dramatic changes in the film conductivity.⁷⁻¹⁰

Therefore, when the electrochemical properties of the polymeric films are investigated, a large number of frequently mutually dependent system parameters should be considered, such as:

- applied electrochemical potential;
- chemical composition and concentration of the electrolyte—anionic and cationic content, pH, type of solvent, size and charge of the ions, specific interactions with the polymer;
- chemical composition of the PANI film, which is often being influenced by the composition of the solution and film synthesis method used during the electropolymerization, as well as the ageing effects;
- film thickness, morphology, permittivity, porosity, density, and swelling
- ionic trapping in the film; and
- temperature effects on the rate of electron transfer, ionic mass transport, and diffusion coefficient of the chain and segmental motions responsible for the electron hopping process.

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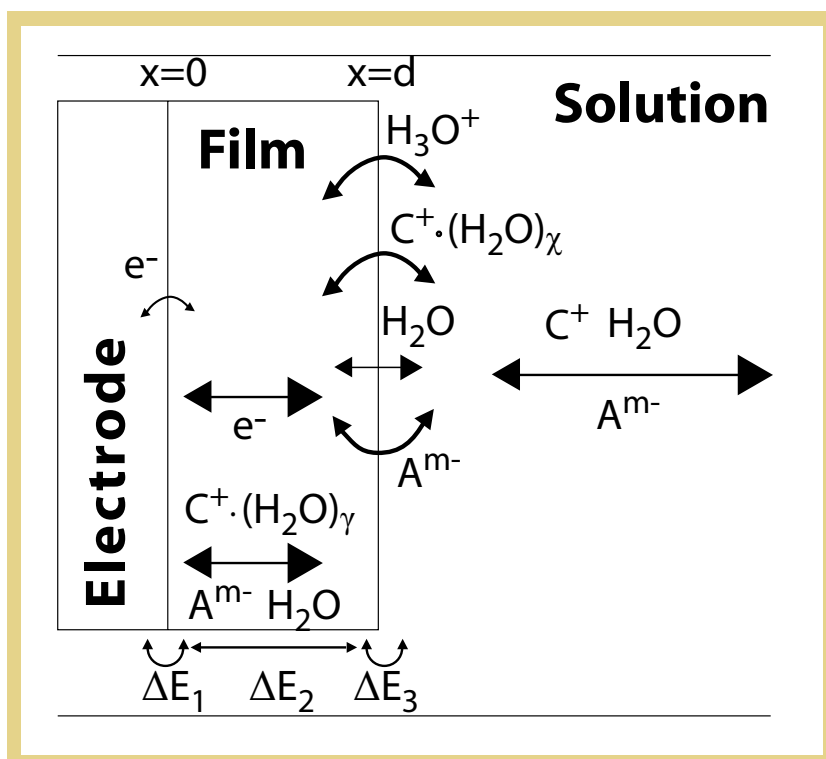


Fig. 2. Schematic diagram of the electrode/electroactive film/solution system.⁴

Electrical Models for PANI Films

The featured classic article¹¹ became one of the very first studies of electron-conducting polymers, in which the technique of the electrochemical impedance was applied to *in situ* characterization of conduction mechanisms and charging/discharging processes. These data showed an essential variation of the non-stationary redox response of a PANI film depending on the oxidation state of the polymer: an almost perfect quasi-equilibrium variation of the charge of the film, following the instantaneous potential values, was observed at high oxidation state, while a pronounced effect of the slow charge transport across the film manifests itself at lower bias potentials. The paper demonstrated that two time constants were present in the potential region where switching between nonconductive and conductive forms of polyaniline occurs, which were simulated with a parallel combination of a capacitance and a transmission line. The exact nature of these potential-dependent processes remains unclear even today, but the paper suggested several thought-provoking possible interpretations of the PANI film physical-chemical identity:

1. A two-phase bulk polymer structure—this interpretation is typical of dielectric spectroscopy analysis of polymers where “more conducting” and “more insulating” segments are expected to display very different electrical properties. (As it will be shown later, in the literature this interpretation has often evolved into a number of “spatial distributed” or “temporal distributed” film theories based on differences in the localized electrical properties of various film segments.)
2. A single homogeneous phase representation, where a combination of double layer capacity and diffusion controlled faradaic process is responsible for oxidation-reduction of the polymer, resulting in appearance of a “transmission line” distributed circuit element in the equivalent circuit model. The large capacitances exhibited by conducting polymer electrodes are usually attributed to the double layer capacitance and pseudocapacitance originating from the redox process of the polymer.

3. A porous phase, exhibiting a pseudo-capacitance charging due to a thin layer behavior of the film and a fast electron-transfer process confined to the pores in the film and double layer capacitance of a porous material.

The featured classic article was followed by a large number of papers dedicated to the EIS characterization of conducting polymers. The general impedance theory of conductive polymer films was developed²⁻³ and the general response of electron-ion conducting films in solution-polymer-metal system⁶ can be modeled as (Fig. 3):

- High frequency impedance response to charge carriers in bulk polymer represented by a parallel combination of film resistance R_{BULK} and capacitance C_{BULK} (or more often $C_{\text{PE}_{\text{BULK}}}$) in series with uncompensated solution resistance R_{SOL} .
- Two parallel combinations of charge transfer resistance R_{CT} and double layer capacitive $C_{\text{PE}_{\text{DL}}}$ features at medium frequency representing the electrode-polymer interface (electron transfer) and polymer-solution interface (counterion transfer).
- Ionic and electronic diffusion-migration limited segment resulting in either Warburg response (W) followed by a capacitive line (constant phase element) reflecting the pseudo-capacitive charging of the film ($C_{\text{PE}_{\text{L}}}$) or a transmission line at low frequencies.

The variations of these EC parameters have been examined in the literature as a function of temperature, film thickness, applied electrochemical potential, concentrations, and types of supporting electrolytes. The kinetic models of conductive polymers differ from one another due to the diversity of opinions about the origin of the experimentally determined parameters. Thus, double layer capacity has been ascribed either to the metal-polymer¹²⁻¹⁴ or the polymer-solution¹⁵ interfaces. Warburg-like domains have been attributed to diffusion or to conduction control of charge transport,²⁻³ whereas $C_{\text{PE}_{\text{L}}}$ has been either considered as a bulk¹³⁻¹⁴ or an interfacial capacitance.¹⁶ Concerning the conductivity of the polymer film, different conduction mechanisms have been considered (metallic, ionic, variable range hopping, fluctuation-induced tunneling, or due to the electrolyte in the pores of the film).¹⁷⁻¹⁹ However, despite seemingly contrasting ways of describing the polymer phase in these approaches, the experimental and computational EIS results concerning the responses to *dc* and *ac* perturbations often turned out to be similar or even identical.

This ambiguity is typical of the EIS analysis in general, where one cannot assume that an equivalent circuit that produces a good fit to a data set represents an accurate physical model of the system.

Impedance modeling included several major developments along the lines represented in the featured classic article¹¹ as well as several possible combinations of these original theories. For example, a “brush-like” model was developed based on ordering of the polymeric chains with macropores filled with electrolyte, which represents the capacitive charging and redox reactions at walls of the pores with a transmission line.²⁰ Very high capacitances dominating the conductive region of the potential window arise from diffusion-controlled movements of counterions (protons and anions) leaving or entering the film at the film/solution interface and being blocked at the film/metal interface. Earlier it was proposed to distinguish two processes during the redox transformation of the polymeric films, a faradaic type in which the charge carriers are generated in a reversible electron transfer step and a (non-faradaic) capacitive type connected to the movement of the carriers to the interface, a charge accumulation without creating new

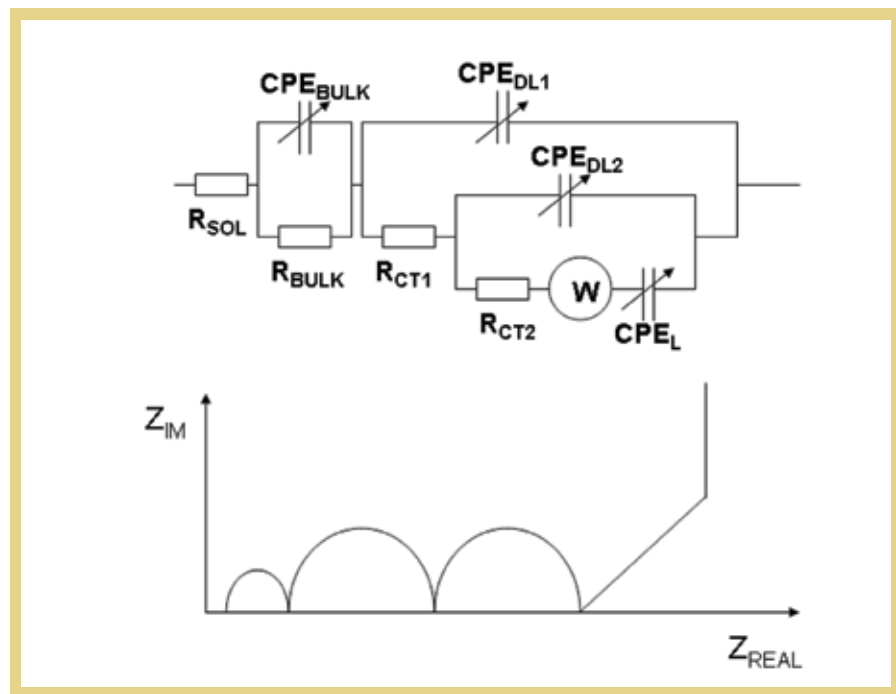


Fig. 3. General equivalent circuit and a typical complex impedance plot representing an electrode/electroactive film/solution system.

carrier.²¹ However, the overlapping oxidation processes, and the inseparability of the current components in pure electrical measurements, often make a clear distinction between these two processes difficult.

Very often, modeling of PANI films have been based on attempts to separate two different charging processes in the film, representing an evolution from the first proposed mechanism based on two different polymer structures. A number of studies were based on representation of these separate charging processes as related to the “fast” vs. “slow” charging properties of these polymer segments determined by their respective morphology, location within the film, chemical composition, and response to the applied ac field. For example, two different diffusion rates are assumed for the doping ion, depending on whether the capacitive doping is related to the ions moving into more closed aggregates of compact polymeric chains or to a bulk phenomenon kinetically controlled by the diffusion of counterions between the large polymeric chains.²²⁻²⁴

Another theory²⁵ considered a similar spatial two-phase distribution with shallowly trapped ions in the bulk of the films and deeply trapped ions in the double layer at the film/electrode interface (Fig. 4).²⁶ A more detailed mechanism of spatial and temporal charging was proposed as a result of external oxidation potential perturbation. It was suggested that PANI oxidation commences at the electrode/PANI interface, and the reaction front moves along the individual polymer chains towards the film/solution interface, representing more of a protonic charge compensation as sites deep inside of nonconducting PANI film react, while at more positive potentials the mechanism reflects oxidation of outside film layers with more anion injection. As proton expulsion occurs during the oxidation, the inner PANI film experiences an increase in local pH, and the outer regions of the film will continue to be influenced by acidity of the bulk solution. Proton injection into a fully conducting PANI film during reduction is likely to occur first at the outer film/solution interface.²⁷ Another type of gradient distribution takes into account mixed electron-ion conduction in the polymer, with ions conducting through pores and electrons through the chains in the polymer.²⁸ If the electronic conductivity is much higher than ionic conductivity, the charge “leaks” from the polymer with the higher conductivity toward the electrolyte surface. The exchange reaction begins at the film/solution interface and propagates through the porous coating into the interior to the electrode. Otherwise, if ionic conductivity is much higher than electronic conductivity, the charge leaks along more conductive pores, and oxidation begins at the electrode/polymer interface and gradually propagates into the interior of the polymer coating.

Additionally, it was proposed to assign the current to redox processes connected to a series of polymeric segments of different length,²⁹ to the existence of parallel domains of

conductive and resistive zones arranged perpendicularly to the electrode,³⁰ and to a hopping motion charge conduction mechanism represented by a transmission line EC element.³¹ The impedance spectra were analyzed as a function of the polymer characteristic parameters through a computational simulation stressing the effects of both thickness and thickness distribution of the polymer films, suggesting that the ohmic resistance determined from EIS data is connected with ionic conductivity, including the cation incorporation, and not with electronic conductivity.²⁵ Film thickness is being viewed as the predominant factor for giving higher capacitances with counterion charging playing a major role.²⁷

Concluding Remarks

The use of polyaniline and other conductive polymers as new materials in value-added industrial and consumer products is opening up entirely new opportunities for polymeric materials. These include electroactive inks, paints, coatings, and adhesives; electrochromic “smart” windows; transparent and corrosion protective films; intercalating electrodes in advanced batteries; super-capacitors; high performance fibers, drain-source junctions in MOSFET-like devices; anti-static products; electrocatalytic materials; and ion-specific electrochemical biosensors. Conducting polymers offer a number of potential advantages in electrochemical sensors, for example as electrode materials not subject to fouling or as substrates for enzyme immobilization. There have been enzyme-modified PANI electrodes reported in detecting glucose using a “ping-pong” mechanism where the polyaniline responds with quantitative conductivity changes to hydrogen peroxide released as a result of interaction between the enzyme and the substrate.¹ PANI-based sensors were used to detect acidity changes in aqueous and non-aqueous environments based on protonation/deprotonation of PANI.³² The future possibilities may include conductive and semi-conductive shielded cable jackets, light emitting diodes, microelectronic devices, and conducting fibers.

Clearly, the electrochemical impedance analysis of PANI films in the featured article¹¹ has provided deeper initial insight into the mechanisms of conduction, doping and charge storage, as well as greatly furthered the theory of the impedance method as a major material science characterization technique. Although the models that have been used to derive the expression for the impedance differ from one another, reflecting the diversity of opinions about the mechanism of charge transport processes occurring in these films, it has become clear that a somewhat reliable physical description of the experimental impedance data can be obtained. However, no unified approach to data analysis has been used, most probably because a search for a uniform kinetic model properly designed to fit conducting polymers continues.

In almost every case, the behavior of real systems shows deviations from the theoretically expected parameters. Therefore, additional refinements of the models are needed, taking into account interactions between the redox sites, intermolecular and intra-molecular charge transport, possible chemical steps associated with charge transfer, nonuniform film thickness and porosity, ionic relaxation processes, and diffusion coefficients distribution.

Recent attempts to find the analytical expression for the transport equations inside the film and the solution, accounting for both ionic and electronic mobile charge carriers inside the film, electron and ion exchange with the polymer, redox couples, and charging of the interfaces³³ can lead to new insights on the nature and representation of the charging process and its dependence on the oxidation level of the film. Finally, application of emerging experimental techniques such as non-linear impedance analysis is also noted.

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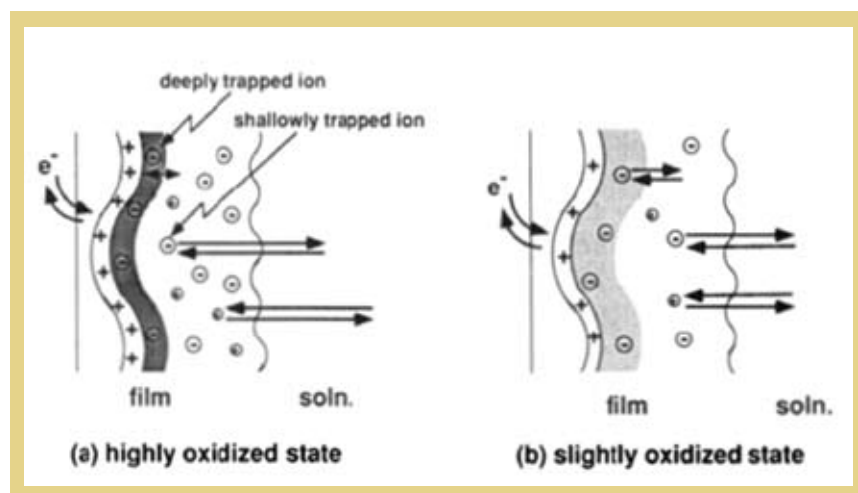


Fig. 4. Ion transport model in conductive films as a function of dc potential with “deeply trapped ions” responsible for “slow” faradaic processes and “shallow-trapped ions” responsible for “fast” kinetic processes.²⁶

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