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Charge transfer processes in conducting polymer films

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Abstract. The available models of charge transfer processes in electroactive polymer films are considered. Examples of interpretation of the data of electrochemical measurements using model approaches are given. The emphasis is placed on the interpretation of the results on the impedance of modified electrodes. On this basis, conclusions concerning the most topical research problems and the description of the processes in question are drawn. The bibliography includes 122 references.

I. Introduction

The laws of electrode processes in electroactive polymer films have been the subject of intensive research in recent decades. At present, this is an individual investigation direction called electrochemistry of modified electrodes. Research in this field became particularly intensive since the discovery of the so-called 'synthetic metals' (conducting polymers with conjugated bonds) in the late 1970s.[1] Incessant interest in such polymers is due to prospects for their practical use as materials for power sources, various electrochromic and optoelectronic devices, *etc*.[2–10] Until very recently, most studies in this field concerned the search for novel systems in order to fabricate films whose properties will fulfill practical demands. Studies on the laws of transport processes in such systems are scarce. The fact that the kinetics and mechanisms of charge transfer in electroactive polymer films have been poorly studied is due to the lack of information on their structural features. The stoichiometry and products of the electrode reactions are sometimes unclear. Often, it is unknown which proportion of potentially active film fragments is involved in the electrode process and whether or not are the film properties changed with the film thickness. The authors of the present review do not pretend to highlight all aspects of research in this field. Here, it is appropriate to place the emphasis on theoretical approaches to the description of charge transfer in various polymers and on generalisation of quantitative data on the kinetics of these processes.

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A polymer-modified (from this point on, 'modified') electrode is a conducting substrate coated with an organic or inorganic electroactive polymer film contacting an electrolyte solution. Usually, two main classes of such films include electron-conducting (or simply conducting) polymers and redox polymers.[8–10] The first class comprises organic polymers with a conjugated system of π-bonds. Here, the conductivity is due to delocalisation of electrons or 'holes' that appear upon the oxidation (doping) of the polymer. Typical conducting organic polymers with conjugated bonds include, *e.g*., polymers based on aniline and its derivatives, polymers based on simple and substituted five-membered heterocycles (polythiophenes, polypyrroles), *etc*. A feature of this class of organic polymers is the ability to undergo reversible redox transitions involving the so-called dopants (anions, hydrogen ions). Redox transitions induce abrupt changes in the polymer conductivity, from quasi-metallic conductivity to semiconductor one.

The class of redox polymers comprises polymer structures containing immobilised redox active centres. Electron transfer between these centres determines relatively low electronic conductivity of such polymers. Electroactive centres can be constituents of the polymer chain or be bound to functional groups of the polymer. Typical redox polymers include polynuclear complexes based on metal hexacyanoferrates, polyoxotungstates and polyoxomolybdates as well as ion-exchange polymers with incorporated (electrostatically bound) redox active cations or anions.

In most cases electroactive polymer films are synthesised on the surface of electron-conducting substrates by electrochemical polymerisation of monomeric organic compounds or metal complexes.

Electrochemically active centres in the redox polymers are metal ions, which can change the oxidation state and thus participate in electron exchange processes. The conductivity of a redox polymer is governed by the product of the electron donor concentration by the electron acceptor concentration and reaches the maximum value at the formal potential of the redox system.

The electrochemically active fragment of conducting polymers is the double bond. Elimination of an electron from the double bond (oxidation) leads to the formation of a radical cation in the initial stage. Experimental EPR studies of conducting polymer films confirm the presence of unpaired electrons in the films.[2,3]

A radical cation that formed is partially delocalised over a polymer chain fragment of size of a few (usually, 4 – 6) monomer units. This leads to deformation of the polymer structure and polarisation of the environment (this gave the name 'polaron' to the chain fragment containing the radical cation). Polarisation of the environment and interaction with counterions lead to stabili-

sation of the radical cation. If the next electron is removed from the same polymer chain fragment, a dication or bipolaron is formed. At present, the polaron theory of conductivity has been recognised as the main model for explanation of the electronic conductivity of polymers with conjugated bonds. According to this theory, the electronic conductivity is due to the motion of polarons and bipolarons along the polymer chain in an electric field and occurs by reorganisation of the double and single bonds and by electron hopping between chains.

In spite of some distinctions between these classes of polymers, common to both of them is a mixed electronic-ionic mechanism of conductivity. Indeed, a negative or positive charge injected into a film should be compensated by injection or removal of electrolyte ions absorbed in the film in order to meet the electrical neutrality condition for the entire film. Therefore, in both cases theoretical description of charge transfer has much in common; in essence, it uses the same model of electron hopping mechanism of charge exchange between adjacent redox centres (or delocalised holes and electrons in conducting polymers), accompanied by transfer of counterions.[4–10] Considering the concepts underlying the interpretation of data on the electrochemical properties of electroactive polymer films, two approaches to construction of theoretical models of these systems should be pointed out. The first approach has been best developed and treats the film as a system possessing homogeneous properties.[5,11–19] Analysis of the response of a metallic electrode (conducting substrate) coated with such a film and contacting an electrolyte solution involves the division of the overall process into certain stages, namely, charge transfer in adjacent electrolyte and charge injection into and charge transfer inside the film. The second approach, which has been intensively developing recently, takes into account inhomogeneous structure of the film and, in particular, microcrystallite structure of the film, *i.e.*, the presence of pores filled with electrolyte.[20–28] Apparently, electrolyte ions can be absorbed in (and removed from) such inhomogeneous film not only from the outer interface with the solution but also from the inner interfaces corresponding to pore–polymer interfaces.

From the aforesaid it follows that modified electrodes should be studied by various methods. Apparent correspondence between the electrochemical properties of the modified electrodes and the structure and morphology features of the modifier films requires the use of various structural-physical methods. At the same time it is desired that the structure and properties of films be changed in a target fashion using chemical techniques. Often an electrode process is accompanied by changes in the spectral characteristics of the films; this makes spectroelectrochemical methods of investigation necessary (see *e.g.*, reviews[29,30]). An important role is also played by the quartz microbalance method,[31–36] which in many cases helps to reliably determine the nature of counterions incorporated into polymer film and the degree of changes in the viscoelastic properties of the film in the course of the electrode process. The most widely used electrochemical methods of investigation of modified electrodes include cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Chronoamperometry (CA) is somewhat more rarely used. Multistage character of electrode processes in such systems, the presence of at least two interfaces (film–solution and film–metallic electrode or another conducting substrate, *e.g.*, semiconductor, graphite, glassy carbon) complicate the interpretation of experimental data.

Both the use of methods of investigation of modified electrodes and processes occurring in them and the difficulties in the interpretation of measurement results require elaboration of relevant theoretical concepts. A broad spectrum of problems and methods make it impossible to correctly describe all aspects of research in the field of modified electrodes in the framework of a small review article. Therefore, in this work we will restrict ourselves to consideration of electrochemical aspects of this avenue of research (*i.e.*, the available models for the description of charge transport in the systems under study and illustration of the use of such models in studies of electrode processes occurring in particular systems).

Electrochemical impedance spectroscopy is the most efficient method of studying charge transfer processes. However, the use of this technique often faces some difficulties[37] that are usually due to the need of taking into account a large number of factors responsible for charge transfer in real systems (*i.e.*, to multiparametric character of analysis). Studies on the impedance of the redox polymer and conducting polymer films carried out to 1989 were briefly outlined by Musiani.[38]

The possibility of using different models of the systems under study and different transport schemes *a priori* makes the interpretation of the results obtained somewhat ambiguous. Therefore, often a particular interpretation is predetermined by the choice of a certain equivalent electric circuit as a model for the system under study or by introducing a number of additional elements corresponding to peculiar features of the impedance spectra into the available circuits. This manner of data interpretation is highly popular and can be treated as a specific approach involving the use of analogue electric circuits. Since the approach uses no particular model, it can be employed for analysing the electrical responses of modified electrodes in the case of both homogeneous and inhomogeneous films and, in particular, porous polymer films.

II. Method of equivalent circuits

As mentioned above, electroactive polymer films exhibit a mixed electronic-ionic conductivity, *i.e.*, electron transfer in a film is accompanied by transfer of counterions. To visualise this process, Albery *et al.*[20–23] proposed an equivalent circuit (Fig. 1) comprised of transmission lines corresponding to the system's con-

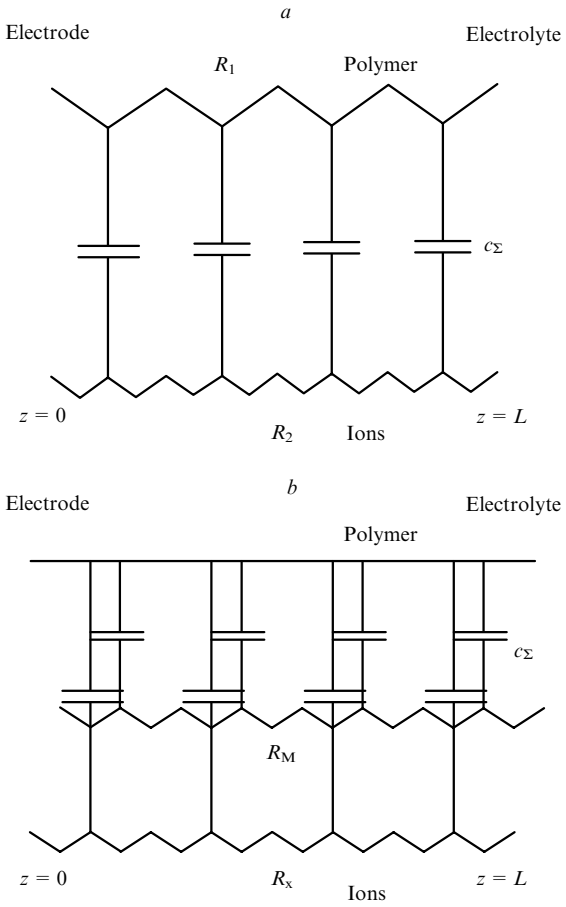


Figure 1. Transmission lines for two particles (electron and ion) (*a*) and for three particles (electron, cation M^+ and anion X^-) (*b*).[22]

ductivity with respect to each type of particles and connected by capacitors. The capacitors take into account the possibility of redox process in the film upon injection of a negative or positive charge and compensation of this charge due to incorporation (removal) of corresponding ions. Initially, this equivalent circuit was proposed for the description of porous electrodes. Albery *et al*. considered two phases of the film, namely, the polymer and pores. The film-related impedance is represented by a finite transmission line consisting of two resistors, R_1 and R_2, and one capacitance (see Fig. 1 *a*). Here, R_1 is the resistor describing the motion of electrons in the polymer and R_2 is the resistor describing ion transfer in pores. Consideration of this circuit shows that if $R_1 \ll R_2$ (electronic conductivity is much higher than ionic conductivity) the charge 'leaks' from the polymer with the higher conductivity towards the electrolyte surface. The exchange reaction begins at the film – solution interface and propagates through the film (porous coating) into the interior to the electrode. Otherwise, if $R_1 \gg R_2$ (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. The Albery theory allows the pore-to-polymer volume ratio, diffusion coefficient and thickness of the coating to be determined. Qualitatively, the model of infinite or (in simplified form) finite transmission lines describes conducting polymer films irrespective of their structure (porous or not). However, this only indicates the correctness of representation of films by this equivalent electric circuit. Physical meaning of the model is still to be clarified, in particular in the cases of frequency-dependent elements of the circuit (see below). Often, for the sake of simplicity the transmission lines in the equivalent circuit shown in Fig. 1 *a* are replaced by an element called the Warburg impedance (Z_W) or diffusion impedance (Z_d).

In addition to charge transfer in bulk film, which is characterised by the transmission lines, the EIS spectrum of modified electrodes is affected by the charge injection processes at the conducting substrate – film and film – solution interfaces. This effect is usually included by introducing the so-called *RC*-chain (element consisting of a resistor R_{ct} and capacitor C_{dl} connected in parallel) into corresponding equivalent circuit. The resistor describes hindered injection of charge carriers through a certain interface and the capacitor describes the need of charging the electric double layers for the injection to occur. The equivalent circuits often include a resistor R_s responsible for the resistance of the region of the bathing electrolyte solution from the film to the tip of the electrolytic salt bridge. Therefore, the simplest equivalent circuit of a homogeneous electroactive film, which takes into account the effect of one interface and charge transfer in bulk film, has the form shown in Fig. 2 *a*.

Figure 2 *a* also shows an ideal spectrum of this circuit in the complex coordinates ($-iZ_{Im}$, Z_{Re}) that are usually called the Nyquist coordinates. If the relaxation times characteristic of different stages of charge transfer differ appreciably, the overall impedance diagram reveals different frequency domains corresponding to each electrode process included. In the high-frequency limit one should expect the electrolyte solution resistance equal to R_s. At relatively lower frequencies, the impedance is due to a process at the electrode – film and(or) film – electrolyte interface and the spectrum exhibits a semicircle (sometimes, two semicircles). The time constant τ (relaxation time or 'characteristic time') of the semicircle is governed by the product of the charge transfer resistance by the double layer capacitance

$$\tau = R_{ct}C_{dl}.$$

These two parameters can be determined using the diameter, D, and frequency, ω_{max}, at the maximum of the semicircle (see Fig. 2 *a*):[37]

$$D = R_{ct};$$

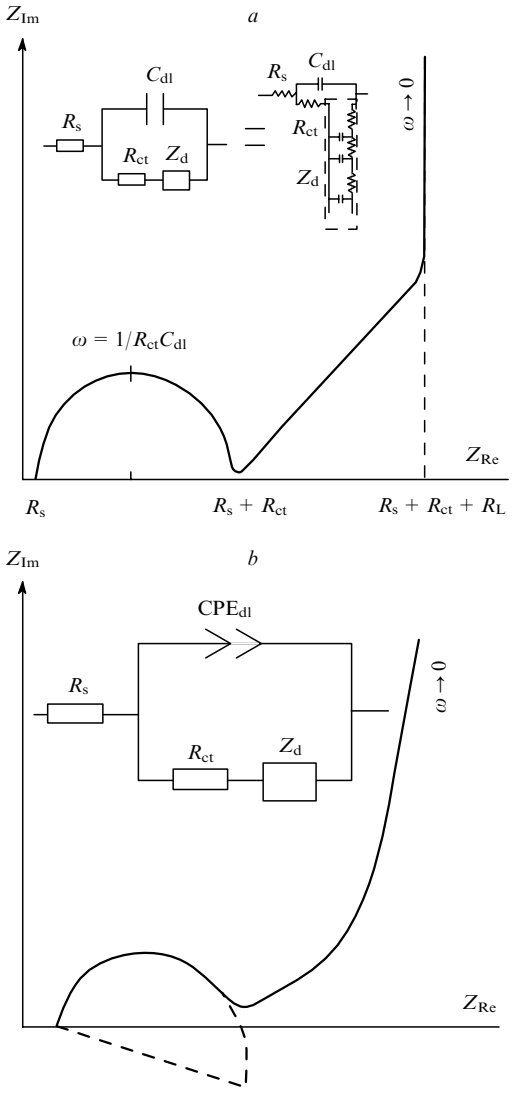


Figure 2. Simplest equivalent circuits for interpretation of the impedance of modified electrodes: conventional Randles circuit (*a*) and modified circuit (*b*) corresponding to the limiting effect of charge injection into film and the corresponding impedance spectra plotted in the complex coordinates (negative imaginary component of the impedance $-iZ_{Im}$ *vs*. real component Z_{Re}).

$$C_{dl} = \frac{1}{\omega_{max}R_{ct}}.$$

At lower frequencies, the major contribution to the frequency characteristic of the impedance comes from diffusion. Here, two regions can be considered, a linear region with a phase angle of $\pi/4$ corresponding to semi-infinite diffusion and treated as the Warburg impedance, Z_d, and a second linear region at more lower frequencies with a phase angle of $\pi/2$. Considering that the diffusion of ions in solution occurs much faster than in the film (*i.e*., in the solid), it is reasonable to assume that mass transfer is governed by the diffusion of current carriers in the film. The region of very low frequencies with a phase angle of $\pi/2$ can be treated as a pure capacitive response of the system. In this region the diffusion is gradually limited by charge accumulation within the film as the frequency decreases, which leads to the limiting capacitance C_{lf} that can be calculated from the equation [37]

$$C_{lf} = \frac{L^2}{3D_{eff}R_L},$$

where L is the film thickness, D_{eff} is the effective coefficient of diffusion in the film and R_{L} is the limiting resistance (intercept on the real axis of the impedance).

It should be noted that in practice the impedance spectra are often inconsistent with the simplest model mentioned above;[39–43] sometimes they exhibit a bent semicircle centred below the real axis (see Fig. 2*b*). In addition, the pure capacitive behaviour predicted by the model (see above) is not observed even at very low frequencies. In many practically used models this deviation from the ideal behaviour is taken into account by replacing the capacitance by the so-called constant phase element (CPE)[37] whose impedance is given by

$$Z(\omega) = \frac{1}{T(\mathrm{i}\omega)^{\varphi}},$$

where T is a constant measured in $\Omega^{-1}\ \mathrm{s}^{\varphi}$ and the exponent φ ($|\varphi| \leqslant 1$) determines the phase shift equal to $(\pi/2)\varphi$. The smaller the φ value ($0 < \varphi < 1$), the larger the shift of the semicircle. The CPE corresponds to a capacitor with the capacitance T at $\varphi = 1$, to an induction coil at $\varphi = -1$, to a resistor at $\varphi = 0$ and to the Warburg impedance Z_{W} at $\varphi = 1/2$ (see below).

The introduction of the CPE for the description of experimental data is a formal procedure, because the physical meaning of this element is still unclear, except for the particular cases mentioned above. The CPE is more likely introduced to simplify calculations rather than understand the actual nature of the processes occurring in the film. Nevertheless, the use of the CPE in equivalent circuits has been a routine step for many authors,[41–43] in particular, in the description of the frequency-dependent capacitance of polymer films. The reasons for this dependence (frequency dispersion of capacitance) have been the subject of extensive literature based on the concepts of structural-chemical inhomogeneity in films, high roughness of interfaces and possible trapping effects (presence of mobile charge carrier traps in the form of certain film fragments). In these cases the frequency-dependent capacitance $C(\omega)$ is usually described by the semi-empirical relation

$$C(\omega) = \frac{C_0}{1 + (\mathrm{i}\omega\tau)^{1-\alpha}}. \qquad (1)$$

Here C_0 is a constant capacitance, τ is the characteristic time of the process responsible for the observed frequency dispersion of capacitance and α is an empirical exponent. It should be noted that as a rule the use of expression (1) is based on the De Levie theory for porous electrodes.[44] In this theory and its more recent versions the capacitance $C(\omega)$ does obey the relation of type (1). Experimental criteria for validation of the use of the porous film model include effects of film thickness and concentration of the bathing electrolyte, specific to these systems. Numerous investigations showed that variation of the film thickness usually leads to a change in the film morphology. As a rule, the degree of film porosity increases with the film thickness, thus affecting the magnitudes of the parameters to be determined. The contribution of ion transfer also changes, namely, increases on going to more porous films. Therefore, in such films one can expect an increase in the effective diffusion coefficient of current carriers with an increase in the concentration of the bathing electrolyte. Practical convenience of the use of the transmission line model lies in that it allows one to divide the impedance spectrum into characteristic regions [high-frequency semicircles and the diffusion (Warburg) impedance and low-frequency capacitance regions] responsible for different stages of charge transfer in films and thus to make qualitative conclusions about the mechanism of this process. At the same time quantitative interpretation of experimental data using the model mentioned above is impossible, because this requires the use of corresponding theoretical results.

Prior to going to a brief outline of the results for a homogeneous modifying polymer film a circumstance not discussed above should be pointed out. The case in point is the choice of the fashion in which different elements of an equivalent circuit are connected to one another. Indeed, according to the Albery model, there are at least two transmission lines describing transfer of electrons and counterions in the film. Apparently, in the case of the substrate–film interface the *RC*-element corresponding to injection of electrons into the film (or *vice versa*) should be connected to the electron transmission line. But at the same interface, the transmission line for counterions should be connected to the substrate through a capacitor, because the charging of the interface will to a greater or lesser extent be determined by the dynamics of these ions in the electric double layer surrounding the substrate (see Ref. 45 and Fig. 3). A similar connection should also correspond to the film–solution interface (or polymer–pore interface in the case of porous film structure), but the difference is that now the *RC*-element is connected to the counterion transmission line and placed before the resistor R_{s}. In the absence of electron transfer at this interface the electron transmission line should terminate with a capacitor (see Fig. 3) or with the second *RC*-element in the presence of electron acceptors in the solution.

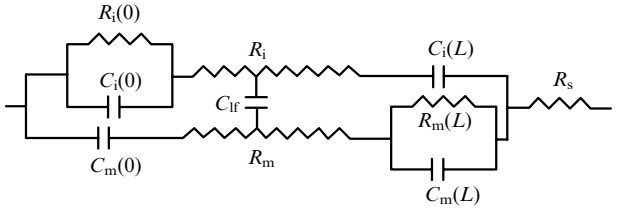


Figure 3. Equivalent circuit representing an electric model of polymer film with two charge carriers.
R_k is the bulk film resistance with respect to the kth current carrier, $R_k(z)$ and $C_k(z)$ are respectively the resistance and capacitance of the film interfaces at the coordinate z ($z = 0$ at the metal–film interface and $z = L$ at the film–solution interface); k = i for electrons and k = m for counterions; C_{lf} is the low-frequency film capacitance; and R_{s} is the resistance of the bathing electrolyte.

Thus, detailing of the equivalent circuit of the modified electrode suggests the need of introducing at least three parameters (two capacitors and a resistor) for each interface in order to correctly describe its charging. Actually, yet another, fourth parameter should be added to the three ones, as was shown by Vorotyntsev *et al.*[16,17] and will be considered below. Therefore, in the general case processing of experimental data using corresponding theoretical results can face certain problems. Even with a certain set of necessary parameters, the results of experimental data processing will cast some doubt. The reason is the lack, up to date, of a correct theory that would provide a basis for the interpretation of experimentally observed changes in such relatively simple parameters as the charge transfer resistance R_{ct} and interface capacitance C_{d} with the potential and other variable experimental parameters. To make no naked assertion, note that experimental C_{dl} values (usually, a few $\mu\mathrm{F\ cm}^{-2}$, see below) have no comments. At best, mention is made that these values are small compared to the double layer capacitances in electrolyte solutions. The situation with interpretation of the R_{ct} values is somewhat different. They are often interpreted using the Butler–Volmer equation in order to write the expression for the rates of injection of current carriers into the film.[12] However, this equation does not include the effect of the electric double layer on the rates of heterogeneous charge transfer (the so-called Frumkin correction). Therefore, application of the Butler–Volmer equation to conducting polymers is at least a moot question. The expressions for injection currents used by Vorotyntsev *et al.*[16,17] and Láng and Inzelt[46] were linearised with respect to small deviations of the concentrations and potential jumps. This representation of the injection currents is correct if small-amplitude methods (in partic-

ular, EIS) are used, but consideration of the shape of the R_{ct}-*vs.*-electrode potential plot (provided that relevant data are available) in this case is impossible. It seems obvious that correctness of data interpretation can only be confirmed by attaining agreement between the observed changes in the measured parameters of the impedance spectra as functions of the electrode potential and some theoretical concepts. Such an agreement is even more necessary in the case of multiparametric processing of impedance data, as often occurs in studies of modified electrodes (see below).

From the aforesaid it follows that research on charge transfer in the systems in question involves a particular investigation line, *viz.*, elaboration of theoretical concepts appropriate for minimisation of the number of descriptor parameters.

III. Homogeneous film model

A correct formulation of the problem of the impedance of a modified electrode and its solution for homogeneous conducting polymer films were reported by Vorotyntsev [16] and then extended [17] to the case where the bathing electrolyte contains a redox pair that provides the possibility for electrons to leak from the film surface. The importance of these results is not limited to the case of homogeneous conducting films separating the substrate and solution (or two metallic substrates or two solutions, see Refs 16 and 17). We believe that they should be taken into account, in one form or another, when using the porous models of such films. However, up to date general character of the analysis performed in these studies prevents the use of the results obtained. In this connection it seems appropriate to dwell here on some important aspects of the analysis,[16] restricting ourselves to the case of modified electrode. In contrast to the non-model approach [16] in this review we will employ a model one in order to find out the possibility of obtaining analytical expressions for some parameters reported by Vorotyntsev *et al.*[16, 17]

For a homogeneous electroactive film containing only two types of current carriers the electron and counterion flux densities j_{im} and j_m, respectively, are given by the following equations:[11]

$$j_{im} = -D_{im}\left\{\frac{\partial C_R}{\partial z} - C_R(1-\theta_R)\left[\frac{\partial \Phi}{\partial z} - \alpha_0\frac{\partial \theta_R}{\partial z}\right]\right\},$$
$$j_m = -D_m\left\{\frac{\partial C_m}{\partial z} + z_m C_m\frac{\partial \Phi}{\partial z}\right\}, \qquad (2)$$

where D_{im} and D_m are the electron and counterion diffusion coefficients, respectively; C_R is the concentration of the reduced fragments (sites); z is the distance from the substrate–film interface; $\theta_R = C_R/C$ is the coverage of the film fragments involved in electron transfer following the reaction

$$Ox + e^- \rightleftharpoons Red,$$

with the reduced form. Here $C = C_R + C_{Ox} \neq f(z)$ is the total concentration of such fragments; C_{Ox} is the concentration of oxidised fragments (sites); α_0 is a dimensionless (in units of RT) attraction constant determined by the energies of the interactions between film fragments and the nearest environment; C_m and $z_m = \pm 1$ are respectively the concentration of counterions in the film and the charge of these mobile charge carriers; $\Phi(z) = F\varphi(z)/RT$ is the dimensionless electric potential (*vs.* adjacent bulk electrolyte) and $\varphi(z)$ is the dimension value of this potential (see also Ref. 19 and references cited therein). Conditions for conservation of current carriers (electrons localised on the reduced fragments and counterions) in the film are given by the equations

$$\frac{\partial C_R}{\partial t} + \frac{\partial j_{im}}{\partial z} = 0,$$
$$\frac{\partial C_m}{\partial t} + \frac{\partial j_{im}}{\partial z} = 0, \qquad (3)$$

which correspond to the absence of chemical reactions (*e.g.*, binding of counterions to film fragments) in the bulk film under study. The expression for the resulting current density, $I(z,t)$, due to the electron and counterion fluxes (j_{im} and j_m, respectively) is obvious:

$$I(z,t) = F(z_m j_m - j_{im}). \qquad (4)$$

Equations (2)–(4) are supplemented with the Poisson equation

$$\frac{\partial^2 \Phi(z)}{\partial z^2} = -\frac{4\pi F^2}{\varepsilon_f RT}\{z_m C_m(z) + (z_0 - 1)C_R(z) + z_0 C_{Ox}(z)\}, \qquad (5)$$

where z_0 is the charge of the oxidised form and ε_f is the dielectric permittivity of the film. An analogous Poisson equation

$$\frac{\partial^2 \Phi(z)}{\partial z^2} = -\frac{4\pi F^2 C_s}{\varepsilon_s RT}\{\exp[-\Phi(z)] - \exp[\Phi(z)]\} \qquad (6)$$

should also be written for the bathing electrolyte, *i.e.*, for the distances $z > L$, where L is the film thickness, C_s is the volume concentration of a solution of symmetric (1–1-charged) electrolyte and ε_s is the dielectric permittivity of the electrolyte. Writing Eqn (6) also implies zero concentration gradients in the bulk electrolyte during measurements.

Gabrielli *et al.*,[12] Deslouis *et al.*[47] and the Mathias and Haas [11] solved Eqns (2)–(5) ignoring the electric double layers at film interfaces. Láng and Inzelt [46] have found an approximate solution to the problem taking into account the deviation from electrical neutrality. In contrast to these studies the derivation [16, 17] of the expressions for the impedance seems to be very correct. In particular, it was assumed that the equilibrium potential and current carrier concentration distributions are retained within the diffuse parts of the electric double layers of the film even when the potential applied to the electrode is altered at relatively high frequencies. Indeed, relaxation of these distributions should occur almost instantaneously, because the Fourier parameters, $(1/\kappa_f)^2/D_{eff}$, of these layers are very small [$1/\kappa_f$ is the thickness of the diffuse part of the electric double layer (EDL) of the film at the left or right boundary, D_{eff} is the effective diffusion coefficient of charge carriers in the film]. Therefore changes in the concentration and potential in these layers should occur under quasi-stationary conditions. Grafov and Chernenko [48, 49] first showed that in this case the potential and concentration distributions within diffuse layers should be equilibrium in character. This allowed the thermodynamic theory of interfaces (in particular, the Gibbs adsorption equation) to be employed [16, 17] for the description of the charging of the EDL in electroactive polymer films. Some important aspects of this analysis will be considered in detail in the text below. At the same time we will show the possibility of decreasing the number of description parameters.

It is convenient to begin with the determination of the injection rates of current carriers into the film. Let us make some simplifications, namely, assume that injection of counterions into the film is limited by partial desolvation of the counterions at the film–solution physical border. With this assumption the equation for the injection rate $J_m(L,t)$ of these ions has the form

$$J_m(L,t) = z_m F[\sigma_m C_M(L,t) - \rho_m C^s_m(L,t)], \qquad (7)$$

where $C_M(L,t)$ is the concentration of counterions at the film surface as viewed from the adjacent solution, $C^s_m(L,t)$ is the concentration of the same counterions at the film surface as viewed from the film and σ_m and ρ_m are respectively the rate constants for injection. Since this stage is assumed to be the limiting stage for the incorporation (removal) of ions into the film, the concentrations $C_M(L,t)$ and $C^s_m(L,t)$ should respectively be related to the concentration, C_0, of injected ions at the end of the diffuse layer in the solution and the concentration, $C_m(L,t)$, at the end of the diffuse layer in the film on the same side of the film by some equilibrium relationships. Taking into account these interrelations, Eqn (7) can be rewritten in the form

$$J_m(L,t) = z_m F\left\{\sigma_m C_0 \exp\left[\frac{-z_m F(\varphi_f(L,t) - \varphi_s(t))}{RT}\right] - \right.$$
$$\left. - \rho_m C_m(L,t) \exp\left[\frac{z_m F(\varphi(L,t) - \varphi_s(L,t))}{RT}\right]\right\}, \quad (8)$$

where the potentials $\varphi_s(L,t)$ and $\varphi_s(t)$ correspond to the physical boundary of the film as viewed from the adjacent solution and to the end of the diffuse layer in the same solution, respectively. The potential $\varphi_f(L,t)$ is equivalent to the potential ψ_0 in the double layer theory and corresponds to the shortest distance (as viewed from the film) between counterions and the film – solution interface. For instance, the difference $[\varphi_s(L,t) - \varphi_f(L,t)]$ is a consequence of the presence of the Helmholtz compact layer at the interface in question (Fig. 4). However, roughness of the film surface in real systems means that there is no continuous Helmholtz plane corresponding to the smallest separation between ions and the interface. This makes it possible to average the location of these ions along an apparent interface assuming equality of the potentials $\varphi_s(L,t)$ and $\varphi_f(L,t)$. In other words, is seems appropriate to use the Gouy model without dense layer for this interface. Then Eqn (8) takes a simplified form:

$$J_m(L,t) = z_m F \exp\left[\frac{-z_m F(\varphi_s(L,t) - \varphi_s(t))}{RT}\right]\left\{\sigma_m C_0 - \right.$$
$$\left. - \rho_m C_m(L,t) \exp\left[\frac{z_m F(\varphi(L,t) - \varphi_s(t))}{RT}\right]\right\}. \quad (9)$$

The equation for the rate of electron injection can be derived by analogy. In particular, assuming that the limiting stage involves transfer of an electron to the first layer of the polymer lattice adjacent to the substrate, the equation for the injection rate can be written as follows:

$$J_{im}(0,t) = -F\{\sigma_e[1 - \theta_R^f(0,t)] - \rho_e \theta_R^f(0,t)\}, \quad (10)$$

where $\theta_R^f(0,t)$ is the coverage of the first lattice layer with the reduced fragments. Here we assume the possibility of electron transfer within the layer only on fragments in the oxidised form and from fragments in the reduced form. This is taken into account in Eqn (10) by the factors $[1 - \theta_R^f(0,t)]$ and $\theta_R^f(0,t)$, respectively, Similarly to the film – solution interface, the situation at the interface in question could also be described using the Gouy model $\varphi_s(0,t) = E(t)$, where $E(t)$ and $\varphi_s(0,t)$ are respectively the electric potentials of the substrate and of the first layer of the film. However, equipotentiality of the substrate surface, which is due to high surface conductivity, points that here it is more appropriate to use the Stern model $[\varphi_s(0,t) \neq E(t)]$. With allowance for this fact and for the equilibrium form of the relation between θ_R^f and the coverage $\theta_R(0,t)$ at the interface between the diffuse layer adjacent to the substrate and the electrically neutral region of the film [at $z \approx 1/\kappa_f(0)$], we get

$$\frac{\theta_R^f(0,t)}{1 - \theta_R^f(0,t)} \approx \exp\left\{\frac{F[\varphi_s(0,t) - \varphi(0,t)]}{RT} + \right.$$
$$\left. + \alpha_0[\theta_R(0,t) - \theta_R^f(0,t)]\right\} \frac{\theta_R(0,t)}{1 - \theta_R(0,t)}. \quad (11)$$

It should be noted that, in particular, relationship (11) follows from the first equation of the system (2) at $j_{im} = 0$. Substituting the coverage $\theta_R^f(0,t)$ from Eqn (11) to Eqn (10) gives

$$J_{im}(0,t) = -F \exp\left\{\frac{\alpha F[\varphi_s(0,t) - E(t)]}{RT} - \alpha\alpha_0\theta_R^f(0,t)\right\} \times$$
$$\times \left\{\sigma_e^0 - \rho_e^0 \exp\left[\frac{F\{E(0,t) - \varphi(0,t)\}}{RT} + \alpha_0\theta_R(0,t)\right]\frac{\theta_R(0,t)}{1 - \theta_R(0,t)}\right\} \times$$
$$\times \left\{1 + k_e \exp\left[\frac{F\{\varphi_s(0,t) - \varphi(0,t)\}}{RT} + \right.\right.$$
$$\left.\left. + \alpha_0\{\theta_R(0,t) - \theta_R^f(0,t)\}\right]\frac{\theta_R(0,t)}{1 - \theta_R(0,t)}\right\}^{-1}. \quad (12)$$

As above, here $\varphi(0,t)$ is the potential at the end of the diffuse layer adjacent to the substrate; α is the transfer coefficient of electron injection into the film; and the constants σ_e^0 and ρ_e^0 are the pre-exponents in the expressions for the rate constants σ_e and ρ_e, respectively:

$$\sigma_e^0 = \sigma_e \exp\left\{\frac{-\alpha F[\varphi_s(0,t) - E(t)]}{RT} + \alpha\alpha_0\theta_R^f(0,t)\right\},$$

$$\rho_e^0 = \rho_e \exp\left\{\frac{\beta F[\varphi_s(0,t) - E(t)]}{RT} - \beta\alpha_0\theta_R^f(0,t)\right\},$$

and for the sum of the transfer coefficients one has $\alpha + \beta = 1$.

Under conditions for small-amplitude methods, Eqns (9) and (12) can be linearised with respect to small deviations of the concentrations $z_m\delta C_m = \delta C_R$ and potential, which leads to the following expressions for the fluxes $J_m(L,t)$ and $J_{im}(0,t)$:

$$J_m(L,t) = -\frac{I_m^0}{C_m^0}\delta C_m(L,t) - z_m F I_m^0 \frac{\delta[\varphi(L,t) - \varphi_s(t)]}{RT},$$
$$J_{im}(0,t) = \frac{\Lambda_0 z_m I_{im}^0}{C_R^0(1 - \theta_R^0)}\delta C_m(0,t) + F I_{im}^0 \frac{\delta[E(0,t) - \varphi(0,t)]}{RT}, \quad (13)$$

where $\Lambda_0 = 1 + \alpha_0\theta_R^0(1 - \theta_R^0)$, $\theta_R^0 = C_R^0/C$ is the equilibrium coverage and 'δ' on the left of a variable denotes its deviation from the equilibrium value. The densities of the exchange currents I_m^0 and I_{im}^0 in Eqn (13) are given by

$$I_m^0 = z_m F \sigma_m C_0 \exp\left\{\frac{-z_m F[\varphi_s(L) - \varphi_s]}{RT}\right\} =$$
$$= z_m F \rho_m C_m^0 \exp\left\{\frac{z_m F[\varphi(L) - \varphi_s(L)]}{RT}\right\},$$
$$I_{im}^0 = -F\sigma_e^0 \exp\left[\frac{\alpha F\{\varphi_s(0) - E\}}{RT} - \alpha\alpha_0\theta_R^0\right] \times \quad (14)$$

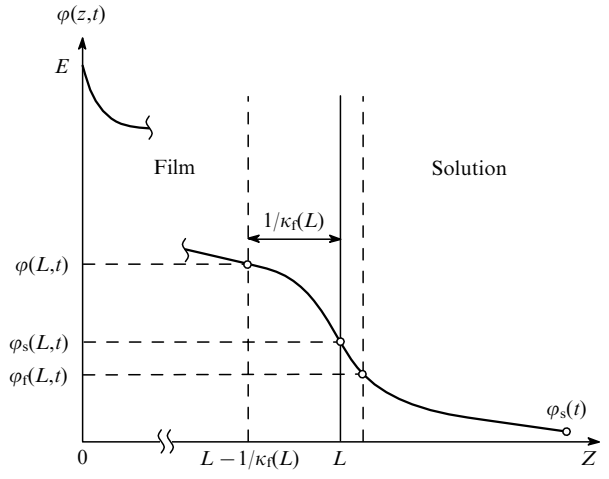


Figure 4. Schematic view of potential distribution $\varphi(z,t)$ in the vicinity of the film – solution interface.
$1/\kappa_f(L)$ is the thickness of the diffusion layer film adjacent to solution; for other notations, see text.

$$\times\left\{1+\exp\left[\frac{F\{\varphi_s(0)-\varphi(0)\}}{RT}+\alpha_0(\theta^0_R-\theta^f_R)\right]\frac{\theta^0_R}{1-\theta^0_R}\right\}^{-1}=$$
$$=-F\rho^0_e\exp\left[\frac{F\{\alpha\varphi_s(0)+\beta E-\varphi(0)\}}{RT}+\alpha_0\theta^0_R-\alpha\alpha_0\theta^f_R\right]\times$$
$$\times\frac{\theta^0_R}{1-\theta^0_R}\left\{1+\exp\left[\frac{F\{\varphi_s(0)-\varphi(0)\}}{RT}+\right.\right.$$
$$\left.\left.+\alpha_0(\theta^0_R-\theta^f_R)\right]\frac{\theta^0_R}{1-\theta^0_R}\right\}^{-1}, \quad (15)$$

where the superscript '0' denotes the equilibrium values of corresponding variables (this is also indicated by the absence of the symbol 'δ'); besides, for the equilibrium state of the system, which is assumed in derivation of Eqns (14) and (15), one has $\varphi(0)=\varphi(L)$ and $\varphi_s=0$.

Although the relations derived are in essence phenomenological (in the sense that they include the rate constants σ^0_e and ρ^0_e determined only from measurements), the dependences of the exchange currents on the electrode potential, E, and concentration, C_0, following from Eqns (14) and (15) can be checked experimentally. By comparing this type of theoretical dependences with experimental results it is possible to assess the correctness of the models used in processing of corresponding data. As an example, it is appropriate to analyse the simplest situation, *viz*., insignificance of short-range effects ($\alpha\approx 0$) and applicability of the Gouy model to the substrate–film interface. In this case one has $\varphi_s(0)=E$ and from two alternative definitions of the exchange current of electron injection (15) the expression follows:

$$\frac{\theta^0_R}{1-\theta^0_R}=\frac{\sigma^0_e}{\rho^0_e}\exp\left\{\frac{F[\varphi(0)-E]}{RT}\right\}, \quad (16)$$

where $\sigma^0_e/\rho^0_e=k_e$ apparently has the sense of the partition coefficient of electron between the film under study and the substrate. As should be expected, Eqn (16) follows from the first equation of the system (2) at j_{im} and α_0 equal to zero. Substituting Eqn (16) into Eqn (15) suggests that for this model of the film–substrate interface the exchange current I^0_{im} is independent of the electrode potential:

$$I^0_{im}=-F\sigma^0_e \text{ at } \varphi_s(0)=E \text{ and } \alpha_0\approx 0.$$

We can also make certain that the exchange current I^0_{im} depends on the potential E if the same interface can be described by the Stern model. The form of this dependence will be reported elsewhere. Seemingly, the possibility of deriving, in the framework of the model approach employed, relationships for other impedance parameters of the modified electrode, namely, the film interface capacitance, transference numbers for the diffuse layers and the asymmetry factors does not require special comments. We will only point to this possibility.

In describing the impedance of the systems considered by Vorotyntsev *et al.*[16,17] an important role was played by the choice of convenient variables to be analysed, namely, the charges

$$\delta q_s(k)=Fz_s\int_{1/k_f(k)}\delta c_s\mathrm{d}z$$

in the diffuse layers of the film [$1/k_f(k)$ is the thickness of the diffuse layer at the kth interface ($k=0, L$), $s=$ m, R is the index of the charge carriers under consideration]. A local change in the concentration of the sth sort of current carriers, $\delta c_s(z)$, due to application of an ac voltage, δE, to the system corresponded to the division [16,17] of the total concentration, C_s, of this sort of particles into two components, $C_s=\delta n_s+\delta c_s$. The first component corresponds to the concentration that fulfils the condition for local electrical neutrality, that is, $z_m\delta n_m(z)=\delta n_R(z)$, while the second component corresponds to the deviation of the concentration of these particles from the 'electrically neutral' value δn_s. Clearly, the second component differs from zero only within the bulk charge regions (diffuse layers of the film in the vicinity of the film–substrate and film–electrolyte solution interfaces). If we know the dependence of the charges $\delta q_s(k)$ in the diffuse layers on the increments of the concentration $\delta n_R(k,t)=z_m\delta n_m(k,t)$ and the potential jump in the kth diffuse layer $\delta\Delta\varphi(k)$, Eqns (2)–(6) can be solved correctly.[16,17] Eventually, this makes it possible to derive the expression for the impedance of the system under study. Without dwelling on details of the solution we will note that the $\delta q_s(k)$ values were determined[16,17] owing to the use of the Gibbs equation at the film interfaces

$$\mathrm{d}\sigma(k)=q(k)\mathrm{d}\delta\Delta\varphi(k)+\sum_{s=R}^{s=m}\Gamma_s(k)\mathrm{d}\mu_s(k).$$

Here, summation was performed over two components (electrons localised on the reduced fragments of the film and counterions) ignoring a possible contribution of solvent molecules incorporated into the film. Since, owing to the condition for electrical neutrality, the increments of the chemical potentials $\mathrm{d}\mu_s(k)$ are interrelated

$$\delta n_R(k)=z_m\delta n_m(k),$$

the tension $\sigma(k)$ (at the kth interface) depends on only two variables [$\delta\Delta\varphi(k)$ and $\delta n_R(k)$]. Based on the fact that the derivative $\partial^2\sigma(k)/\partial[\delta\Delta\varphi(k)]\partial[\delta n_R(k)]$ is independent of the order of differentiation with respect to the variables $\delta\Delta\varphi(k)$ and $\delta n_R(k)$, expressions relating the charges $\delta q_s(k)$ to the total charge increments $\delta q(k)=\delta q_m(k)+\delta q_R(k)$ and $\delta n_R(k)$ were obtained:[16,17]

$$\delta q_m(k)=\eta_m(k)\delta q(k)-C^{(k)}_f\left[\frac{\mathrm{d}\mu_m(k)}{z_mF}-\frac{(-1)^{z_m}\mathrm{d}\mu_R(k)}{F}\right],$$

$$\delta q_R(k)=\eta_R(k)\delta q(k)-C^{(k)}_f\left[\frac{\mathrm{d}\mu_m(k)}{z_mF}-\frac{(-1)^{z_m}\mathrm{d}\mu_R(k)}{F}\right].$$

Derivation of these relations requires the introduction of the (i) transference numbers for the diffuse layers [$\eta_m(k)$, $\eta_R(k)$] with respect to corresponding current carriers and (ii) asymmetry factor $C^{(k)}_f$, which are generally different for different film interfaces. The introduction of the $\eta_m(k)$ and $\eta_R(k)$ numbers is due to the necessity of taking into account the contributions of the $C_i(k)$ and $C_m(k)$ capacitors (see circuit in Fig. 3) to the resulting capacitance, $C(k)$, of the kth interface, whereas the factor $C^{(k)}_f$ describes the effect of the concentrations of both types of current carriers [at $z=1/\kappa_f(0)$ and $z=L-1/\kappa_f(L)$] on the charging of this interface. Since the sum of the transference numbers for the diffuse layers with respect to electrons and counterions equals unity [16,17] [$\eta_R(k)+\eta_m(k)=1$], the total number of phenomenological parameters for the description of each interface appears to be equal to four (with inclusion of the interface capacitance and exchange current for one or another stage of injection). This means that in the general case the overall expression for the impedance of a modified electrode

$$Z(\omega)=R_f+R_s+Z(0,\omega)+Z(L,\omega)+$$
$$+Z_f(t_m,D_{eff},\Lambda_0,\eta_m(k),C^{(k)}_f,C(k),I^0_{im},I^0_m,\omega) \quad (17)$$

should contain not only the parameters of transport in the bulk film, namely, t_m, D_{eff} and Λ_0 (where t_m is the transference number of counterions in the bulk film) but also additional eight parameters characterising the charging and injection at the film interfaces.

A salient feature of the impedance $Z(\omega)$ is as follows. Generally, the impedance is not an additive sum of the solution resistance R_s, instantaneous resistance of bulk film $R_f=RTL/\alpha F^2D_{eff}$, and the impedances of both interfaces:

$$Z(0,\omega)=\left[\frac{F|I^0_{im}|}{RT}+i\omega C(0)\right]^{-1}$$

and

$$Z(L,\omega) = \left[\frac{F|z_m I^0_m|}{RT} + i\omega C(L)\right]^{-1},$$

and the diffusion impedance of the bulk film. The impedance component Z_f in expression (17) includes cross-effects that characterise both the direct effect of the current carrier concentration gradients that appear in the bulk on the charging of the diffuse layers and the reverse effect of the charging of these layers on transport in the bulk film. The necessity of these effects apparently follows from relations (13), according to which the rate of charge carrier injection into the film is determined by not only the potential jump at the kth interface but also the concentration shifts $\delta C_m(k,t) = \delta n_m(k,t)$ at the boundaries of the electrically neutral bulk film adjacent to the diffuse layers. Only for the frequencies at which the reactive components of the interface impedances are small compared to the active components of the interface impedances

$$\frac{F|I^0_{im}|}{RT} \gg \omega C(0) \text{ and } \frac{F|z_m I^0_m|}{RT} \gg \omega C(L),$$

expression (17) is transformed into the following relationships

$$Z(\omega) = R_f + R_s + \frac{RT}{F|I^0_{im}|} + \frac{RT}{F|z_m I^0_m|} + \\ + \frac{(t^2_{im} + t^2_m)RT}{F^2 A(i\omega D_{eff})^{1/2}} \left\{\frac{\Lambda_0}{C^0_R(1-\theta^0_R)} + \frac{1}{z^2_m C_m}\right\}, \quad (18)$$

$$Z(\omega) = R_f + R_s + \frac{RT}{F|I^0_{im}|} + \frac{RT}{F|z_m I^0_m|} + \\ + (1 - 3t_m t_{im}) \left\{\frac{\Lambda_0}{C^0_R(1-\theta^0_R)} + \frac{1}{z^2_m C_m}\right\} \frac{LRT}{F,^2 A(3D_{eff})}, \quad (19)$$

for the limiting cases of high ($\omega L^2/D_{eff} \gg 1$) and low ($\omega L^2/D_{eff} \ll 1$) frequencies, respectively. Expressions for the Warburg impedance components follow from Eqns (18) and (19) and have the form

$$\mathrm{Re}Z_w(\omega) - \mathrm{Re}Z_w(\infty) = -\mathrm{Im}Z_w(\omega) = \frac{RT(t^2_{im} + t^2_m)}{C_{eff}F^2(2\omega D_{eff})^{1/2}}$$

at $\omega L^2/D_{eff} \gg 1$, where

$$\mathrm{Re}Z_W(\infty) = R_f + R_s + \frac{RT}{F|I^0_{im}|} + \frac{RT}{F|z_m I^0_m|};$$

$$C_{eff} = \left[\frac{\Lambda_0}{C^0_R(1-\theta^0_R)} + \frac{1}{C^0_m}\right]^{-1},$$

and for the low-frequency limiting imaginary component of the impedance

$$-\mathrm{Im}Z_w(\omega) = \frac{1}{\omega F^2 C_{eff} L} \quad \text{at} \quad \omega L^2/D_{eff} \ll 1.$$

They are most widely used in processing the data on the impedance of modified electrodes. In the Gabrielli model,[12] the components of the interface impedances ($RT/F|I^0_{im}|$ and $RT/F|z_m I^0_{im}|$) from relations (18) and (19) are in essence formally replaced by the impedance

$$Z(0,\omega) = \left\{\frac{F|I^0_{im}|}{RT} + i\omega C(0)\right\}^{-1}$$

and

$$Z(L,\omega) = \left\{\frac{F|I^0_{im}|}{RT} + i\omega C(L)\right\}^{-1},$$

respectively. From consideration of Refs 16 and 17 given above it is clear that this replacement as well as representation of the impedance by expressions (18) and (19) may appear to be quite incorrect. It should be noted again that in the framework of the model described all eight parameters (see above, except for the rate constants for injection σ^0_e and ρ^0_e) characterising the charging of the film interfaces can be expressed through the bulk film properties, electrode potential and electrolyte concentration. This was demonstrated above taking the injection rate as an example. As to calculations of other parameters, relations [16] between them and the electrode potential and electrolyte concentration exemplify the realisation of this possibility for a system consisting of two metallic electrodes and a binary electrolyte solution. Extension of these results to the modified electrode will be reported elsewhere. Here we can only mention that carrying out such an analysis (or similar analysis in the framework of other models) will indicate that only the parameters of charge transport in bulk polymer films should be taken into account.

IV. Experimental results on the impedance of modified electrodes

Among the best studied and at the same time simplest systems are inorganic redox polymer films, in particular, films based on various metal hexacyanoferrates. They belong to zeolite-type inorganic compounds with rigid crystal lattice and alkali metal cations can migrate into and out of the film structure. Since the lattice structure of such films has been well studied and the stoichiometry of corresponding compounds established reliably, they can be treated as convenient systems for experimental evaluation of the available concepts of charge transfer in electroactive polymer films.

The kinetics of electrode processes in Prussian blue (PB) films was studied by the EIS method.[50–54] The EIS spectra of the PB films deposited on a platinum substrate exhibited no high-frequency semicircle and the major portion of the spectrum corresponded to the Warburg diffusion impedance.[53,54] Analysis of the EIS spectra obtained in the framework of the homogeneous film model showed [53] that the model correctly describes diffusion-controlled charge transport in the film. It was established [53,54] that a decrease in the film thickness leads to shortening of the Warburg region $Z_d(\omega^{-1/2})$, however, as should be expected from theoretical predictions [see Eqn (18)], this is not accompanied by significant changes in the slope. The diffusion coefficients D_{eff}, calculated for the first redox process, namely, recharging of outer-sphere ions Fe^{3+}/Fe^{2+}, were found to depend on the nature of the cation of the bathing electrolyte and decreases in the order $K^+ > NH_4^+ > Cs^+$. It was also found that for both redox processes the plots of the diffusion coefficients *vs.* the initial potential of the PB film exhibit maxima near the formal potentials. This is consistent with the published data.[51]

At the highest frequencies, the impedance spectra of the PB films synthesised on an oxide ($SnO_2 + In_2O_3$) conducting substrate in 1 M KCl solutions exhibited semicircles characteristic of retarded interfacial charge transfer.[50–52] At lower frequencies, the Warburg impedance region was followed by a poorly pronounced initial part of the capacitive behaviour of the film. The resistance, R_{ct}, of 'thick' PB films (film thickness > 1 μm) reached a value of 3.3 Ω at the formal potential of the first redox process and was treated as the resistance of the electrode–film interface. This conclusion is consistent with the published data,[53,54] from which it follows that replacement of the oxide substrate by a platinum substrate should lead to disappearance of the semicircle in the spectrum. The coefficients of charge carrier diffusion in the film were calculated from analysis of the impedance response at medium frequencies [42] assuming that the PB film consists of two layers with different transport characteristics, namely, a compact inner layer and a more porous outer layer. It is believed [51,52] that the diffusion coefficients calculated for these layers (4.6×10^{-10} and 1.1×10^{-10} cm^2 s^{-1}, respectively) correspond to slow motion of counterions.

The EIS spectra of cobalt hexacyanoferrate (CoHCF) films on a platinum electrode exhibit a Warburg portion at high frequencies and the capacitive behaviour of the film at low frequencies.[55,56] Deviations from the major linear part of the Warburg plot at the highest frequencies were explained[56] by the bilayer character of the system comprising a relatively thin dense layer and a thicker porous layer.

The diffusion coefficients D_{eff} derived for the compact and porous layers from the slopes of the linear portions are respectively 2.4×10^{-12} and 1.1×10^{-11} cm^2 s^{-1} at $E = 0.4$ V and 8.4×10^{-11} and 3.7×10^{-10} cm^2 s^{-1} at $E = 0.8$ V. The higher diffusion coefficients at 0.8 V can be a consequence of different nature of the redox processes occurring at 0.8 and at 0.4 V. The diffusion coefficients of the CoHCF films are in reasonable agreement with the published data for PB films.

The effect of the substrate material on the high-frequency semicircle in the EIS spectra was also established in studies of indium hexacyanoferrate (InHCF) films in potassium nitrate solutions.[57–59] Replacement of platinum substrate by glassy carbon one as well as an increase in roughness of the platinum surface led to considerable increase in the charge transfer resistance R_{ct} (up to a factor of 7); however, the interfacial capacitance C_{dl} decreased to almost the same extent and the product, $R_{ct}C_{dl}$, remained nearly constant. Changes in the substrate roughness had no effect on the measured effective diffusion coefficient D_{eff}; hence, the bulk film structure is independent of the substrate material. Based on these facts, it was concluded that the process is controlled by charge transfer across the interface between the InHCF films and the support electrode.[58,59]

Another interpretation of the observed impedance spectra was reported[51] in a CV and EIS study of charge transfer on composite electrodes (geometric surface area of 0.2 cm^2) fabricated from a mixture of powdered copper hexacyanoferrate (CuHCF) and impregnated graphite. The EIS spectra of these electrodes exhibited a distorted semicircle which was considered as consisting of two components. The first of them, contributing largely to the high-frequency spectral region, was attributed to electron transfer in the bulk film. The electron diffusion coefficient was estimated from parameters of this component at $D_e = 0.1$ cm^2 s^{-1}. The high D_e value was treated as an indication of the semiconductor conductivity mechanism involving the valence band instead of conventionally assumed hopping mechanism of charge transfer.[60] The second semicircle was ascribed to slow injection of counterions (K^+ ions) into the metal hexacyanoferrate crystallites. However, then the authors of Ref. 60 made a conclusion about the hopping mechanism of charge transfer in the metal hexacyanoferrate crystallites and calculated $D_{eff} = 1.5\times10^{-9}$ cm^2 s^{-1} from the observed portion of the Warburg impedance. Large difference between the D_e and D_{eff} values indicates a slow diffusion of counterions in the metal hexacyanoferrate crystallites.

The charge transfer resistances R_{ct}, determined from the high-frequency semicircle in the impedance spectrum of poly-[$NiMe_2$Salen] films in 0.1 M solutions of tetraethylammonium tetrafluoroborate in acetonitrile, were ascribed to the film–electrolyte solution interface.[52] The R_{ct} values were almost independent of the potential in the region of electrical activity of the film (0.8–1.1 V). Analysis of the impedance spectra at medium and low frequencies permitted the determination of the low-frequency capacitance C_{lf} and the effective diffusion coefficient D_{eff}. The D_{eff} values calculated from the slopes of the Warburg portions of the spectrum using the relationships for the homogeneous film model ($\approx 3\times10^{-7}$ cm^2 s^{-1}) are about two orders of magnitude higher than the D_{eff} value found from the CV current peaks using the Randles–Sevcik equation.[61] It was assumed that this discrepancy is mainly due to the neglect of the short-range forces between film fragments in the calculations using the Randles–Sevcik equation. The observed large half-width of CV peaks points that this effect, which corresponds to large positive values of the attraction constant α_0 [see the system of equations (2)], should also be taken into account.

Among conducting polymers with conjugated bonds, polypyrrole, polythiophene and substituted polythiophene films exhibit a relatively simple electrochemical behaviour. When using non-aqueous solvents, these systems are free from problems that are due to protonation effects and certain redox processes, which is characteristic of, *e.g.*, polyaniline-based polymers.

In most cases the impedance of such systems can to a first approximation be correctly described by the circuit shown in Fig. 2*a*. A similar spectral pattern or certain characteristic parts of the spectrum were found for polypyrrole and its derivatives[6,62–74] and for polythiophene-based polymers.[13,75–93] For instance, the high-frequency semicircle (usually, it is distorted and more correctly, suppressed) and an extended (with respect to frequencies) capacitive response were observed for polypyrrole films on various substrates in solutions of $LiClO_4$ in propylene carbonate[69–73] and in aqueous KCl solutions.[6,74] Similar parts in the impedance spectra were observed for polythiophene derivatives, namely, poly(3-methylthiophene) (PMT),[75–79,85,86] poly(3-octylthiophene) (POT),[80,84,87] poly(3,4-ethylenedioxythiophene)[90–93] and some other compounds.[88,89] It was also reported that the impedance spectra of the reduced or weakly oxidised forms of polythiophenes exhibit not only the high-frequency semicircle regions and low-frequency capacitive responses at medium frequencies but also parts corresponding to the Warburg impedance with slopes approaching unity.[82,83,87] The high-frequency semicircle was most pronounced for little doped polypyrrole.[70,74] The presence of the high-frequency semicircle and noticeable capacitive response was also reported[71] for polypyrrole, poly(3,6-dioxyheptylpyrrole) and poly(3-methylthiophene) films in 1 M $LiClO_4$ solutions in propylene carbonate [for poly(3-methylthiophene) and for solid electrolytes based on poly(ethylene oxide), $(PEO)_{20}LiClO_4$].

Thus, the impedance spectra of polypyrrole- and polythiophene-based polymer films exhibit characteristic portions with well-separated frequency regions corresponding to the kinetics of different stages of charge transfer. This points to common nature of electrode processes in these polymers. Now we will dwell on the results obtained for particular systems in which the impedance parameters were analysed systematically.

From the impedance measurements of polypyrrole films at specified constant frequencies ($f > 10$ Hz) it was found[62] that the plots of the film capacitance, C_p, and conductivity, $1/R_p$, *vs* potential have maxima at the formal potential [$E = (E_{p,k} + E_{p,a})/2$]. Analysis of the frequency dependences of these parameters suggested[62] that polypyrrole behaves as a porous material whose resistance is mainly due to the resistance of the electrolyte filling its pores. High film capacitances (a few mF cm^{-2}) were attributed to the double layer capacitance of the developed inner surface of the polymer. It should be noted that in most studies[65–68] on polypyrrole it was concluded that in the conducting state the rate of charge transfer in the polypyrrole film is controlled by the diffusion of ClO_4^- anions.

Typical impedance spectra exhibiting three noticeable regions (capacitive, Warburg and high-frequency semicircle) were observed for polypyrrole films in various aqueous electrolyte solutions.[70] Using these data, the electron diffusion coefficient for polypyrrole films was calculated, $D_e \approx 10^{-3}$ cm^2 s^{-1}. It was found[62] that the ion diffusion coefficient D_m for the film ($L = 15$ μm) strongly depends on the nature of the anion in the electrolyte, namely, $D_m = 2.5\times10^{-6}$ (Cl^-), 6.2×10^{-7} (ClO_4^-), 8.2×10^{-8} (SO_4^{2-}) and $\sim1\times10^{-9}$ cm^2 s^{-1} (tosylate ion) and weakly depends on the nature of the cation in the electrolyte (H^+, Na^+, Me_4N^+). Particular attention was given[63,64] to analysis of the capacitive regions of the impedance spectra of polypyrrole films. An attempt was made to separate the contributions of the capacitive and Faradaic currents to the overall impedance response. The capacitive component was attributed to the charging of the double layer at the film interface and the Faradaic component was attributed to the incorporation of the dopant anions, ClO_4^-, into compact film fragments.

The impedance spectra of polythiophene films were analysed as functions of the potential and film thickness for asymmetric configuration of the metal – polymer – solution system characteristic of modified electrode and for symmetric configuration (metal – polymer – metal) using air-dry film.[13] The high-frequency semicircle in the spectrum obtained for the asymmetric configuration and the derived parameters of the *RC*-circuit ($R_{ct} \approx 30\ \Omega\ cm^2$ and $C_{dl} \approx 1-5\ \mu F\ cm^{-2}$) were ascribed to the film interface. However, strictly speaking, no experimental facts for identification of this interface (substrate or solution) are available. The calculated[13] diffusion coefficient D_- attributed to the motion of ClO_4^- anions in the film were of the order of $(0.05-1.2)\times10^{-12}\ cm^2\ s^{-1}$. The D_- value increased almost linearly with an increase in the polythiophene film thickness from 0.1 to 1.6 μm, which suggested an inhomogeneous film structure (in particular, formation of a more porous structure with an increase in the film thickness). The diffusion coefficients D_- were calculated with inclusion of the relations for the Warburg constant that follow from the classical electrochemistry. As was shown in a number of studies, these relations require redefinition of parameters which have a more complex sense in the case of modified electrode. Probably, so low D_- values are due to the calculation procedure employed, being not reliable.

The system platinum electrode – PMT film in a 0.2 M $LiClO_4$ solution in MeCN was studied by the electrochemical impedance method.[75] It was established that the impedance spectra of the films of the reduced form of PMT exhibit a semicircle which is gradually transformed into the capacitive response of the film as the frequency decreases. On going to the oxidised form of PMT the diameter of the semicircle noticeably decreases; the charge transfer resistance R_{ct} derived from the diameter of the semicircle was about 15 – 20 $\Omega\ cm^2$. This R_{ct} value was attributed to the bulk polymer resistance assuming the major contributions of the conductivity of the electrolyte in pores of the polymer for the oxidised form of the PMT film and the electron conductivity for the reduced form of the PMT film. However, this assumption was unsubstantiated.[75] The diffuse part of the spectrum, which is usually characterised by a unity slope of the $Z_{Re}(Z_{Im})$ plot, was almost not observed. At the same time, data analysis allowed the authors to find the diffusion impedance component and to determine the coefficient of charge carrier diffusion in the film (D varied from 1.5×10^{-14} to $1\times10^{-12}\ cm^2\ s^{-1}$), which was attrributed to diffusion of the dopant ions in the film. The lowest D values were obtained for thin (about 20 nm) polymer films. Since the coefficient D characterises diffusion of ions both in the compact polymer and in pores, the fact[75] that D values are independent of film thickness indicates that the average size of dense domains (aggregates) and the average pore size behave analogously. It should be noted that very low values of diffusion coefficients[75] are inconsistent with the assumptions of high film porosity and corresponding capacitive response. Besides, at such D values one would observe a large contribution of the diffusion resistance of the film; however, the impedance spectra in the frequency range 10^4-10^{-3} Hz exhibited no Warburg response with a characteristic linear dependence with a slope approaching unity (see above).

The impedance of PMT films was also measured in 0.1 M $NBu^n_4PF_6$ solution in propylene carbonate[77] and in 0.05 – 0.5 M $LiClO_4$ solutions in acetonitrile.[86] Strongly suppressed, poorly pronounced high-frequency semicircles were observed in both cases. The mid-frequency parts of the spectra exhibited some indications of the Warburg impedance and transformed into abruptly rising curves associated with the capacitive response of the films. The charge transfer resistance determined from the diameter of the semicircle (30 – 60 $\Omega\ cm^2$) was attributed to the film – electrolyte solution interface.[77] The estimates of the coefficients of charge carrier diffusion obtained from direct measurements of the electron and ionic components of the conductivity of the PMT film are $D_e = 5.6\times10^{-3}$ and $D_i = 1.6\times10^{-9}\ cm^2\ s^{-1}$. Thus, from the results obtained it follows that the mobilities of electrons and counterions (PF_6^-) in the polymer phase differ by a factor of 10^6 and the overall charge transfer is controlled by the diffusion of counterions in bulk polymer. The dependence[69] of the impedance parameters on the PMT film thickness was explained with allowance for the porous structure of the polymer films. It should be noted that, in spite of considering a porous film, the authors[77] reported the possibility of interpreting the same results in the framework of the homogeneous film model. However, parameters obtained in such a fashion have different physical meaning.

It was found[86] that the high-frequency semicircle in the spectrum becomes more pronounced as the $LiClO_4$ concentration decreases by an order of magnitude; the diameter of the semicircle increases by about a factor of four. The authors[86] concluded that the appearance of the semicircle in the EIS spectra is due to predominant contribution of the impedance of the film – electrolyte solution interface in this frequency range. Slow charge transfer at this interface seems to be due to partial desolvation of dopant anions (ClO_4^-) during incorporation of these ions into the polymer matrix. This conclusion was confirmed by the results obtained in a study[94] on the effect of solvent viscosity and the size of the solvent molecules on the reversibility of the oxidation of poly(3,4-ethylenedioxythiophene) films. Seemingly, yet another argument in favour of this assignment is provided by a decrease in the resistance R_{ct} with an increase in the film thickness; here one can assume that the outer surface of the film becomes looser (see above). A decrease in R_{ct} with an increase in the electrode potential was explained[86] by additional solvation of the polymer molecules upon swelling of the film, which leads to a decrease in the energy barrier to incorporation of the dopant anions into the film. The effective diffusion coefficients, D_{eff}, of PMT films calculated using the homogeneous film model were almost independent of the potential in the range 0.6 – 1.2 V [$D_{eff} = (1.3-2.3)\times10^{-7}\ cm^2\ s^{-1}$].

Impedance measurements of PMT films deposited on platinum in aqueous electrolyte solutions containing different anions were reported.[78] It was concluded that the charge transfer resistance at the film – solution interface contributes largely to the measured impedance. The overall patterns of the impedance spectra of PMT films were also reported;[80,81] however, here the authors made only qualitative conclusions about the appearance of incomplete high-frequency semicircle and low-frequency pseudocapacitive response.

Significantly different impedance spectra of the neutral and oxidised forms of POT were obtained with the Pt/POT-electrode immersed in a 0.1 M solution of $LiBF_4$ in propylene carbonate.[82–84] The spectra of the neutral form of POT (at potentials $E = 0.0-0.7$ V) exhibited a semicircle corresponding to a rather high resistance R_{ct} (about 30 kΩ). The impedance spectrum of the neutral form of POT was explained[82] by the effects of the double layer with $C_{dl} = 2\ \mu F\ cm^{-2}$, which was attributed to the polymer – electrolyte solution interface. For the doped (oxidised) form of POT (at $E = 0.8-1.2$ V) the semicircle becomes more pronounced and its diameter considerably decreases as the degree of film oxidation increases, namely, R_{ct} decreases to 980 – 790 Ω at a potential of 1.2 V. As the potential changes in the range 0.8 – 1.2 V, the capacitance C_{dl} increased by nearly a factor of 1.5 (from 2.8 to 4 $\mu F\ cm^{-2}$) and the low-frequency capacitance C_{lf} changed from 0.76 to 4.1 $mF\ cm^{-2}$. The coefficients of charge carrier diffusion, determined at different oxidation states of the POT film lie in the range $(1-8)\times10^{-8}\ cm^2\ s^{-1}$. Similar measurements for poly(3-octylthiopene) films were carried out in solutions of lithium perchlorate in acetonitrile.[86,87] The pattern of the impedance spectra is consistent with the data obtained for solutions of $LiBF_4$ in propylene carbonate. Three characteristic spectral features were revealed, *viz*., the high-frequency semicircle, the transient spectral region and an abrupt increase in the imaginary impedance component, $-Z_{Im}$, with a decrease in frequency. As the degree of film oxidation increases, the diameter of the semicircle and the transient region at medium frequencies

decreases appreciably (for the neutral form of the polymer, the transient region exhibits the properties of the Warburg impedance). The diffusion impedance components are particularly pronounced when analysing the data in the $-Z_{Im}$, $Z_{Re}-f^{-0.5}$ coordinates. This analysis reveals parallel linear regions indicating diffusion-controlled charge transfer in the film. The diffusion coefficients, which apparently should be associated with the diffusion of counterions (ClO_4^-), depend on the potential and are as follows:

E/V	0.8	0.9	1.0	1.1	1.2
$10^7 D$ /cm^2 s^{-1}	0.29	0.68	1.5	6.3	17

Similar values of the diffusion coefficient of BF_4^- ions ($D_{eff} = 8 \times 10^{-9}$ cm^2 s^{-1} for the potential of the anodic maximum in CV) were reported for POT films.[82]

In contrast to the spectra considered above, in most cases the impedance spectra of polyaniline films and films based on polyaniline derivatives, *e.g.*, poly(*o*-phenylenediamine) (PPD) and poly(*o*-aminophenol) (PAP), have a more complex shape. This manifests itself in the absence of well-defined spectral regions which could be associated with particular processes. In other words, the impedance spectra of these systems cannot be described by simple theoretical relations.

The impedance of polyaniline films was studied in hydrochloric acid.[95] The dependences of the capacitance and conductivity on the potential measured at a constant frequency of 10 Hz exhibit maxima in the region of electrical activity of the film. The authors [96] reported a thorough analysis of the published data [95] and concluded that the properties of the polyaniline film can be explained with allowance for the porous film structure.

Based on the IR spectroscopy and quartz microbalance data for PPD and PAP films, it was established [89,90] that the electrode process in acid aqueous solutions involves hydrogen ions as charge-compensating ions. In contrast to the processes in polyaniline, here anions are involved in the electrode process to a much lesser extent, although some researchers intensively elaborate anion-related concepts.

The EIS spectra of PPD films exhibit a region corresponding to the Warburg impedance and a poorly pronounced low-frequency capacitive response.[97] Analysis of the impedance spectra and estimation of parameters of the processes were carried out in the framework of the homogeneous film model. It was established that the low-frequency capacitance is proportional to the film thickness and the maximum capacitance is reached at the formal potential of the polymer. A minimum of the Warburg constant and the maximum width of the Warburg impedance region were also observed near the formal potential.

The effective diffusion coefficients are of the order of $(1-10) \times 10^{-8}$ cm^2 s^{-1} depending on the film potential.[97] It was concluded that charge transfer is controlled by electron 'diffusion' and the 'electron diffusion coefficient' D was estimated at $D_e = 2 \times 10^{-9}$ cm^2 s^{-1}. At the same time it was reported that the model used is irrelevant to specific features of the processes occurring in the polymer, in particular, to protonation of the redox centers in the film.

A solution study [98] of the impedance spectra of PPD film on glassy carbon in a broad range of pH values allowed the dependence of the film parameters on the concentration of hydrogen ions to be analysed in detail. It was found that at low pH values the impedance spectra were slightly different from the published spectra[97,99] and a high-frequency semicircle appeared in the spectra at pH > 4. The key parameters, *viz.*, interfacial charge transfer resistance R_{ct}, low-frequency capacitance C_{lf} and the effective diffusion coefficient D_{eff} were determined [98] using relations for the homogeneous film impedance. It was established that the capacitance C_{lf} and diffusion coefficient D_{eff} depend on potential and reach maximal values near the formal potential.

An increase in D_{eff} with a decrease in pH value was treated as an indication of the fact that electron transfer is accompanied by intermolecular proton transfer and the shape of this dependence was explained by an increase in the rate constant for homogeneous electron transfer upon protonation of the polymer.

The electrochemical properties of PPD films in solutions of different anionic compositions at different pH values were also studied.[99] The impedance spectra of the PPD films exhibited a 'non-classical' shape, which was probably due to similar values of the characteristic relaxation frequencies corresponding to diffusion and pseudocapacitive charging of the film.

To describe these EIS spectra, the equivalent circuit (see Fig. 2 *a*) was modified [99] by introducing an additional capacitance and a CPE element responsible for occurrence of certain reactions with solution components and for structural features of the film (namely, film porosity). Finally, processing of the spectra gave dependences of the effective diffusion coefficient D_{eff} on the potential E for PPD films. The D_{eff} values calculated using any of the three models employed by the authors vary by several orders of magnitude as the electrode potential increases by 400 mV. These changes in D_{eff} values were explained by strong interaction between electroactive centres in the polymer and counterions.

Analysis of the EIS spectra of PPD films was continued in the next study [46] reported by the same authors. To describe the EIS spectra, they elaborated a new model with inclusion of diffusion and migration of three charge carriers (proton, electron and anion) in bulk film. Expressions for the impedance were derived with allowance for the effects of two interfaces (electrode – film and film – solution). The equivalent circuit proposed for this model is shown in Fig. 5.

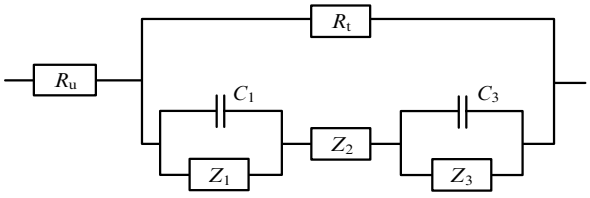


Figure 5. Equivalent circuit of PPD films.[46]
Z_1 and Z_3 are the impedances of the interfaces; Z_2 is the bulk film impedance; C_1 and C_3 are the capacitances of the interfaces; R_t is the shunt resistance responsible for charge leakage; and R_u is the solution resistance.

Among quantitative results obtained,[46] the diffusion coefficients and the double layer capacitances deserve particular attention. Despite the fact that the diffusion coefficients vary by several orders of magnitude as the potential changes (this is similar to study [99]), no comments were made. The interfacial capacitances ($C_1 = 80-200$ and $C_3 = 300-450$ μF cm^{-2}) exceed conventional values of the double layer capacitances. A possible explanation for this anomaly for the metal – film interface (C_1) is provided by roughness of the electrode surface, *i.e.*, larger actual surface area compared to the geometric surface area. However, the effect of adsorptive capacitance on C_1 and C_3 seems to be a more probable explanation.

Analysis of the results obtained in this study revealed some difficulties faced by the authors in constructing their own, 'improved' models of charge transfer in order to describe complex, 'non-classical' impedance spectra with poorly separated frequency regions corresponding to a certain process. As a rule, mathematical formalism employed is rather complicated and includes parameters that are often difficult to compare with real characteristics of the system under study. Besides, a large number of such parameters complicates processing of experimental data, which forces the authors to essentially simplify their models in order to decrease the number of independent variables. Sometimes, this leads to paradoxical consequences as in, *e.g.*, the study considered above. Having elaborated a rather complex model of

charge transfer involving three different current carriers, in processing experimental data the authors had to reduce the number of particles to two, thus returning, in essence, to the well-known formalism.

Dispersion of the low-frequency capacitance, which is characteristic of the impedance spectra of PPD films was investigated.[100, 101] The authors concluded that this phenomenon is due to inhomogeneity of the polymer surface, whereas the surface structure of the conducting substrate and the binding of counterions in the film have no effect on the dispersion of the low-frequency capacitance. This is inconsistent with theoretical consequences reported in other studies,[72, 73] according to which one should observe a noticeable effect of the binding of counterions on the low-frequency capacitance.

Poly(*o*-aminophenol) is one of the nearest analogues of PPD. As in the case of PPD films, studies of PAP films were accompanied by debates concerning the nature of counterions involved in the electrode process. Although a significant role of protons in charge transfer in these films is undoubtful,[102–104] the authors of some studies (see, *e.g.*, Ref. 105) consider the involvement of anions of the bathing electrolyte as counterions. Nevertheless, the scheme [102, 103] involving hydrogen ions as counterions should be considered as the most probable scheme of the redox processes occurring in such films.

The apparent diffusion coefficients of $(3.6 \pm 0.4) \times 10^{-10}$ and $(5.5 \pm 0.3) \times 10^{-10}$ cm^2 s^{-1} for the anodic and cathodic processes, respectively, are two orders of magnitude lower than the values obtained by the same authors for PPD.[102]

PAP films were studied by the EIS method.[106] The EIS spectra were processed using the homogeneous film model.[12] The spectra obtained exhibited the high-frequency semicircle and a characteristic region corresponding to the low-frequency capacitance of the polymer. The following parameters of the semicircle were determined: the electrolyte resistance R_u (2.8 ± 0.5 Ω) and the charge transfer resistance θ attributed to the bulk film. Then the standard rate constant for charge transfer $k_{s,h} = (2.3 \pm 0.4) \times 10^{-6}$ cm s^{-1} and the double layer capacitance $C_{dl} = (8 \pm 2) \times 10^{-6}$ F cm^2 were calculated. By analysing the pseudocapacitive spectral region the low-frequency capacitance, C_{lf}, of the polymer and the effective diffusion coefficient D_{eff} were determined. The latter parameter was almost independent of the potential and equal to 1.3×10^{-11} cm^2 s^{-1}, which, similarly to Ref. 102, is two orders of magnitude lower than the values obtained by the same method for PPD.[97, 98] In spite of apparent simplicity and reliability of this 'classical' approach to processing of the EIS spectra, it casts some doubt when comparing the results obtained in different studies. For instance, the same authors studied [107] the dependence of charge transfer parameters in PAP films on the film thickness and ionic strength of the bathing electrolyte solution; the diffusion coefficients obtained under identical experimental conditions differed from the published data [106] by an order of magnitude. Even higher diffusion coefficients (10^{-8} cm^2 s^{-1}) were obtained [108] for PPD using the equations of the Mathias and Haas model.[11] In spite of different compositions of the bathing electrolytes used [98–100] such a large discrepancy between the diffusion coefficients is hard to explain.

Unlike the Inzelt model, the charge transfer model developed in order to describe the EIS spectra of PAP[109] represents an attempt to allow for the effect of protonation on the EIS spectra. This model was based on the Gabrielli model [12] with inclusion of slow protonation in order to explain a strong effect of the pH values on the electrochemical properties of PAP and related polymers. The authors assumed that the proton concentration in the film is constant in time and independent of the electrode potential. Therefore, the distribution coefficient K_p was introduced, which determines the ratio of the concentrations of hydrogen ions in the film and in solution ($[H^+]_{film} = K_p \times [H^+]_{sol}$). Representing the reactions in the polymer by two consecutive stages (protonation and the redox process itself)

$$O + [H^+]_{film} = HO^+,$$

$$HO^+ + e^- = OH,$$

and assuming that the kinetics of the second stage at the electrode–film interface obeys the Butler–Volmer equation, the authors derived the final expression for the film impedance. Using this approach, experimental data were fitted quite correctly, reasonable values of diffusion coefficients were established (2.2×10^{-10} and 0.53×10^{-10} cm^2 s^{-1} for pH values of 1 and 2, respectively) and the acidity constant K_a for the oxidised form of the polymer ($pK_a = 2.93$), consistent with the expected value for deprotonation of the amino group of polyaniline, was determined.[110]

It should be noted that the assumption of constant concentration of hydrogen ions in the film seems to be somewhat incorrect, because in this model protons are counterions and maintain electrical neutrality of the entire film. Mention should be made, also concerning other studies, that the results of approximation using different models for the same systems under study and similar experimental data often provide good agreement between experiment and theory. However, the physical meaning of the parameters obtained is often ambiguous.

The role of porosity in the charging of conducting polymer films has long been discussed in the context of the 'faradaic' and 'capacitive' components of the overall current.[103–111] A number of methods for experimental separation of these contributions were proposed. Among them, the most important is spectroelectrochemical study of conducting polymer films in the UV and visible spectral regions.[111–118] It was assumed that the capacitive current can be determined based on electrochemical measurements carried out along with optical spectral measurements, which contain information on changes in the concentration of the redox species (polarons, *etc.*) in bulk film. However, as was established to date, such a separation is impossible, because the surface and bulk film charging processes occur involving species of the same chemical nature. Therefore, the problem of interpreting the capacitive response is still to be solved.

Recently, spectroelectrochemical studies of conducting polymer films have been widely used to elucidate the nature of quasiparticles generated in films and the mechanism of the redox processes.[119, 120]

When analysing the experimentally determined low-frequency capacitance C_{lf} of electroactive polymer films in the region of redox activity, in most cases C_{lf} is a parabolic function of the potential E with a maximum at an oxidation state θ of about 0.5. This is associated with the maximum value of the product of the concentrations of the oxidised and reduced fragments in the polymer near the formal potential. The experimentally observed dependence of C_{lf} on potential is in qualitative agreement with the theoretical ratio for the low-frequency capacitance, which follows from the homogeneous film model,

$$C_{lf} = \frac{AF^2L}{RT}\left\{\frac{1 + \alpha_0\theta_R^0(1-\theta_R^0)}{C_R^0(1-\theta_R^0)} + \frac{1}{z_m^2 C_m^0}\right\}^{-1}.$$

The C_{lf}–E curve calculated [87] for poly(3-octylthiophene) films is in good agreement with the experimental curve assuming a value of 6.8 for the fitting coefficient (interaction parameter α_0). According to the definition of the parameter α_0, its sign and magnitude indicate a repulsive interaction between redox fragments in the film, with a rather high interaction energy. Similar character of the approximation of the experimental C_{lf}–E curve was established for PPD films.[97] Possible reasons for significant differences between theoretical and experimental curves include structural-chemical inhomogeneity of films leading to dispersion of the formal redox potentials and film swelling effects; both of them are ignored in the homogeneous film model.[87] It seems that these factors affecting the low-frequency capacitance cannot be formally 'included' by the fitting parameter of the model, α_0.

An important feature of the capacitance C_{lf} experimentally observed for certain electroactive polymer films is the frequency dependence of this parameter. Up to now the nature of the frequency dispersion of the capacitance C_{lf} is a debated topic. Considerable attention to this issue was paid by Bisquert *et al.*[72, 73, 121, 122] who reported detailed analysis [72, 73] of the dependence of the low-frequency capacitance on the thickness of polypyrrole film and on the potential. The frequency dispersion of capacitance was explained [73] by film porosity and the experimental data were treated in the framework of the modified Albery model for charge transmission lines. However, from this analysis it follows that the specific low-frequency capacitance $C = C_{lf}/L = 100-200$ F cm^{-3} is almost independent of film thickness. This points to a linear dependence of C_{lf} on the film thickness and, with allowance for the available data on noticeable changes in the morphology of polypyrrole films with an increase in the film thickness, suggests the volume character of the film charging rather than formation of charged double layers on the large inner surface of the porous film. In this case the dispersion of capacitance was associated [73] with effects of diffusion length (pore size and polymer grain size) distribution for charge carriers over the bulk polymer and with the binding of counterions in the film.

The data obtained in the impedance studies [58, 59] of indium hexacyanoferrate films are of interest in the context of the problem of dispersion of the low-frequency capacitance. It was found that for potassium nitrate solutions the capacitive response fits well by a linear dependence of $-Z_{Im}$ on ω^{-1}, whereas a considerable change in the slope $\partial(-Z_{Im})/\partial(\omega^{-1})$ with frequency was observed for lithium nitrate solutions. These results were explained [59] by the binding of lithium ions to negatively charged film lattice fragments. The absence of dispersion of the capacitance of the InHCF film in the case of K^+-containing solutions points that most of potassium ions in these films are in free state. As to the Li^+-containing solutions, it seems likely that the contributions of the free and bound forms of counterions vary with frequency, thus being responsible for the observed frequency dependence of C_{lf}.

V. Conclusion

Analysis of electrochemical aspects of research on modified electrodes reveals that specific features of charge transfer in these systems due to mixed electron-ionic conductivity have, in principle, become understandable. Experiments showed that a large number of systems exhibit such features as simultaneous appearance of high-frequency semicircles and the presence of diffusion portions (Warburg impedance) in the EIS spectra and the absence of dispersion of the low-frequency capacitance, *i.e.*, behaves consistently with the homogeneous film model. However, quantitative agreement between experiment and theory is a long way in the future. The case in point consists in *a priori* uncertainty of the extent to which the charge transport parameters obtained correspond to real processes (in particular, processes at polymer film interfaces) rather than possible errors in determinations, which are usually performed using the simplified theory of homogeneous film impedance by Mathias and Haas. Therefore, the development of the theory of injection of current carriers into films and obtaining relevant experimental data are topical problems of investigations in the field of charge transport in modified electrodes.

A recent trend towards allowance for the structure of real polymer films and film morphology effects on the electrochemical properties indicates a new step in research on modified electrodes. Researchers have been refining their understanding of such systems. In this connection not only the problems considered above but also construction of correct models with inclusion of the film structure and their experimental evaluation seem to be important. And, as earlier, search for novel systems based on electroactive polymer films and fulfilling practical demands remains a task of paramount importance.

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