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REVIEW PAPER

SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF POLYPYRROLE, POLYANILINE AND POLY–3–METHYL THIOPHENE

In this article, the results of a study of the electrochemical polymerization of pyrrole and the chemical polymerization of pyrrole, aniline and 3–methyl thiophene initiated by FeCl$_3$ are presented. The electrochemical properties of the synthesized electron conducting polymers (polypyrrole, polyaniline and poly 3–methyl thiophene) were measured. A new reactor for the synthesis of polypyrrole at a constant initiator concentration – K$_3$Fe(CN)$_6$ – was developed and for the first time corresponding constants of the pyrrole polymerization reaction were determined. It has been proved that polypyrrole and polyaniline can be used as electrode materials for positive electrodes in lithium rechargeable power sources and that thin layers of these polymers can be successfully applied for the corrosion protection of iron.

In recent years considerable attention has been dedicated to the study of synthesis, structure and properties of conducting polymers [1–4]. The interest in conducting polymers has significantly increased since 1987, when their application in a variety of important technological sectors commenced, i.e. rechargeable batteries (1987), conductive coatings for textile (1990), plating bath for Cu deposition and printed circuit boards (1990), electrolytic capacitors (1991), conducting films (1991), antistatic electronic component carriers (1992), high capacity (4 Mb) magnetic disks (1992), camouflage coverings (1991), emitting diodes (1994), solid state lasers (1995), solar cell elements and corrosion protection of iron (1996) [1, 2, 5, 6].

Among conducting polymers, polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives have attracted attention mainly because of their higher chemical and thermal stabilities compared to those of other conducting polymers, such as polyacetylene, polyphenylene, etc..

PPy, PANI and PTh in the doped state can be obtained directly by electrochemical and chemical oxidative polymerization of pyrrole (Py), aniline (ANI) and thiophene (Th), respectively, or by subsequent treatment of the synthesized polymers with dopants [4].

Electrochemically PPy, PANI and PTh can be prepared in the shape of freestanding, insoluble films of high conductivity (several hundreds of Scm^{-1}), possessing good mechanical properties and environmental stability [7]. Electropolymerization of Py in a matrix of another polymer (such as PVC, PVA, etc.) yields a conductive alloy film, which has stronger mechanical properties due to the polymer matrix but has lost some of the conductivity of pure PPy. The disadvantage of the electrochemical method is the very small degree of utilization of Py and electrolyte (which serves as a counter ion source) of only a few percents [7].

Chemically prepared PPy, PANI and PTh are in the form of an insoluble black powder of somewhat lower conductivity (several tens of Scm^{-1}) [8]. The advantage of the chemical synthesis is that it is usually performed in water to a very high yield (40–80 wt%). PPy properties can be modified by chemical synthesis of PPy both on a somewhat swollen surface of another polymer (e.g. PMMA) and in the pores of macroporous membranes. In the first case, thin films of PPy of rather high conductivities are obtained and in the second, electrically conducting composites having high conductivities ($10^{-2} - 10^{-1}$ Scm^{-1}) are produced [9].

In this article, results of a study of the electrochemical and chemical oxidative polymerization of Py, ANI and 3–methyl thiophene (3–MeTh), as well as of the application of the synthesized conducting polymers as electrode material in lithium rechargeable cells and for the corrosion protection of iron are presented. These results have been obtained by intensively studying conducting polymers during the previous ten years at the Department of Physical Chemistry and Electrochemistry at the Faculty of Technology and Metallurgy in Belgrade.

EXPERIMENTAL

In the electrochemical synthesis, PPy films were deposited galvanostatically on a Pt foil by the anodic oxidation of Py from a degassed and slowly agitated reaction mixture. The experiments were performed in a three–compartment cell having a Pt wire counter electrode and a Ag/AgCl reference electrode. Propylene carbonate (PC) and acetonitrile (AN), were used as solvents and LiClO$_4$ and different organic salts were used as electrolytes. The purification of the solvents, Py and the electrolyte salts, as well as the preparation of some electrolyte salts, have been described in a previous paper [10].

The chemical oxidative polymerization of Py, ANI and 3–MeTh was performed in a standard reactor equip-

ped with a stirrer and a reflux condenser. As oxidative agents, the polymerization initiator for all monomers, $FeCl_3$ and $K_3Fe(CN)_6$ were used. A 1.0M solution of HCl or of dodecylbenzene sulphonic acid were used as solvents. The polymerization process started after the addition of the monomer (Py, ANI or 3–MeTh) to a well stirred mixture of the initiator and solvent, after the desired temperature had been attained. The reaction product (PPy, PANI or P3–MeTh) was filtered or centrifuged, washed thoroughly with a 1.0M solution of HCl and of NH_4OH and dried under vacuum at $40^\circ C$ to a constant weight [11, 12]. During the polymerization, PPy and P3–MeTh are produced in the doped state. PANI was doped using a 1.0M solution of HCl during 17h at room temperature.

The electrical conductivity of the polymers was measured by the four–point probe method on samples prepared from doped and dried powders by pressing at 10MPa.

The macroporous membranes for the chemical synthesis in the pores were prepared by the radical copolymerization of a mixture of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) (70/30 and 65/35 w/w) in the presence of cetyl alcohol (CA) and cyclohexanol (CH) [13]. The macroporous membrane was filled with $FeCl_3$ by repeated submerging of the membrane in a saturated deaerated solution of $FeCl_3$ in diethylether (DEE). The membrane filled with $FeCl_3$ was dipped in toluene at room temperature for 18h and then Py was introduced. The Py diffused into the membrane and polymerized [14].

The electrical conductivity was measured by the four–probe method. Scanning electron microscopy was employed to characterize the surface morphology of the prepared MMA–co–EGDMA–PPy composites [14] and of PPy films prepared by electrochemical means [10].

The electroactivity of PPy films (20 μm thick) was studied by cyclic voltammetry. A solution of $LiClO_4$ (1.0M) in a mixture of 1,2–dimethoxyethane (DME) and PC (30/70, v/v) was used as the electrolyte. The PPy film electrodes were assembled in a cylindrical Teflon cell having Li as both the counter and reference electrode. All the electrochemical tests were performed in a glove–box in an Ar atmosphere at room temperature [10,15–17].

PPy films were electrodeposited on iron from aqueous solutions of Py and oxalic acid at a constant current of 1mA cm^{-2}. This method yields strongly adherent polymer layers [18]. The influence of the PPy films on the corrosion behaviour of iron in sulphate solutions was investigated by following the change of the corrosion potential (E_{ocp}) of iron samples coated with a polymer layer with time and by impedance measurements [19–21].

RESULTS AND DISCUSSION

Preparation of PPy films by electropolymerization

The electrochemical process of the Py polymerization can be represented by the overall reaction:

$$nPy + nyA^- \rightarrow [Py^{y+} (A-)_y]_n + 2nH^+ + n(2+y)e \qquad (1)$$
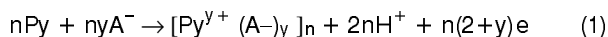
where: n is the degree of polymerization, y is the degree of oxidation (doping) and A^- is the doping anion from the electrolyte.

In one study [10], the effects of the preparation conditions on the conductivity, electroactivity and mechanical properties of electrochemically synthesized PPy layers 10–130 μm thick were investigated. In this sense, the effects of formation parameters (e.g. electrolyte recycling, concentration of monomer, current density, temperature, solvent, amount of water in the reaction mixture and film thickness), the nature of the counterions (e.g. ClO_4^-, p–toluenesulphonate and NO_3^-) and the nature and size of the cations associated with the anions (e.g. Li^+, Na^+, tetraethyl–ammonium, tetrabutyl–ammonium, N–methylpyridinium and poly(1–methyl–2–vinil pyridinium)) were studied.

A rather strong dependence of the PPy film conductivity on the formation parameters was found. The PPy conductivity first increased and then decreased with increasing applied current density, as it is shown in Fig.1. Also, the PPy conductivity increased with increasing monomer concentration up to 0.5M and the
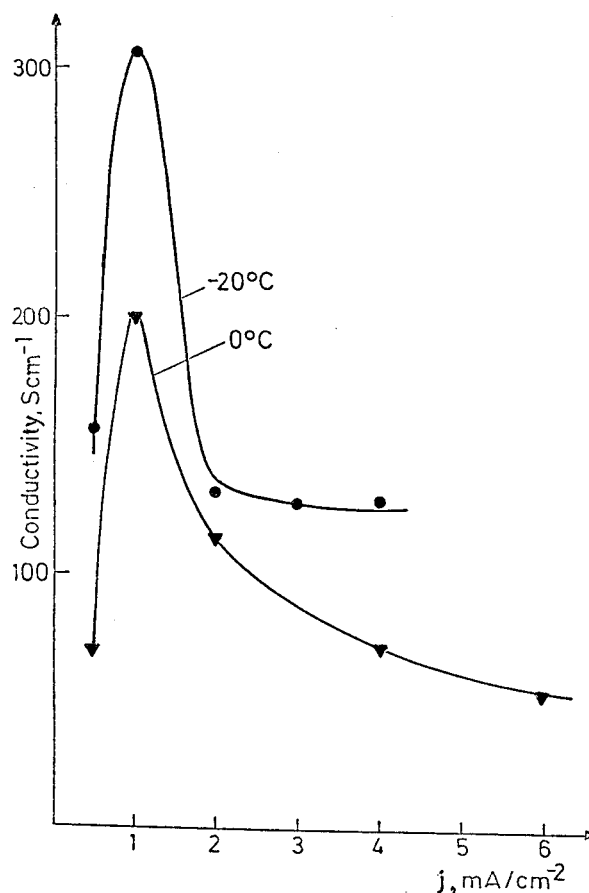

Figure 1. Influence of the current density and temperature on the electrical conductivity of PPy synthesized in 0.1M $LiClO_4$ + 0.5M Py in PC with 3 vol.% of water. The film thickness was 20 μm in each case.

amount of water in the reaction mixture up to 3 vol.%. At concentrations higher than these there was practically no effect in both cases. An increase in the PPy conductivity with decreasing film thickness and temperature was observed. The highest achieved conductivity was 307 Scm^{-1}, which was measured using a 20 μm thick PPy film synthesized at $-20^{\circ}C$ in PC containing 0.1M $LiClO_4$, 0.5M Py and 3 vol.% water at a current density of 1 mA cm^{-2}. When AN was used as the solvent (instead of PC), the PPy conductivities were lower. It was also shown, that recycling the electrolyte, for given conditions of PPy preparation, significantly decreased the PPy conductivity. Therefore, only freshly prepared electrolyte was used in all investigations.

It was found that the nature and size of the cation had no effect on the PPy conductivity. The highest observed conductivities of the PPy synthesized with both tetraethyl ammonium perchlorate and N–methyl–pyridinium perchlorate (NMPP) were quite close to the conductivities of the PPy obtained with $LiClO_4$ as the electrolyte under similar conditions. However, the nature and size of the anion effected both the conductivity and mechanical properties of the PPy. Thus, PPy films of low conductivity but with good mechanical properties were obtained using N–methyl–pyridinium nitrate in both water and PC as solvents. Tetrabutyl ammonium p–toluene sulphonate and N–methyl–pyridinium p–toluene sulphonate as electrolytes gave very satisfactory films of reasonably good conductivities.

The presence of small amounts of water in the reaction medium had a favorable action not only on the conductivity, but also on the mechanical properties and morphology of the PPy film. Generally, films prepared under dry conditions were brittle, had low conductivity and a "brain skin" texture. On the other hand, PPy films prepared in the presence of water had high conductivity, good mechanical properties and a so–called "cauliflower" texture. This texture was developed at very different current densities (e.g. 1 and 8 mA cm^{-2}) but the globules obtained at the higher current density were larger. PPy synthesized with NMPP as the electrolyte instead of $LiClO_4$, had a texture resembling hollow raspberries with a developed film surface.

Chemical polymerization of Py, ANI and 3–MeTh

In the scope of this work, the effect of the initiator concentration, initiator monomer ratio in the reaction mixture, temperature and polymerization time on the yield of synthesized PPy, PANI and P3–MeTh, have been studied in detail. $FeCl_3$ was used as the initiator of the chemical oxidative polymerization of Py, ANI and 3–MeTh in acidic aqueous solutions. Of all the obtained results, only the dependence of the yield and electrical conductivity on the polymerization time are presented in Figs. 2, 3 and 4 for PPy, PANI and P3–MeTh, respectively.
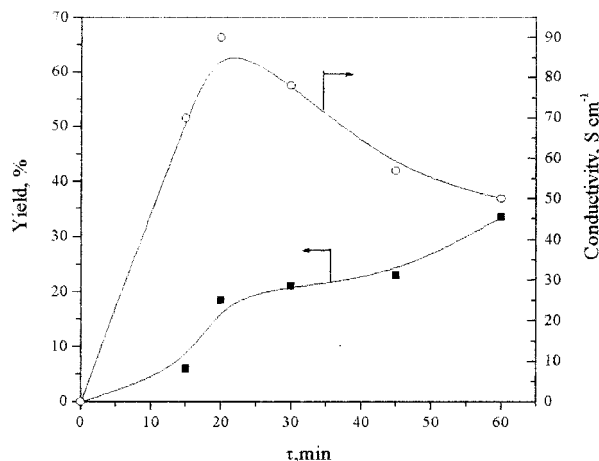

Figure 2. Dependence of the yield and electrical conductivity of PPy on the time of polymerization for $[FeCl_3]^0 = 0.474M$ and $n(FeCl_3)/n(Py) = 2.4$ at $t_p = 0^{\circ}C$.
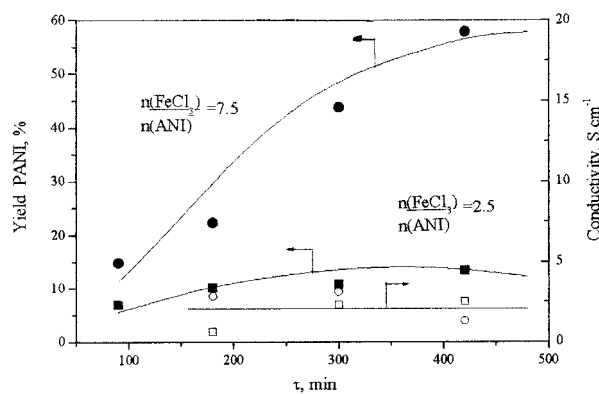

Figure 3. Dependence of the yield and electrical conductivity of PANI on the time of polymerization for $[FeCl_3]^0 = 1.0M$, $n(FeCl_3)/n(ANI) = 2.5$ and $[FeCl_3]^0 = 0.975M$, $n(FeCl_3)/n(ANI) = 7.5$, at $t_p = 35^{\circ}C$.

It can be concluded, on the base of obtained results, that Py, ANI and 3–MeTh have completely different behaviour during the chemical oxidative polymerization in acidic aqueous solutions. The polymerization of Py was performed at $0^{\circ}C$, ANI at $35^{\circ}C$ and 3–MeTh at $25^{\circ}C$. These temperatures are the optimal polymerization temperatures at which the highest yields of corresponding polymers are obtained, so their comparison can be considered as justified. The obtained results show that $FeCl_3$ initiates the polymerization of Py at the highest rate, fallowed by 3–MeTh and finally ANI. This may be related to the fact that $FeCl_3$ is a weak oxidizing agent and that the oxidation of Py starts at 0.7V, Th at 1.6V and ANI at 1.8V relative to SCE.

The curves of the PPy and P3–MeTh electrical conductivity vs. polymerization time exhibit a maximum. The maximal PPy electrical conductivity is 90 Scm^{-1} which is higher than that of PANI and P3–MeTh, but is lower than the electrical conductivity of PPy synthesized electrochemically [10].
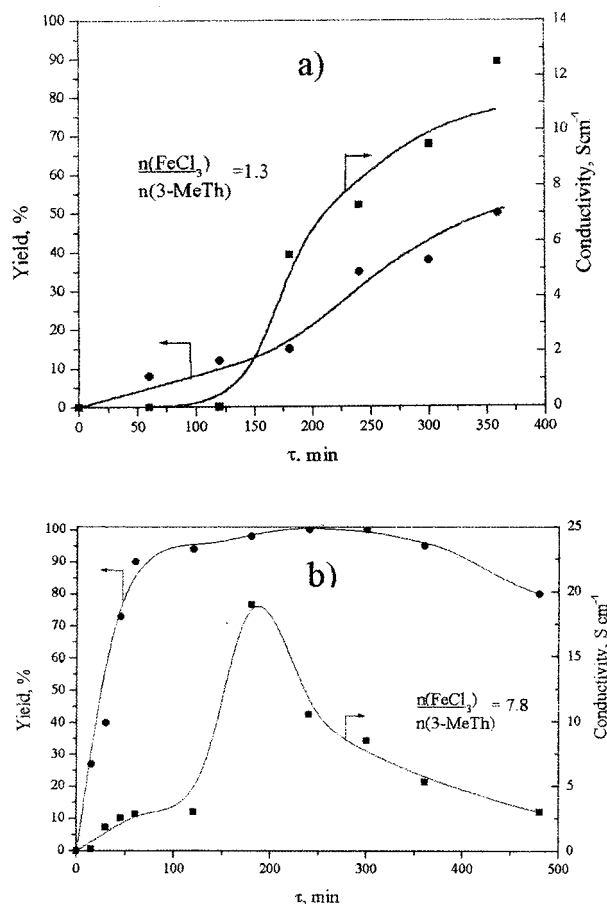
Figure 4. Dependence of the yield and electrical conductivity of P3-MeTh on the time of polymerization for $[FeCl_3]^0 = 0.133M$, $n(FeCl_3)/n(3-MeTh) = 1.3$ (a) and $[FeCl_3]^0 = 0.798M$, $n(FeCl_3)/n(3-MeTh) = 7.8$ (b), respectively, at $t_p = 25^{\circ}C$.

Fig. 4 illustrates that, on changing the (FeCl3)/(3-MeTh) mole ratio from 1.3 to 7.8, the rate of polymerization of 3-MeTh increases significantly, as does the maximal yield of P3-MeTh. However, it is interesting that, in both cases, the electrical conductivity of the synthesized P3-MeTh is practically constant up to 60 and 120 min polymerization time, respectively. The electrical conductivity (Fig. 4b), shows a maximum and then gradually decreases with time similar to the behaviour of PPy (Fig. 2).

The yield of PANI is significantly dependent on the initiator/monomer mole ratio as it is the case with PPy and P3-MeTh, but both the polymerization time and the initiator/monomer mole ratio have practically no effect on the electrical conductivity of the synthesized samples. The reason for such a peculiar behaviour of the electrical conductivity with the polymerization time is probably due to the fact that PPy and P3-MeTh are obtained in the doped state at the end of the synthesis. It is reasonable to assume that the doping process leads to a change in the supermolecular structure of the polymer molecules and also to the formation of defects having as a consequence the lowering of the electrical conductivity. However, in the case of PANI the polymer is

doped after the polymerization process therefore, there is no change in either the molecular structure or electrical conductivity of the synthesized PANI at different polymerization times.

A new method for the chemical polymerization of Py

The overall reaction of the chemical polymerization of Py in the presence of an oxidizing agent (Ox) is usually presented as:

$$nPy + n(2+y)Ox + nyA^- \rightarrow [Py^{y+}(A^-)_y]_n + 2nH^+ + n(2+y)Red, \tag{2}$$
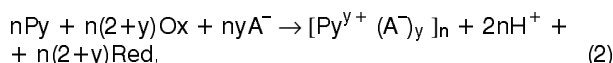
where: Red is the reduced form of the oxidizing agent.

During the chemical synthesis of PPy, the reaction conditions change with time. In addition to the decrease of the reactant concentrations and the change of pH, the oxidation potential of the solution (E), expressed by the Nernst equation, decreases due to the change of the ratio C_{Ox}/C_{Red}:

$$E = E^{\theta} + \frac{RT}{nF} \ln \frac{C_{Ox}}{C_{Red}}, \tag{3}$$

where: E^{θ} is the standard solution potential. According to scheme (2), an extremely large amount of the oxidizing agent is consumed during the chemical polymerization of Py.

For the reasons given above, a cell for the chemical polymerization of Py, in which the oxidation potential of the solution could be kept constant, was constructed [20]. The cell, which is schematically presented in Fig. 5, consists of two compartments 1 and 2, separated by a polymeric anionic membrane (M) which selectively permits only the diffusion of anions from compartment 2 into compartment 1. Two glassy carbon plates, (GC1 and GC2) are used as the anode and cathode, respectively. The electrodes were connected with a DC source through a variable resistor (R) and an ampermeter (A). A Pt indicator electrode (IE) was used to measure the oxidation potential of the solution against SCE.

Compartment 1 was filled with a deaerated aqueons solution of $K_3Fe(CN)_6$ in which freshly distilled Py had been introduced. Immediately after
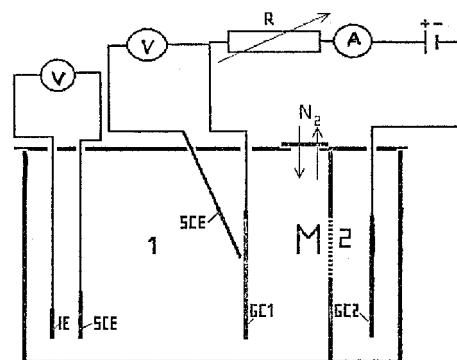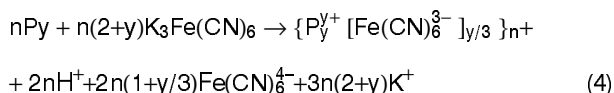

Figure 5. Schematic picture of a two-compartment cell for the chemical polymerization of Py

comencement of the Py polymerization, a current was passed through the circuit connecting the GC1 anode and the GC2 cathode. The current intensity was adjusted to compensate for the consumption of $Fe(CN)_6^{3-}$. Namely, during the chemical polymerization of Py, $Fe(CN)_6^{3-}$ is reduced to $Fe(CN)_6^{4-}$, which was then immediately oxidized on the GC1 anode to $Fe(CN)_6^{3-}$. The ratio C_{Fe}^{3+}/C_{Fe}^{2+} was adjusted at the beginning of the polymerization and then kept constant by maintaining a constant value of the oxidation potential measured using the Pt indicator electrode. In order to prevent electrochemical polymerization of Py on the GC1 anode, its potential was kept at values lower than 0.6V against SCE.

After desired polymerization time, the PPy powder was separated from the reaction mixture by filtration. The aqueous solution of $K_3Fe(CN)_6$ (and some remaining Py) collected as the filtrate was then used again for the polymerization of fresh amounts of Py. Therefore, in this new method of chemical polymerization of Py, electric energy is used instead of an oxidizing agent.

The kinetics of the chemical polymerization of Py by $K_3Fe(CN)_6$

In the chemical synthesis (as well as in the electrochemical synthesis) the polymerization of Py is believed to occur through oxidation the monomer with the creation of cation radicals, followed by a coupling reaction [21]. With $K_3Fe(CN)_6$ as the oxidizing agent, reaction (2) can be written as:

$$nPy + n(2+y)K_3Fe(CN)_6 \rightarrow \{P_y^{y+} [Fe(CN)_6^{3-}]_{y/3}\}_n +$$

$$+ 2nH^+ + 2n(1+y/3)Fe(CN)_6^{4-} + 3n(2+y)K^+ \qquad (4)$$

In order to obtain a deeper insight into the mechanism of the polymerization of Py, kinetic studies are of great importance. However, very little work has been done on this subject so far particularly in the case of chemical polymerization. This is mainly due to difficulties connected to the insolubility of PPy and its black color. The newly developed method of chemical polymerization of Py enables the study of the kinetics of the chemical polymerization of Py [22].

Assuming initially that the polymerization reaction is of the first order with respect to Py, the following rate law for reaction (2) can be written:

$$-\frac{dC_{Py}}{dt} = kC_{Py}\left[C_{Fe(CN)_6^{3-}}\right]^n = kC_{Py}\left[C_{Fe(CN)_6^{3-}}^0\right]^n = k'C_{Py}, \qquad (5)$$

where: k is the rate constant of the overall reaction (4) and n is the reaction order with respect to $Fe(CN)_6^{3-}$, $k' = k [C_{Fe(CN)_6^{3-}}^0]^n$ where the superscript ^{0} refers to the initial concentration. Strictly speaking, the concentration of $Fe(CN)_6^{3-}$ is not constant during the

polymerization, since some $Fe(CN)_6^{3-}$ anions are built into the polymer structure. However, the approximation $C_{Fe(CN)_6^{3-}} = C_{Fe(CN)_6^{3-}}^0 = $ const is acceptable as the decrease in $Fe(CN)_6^{3-}$ concentration is neglectable (about 0.5 %).

The yield of the reaction (x) can be defined as:

$$x = (C_{Py}^0 - C_{Py})/C_{Py}^0, \qquad (6)$$

where: C_{Py}^0 and C_{Py} are the initial and actual Py concentration, respectively. Substituting Eq.(6) into Eq.(5), the relationship is obtained upon integration:

$$\ln(1-x) = -k't. \qquad (7)$$

On the other hand, it can be shown that:

$$x = m_{PPy}^{exp}/\left\{m_{Py}^0(1 + yM_A/3M_{Py})\right\}, \qquad (8)$$

where: m_{PPy}^{exp} is the experimentally determined mass of PPy, m_{Py}^0 is mass of Py introduced into the reactor, y is the degree of doping, which was determined for each sample from elemental analysis, M_A and M_{Py} are the molar masses of the counterion $Fe(CN)_6^{3-}$ and the Py repeating unit, respectively.

If the experimental results satisfy the linear relationship (7) for different values of time, the assumed first order of the polymerization reaction with respect to Py can be considered as correct. The slope of the Eq. (7) gives the value of k'. On the other hand, from the slope of the linear relationship:

$$\ln k' = \ln k + n\ln C_{Fe(CN)_6^{3-}}^0, \qquad (9)$$

the order of the polymerization reaction with respect to an oxidizing agent (n) can be obtained, while from the intercept, the value of the rate constant k can be evaluated.

The linear relationships (7) and (9) are presented in Figs. 6 and 7, respectively.

Fig. 6 shows the first-order plots for the polymerization of Py at 0°C for different concentrations of $K_3Fe(CN)_6$. The values n and k were calculated as 2.6
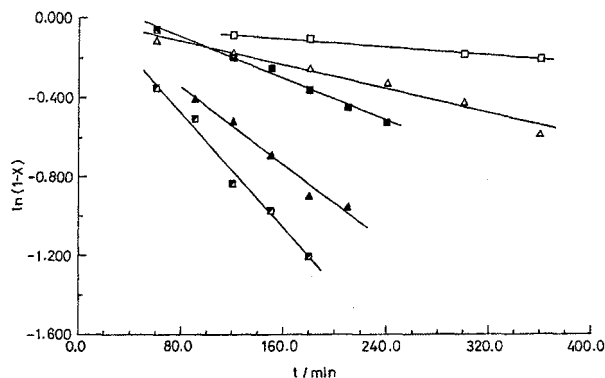

Figure 6. First-order plots for the Py polymerization at H0°C for different concentrations of $K_3Fe(CN)_6$: (□) 0.30; (△) 0.40M; (■) 0.50M; (▲) 0.70M; and (▢) 0.80M, respectively.

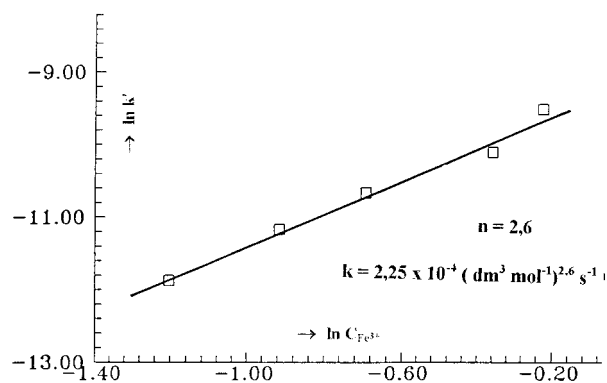*Figure 7. Plot of lnk' as a function of ln $C_{Fe(CN)_6^{3-}}$ according to Eq.(9).*

and 2.25×10^{-4} $(dm^3 mol^{-1})^{2.6} s^{-1}$, respectively. The order of the overall reaction (4) is equal 3.6. The fact that the overall order of the reaction is not an integer indicates that the mechanism of the polymerization reaction is rather complex.

Conducting composites based on MMA–co–EGDMA and PPy

Flat macroporous plates, conditionally denoted as membranes, based on MMA–co–EGDMA were prepared by homogeneous bulk polymerization and then the effect of different parameters on the chemical polymerization of Py in the pores of the membrane was studied [14]. FeCl$_3$ was chosen as the oxidizing agent for the chemical polymerization of Py. In order to ensure an effective filling of the pore with FeCl$_3$ and to preserve the porous structure of the membrane, DEE was used as a solvent for FeCl$_3$, since DEE fulfills all the necessary requirements: it is a good solvent for FeCl$_3$, a nonsolvent for both MMA and EGDMA and has a low surface tension (17.01 10^{-3} Jm^{-2} at $20°C$). If the membrane filled with FeCl$_3$ was just dipped into Py, then monomer polymerization would only occur at the surface and not inside the membrane due to the high rate of the Py polymerization compared to the slow diffusion of Py into the pores under the given conditions. PPy formed in the course of the polymerization plugs the pores at the membrane surface and prevents the diffusion of Py deep inside the membrane. In order to overcome these difficulties, the rate of the Py polymerization was reduced by a combitation of two effects. Firstly, instead of dipping the FeCl$_3$ filled membranes into Py directly, they were submerged in toluene (since it wets both MMA–co–EGDMA and is a nonsolvent for FeCl$_3$) for 18h and then the desired amount of Py was added. Secondly, the oxidation potential of FeCl$_3$ was lowered by adding some FeCl$_2$, since it has been shown that the rate of the Py chemical polymerization depends on the initial oxidation potential of the FeCl$_3$ solution [14].

Electrical conductivities of the order of 10^{-3} S cm^{-1} were obtained for MMA–co–EGDMA–PPy composites prepared from 0.290 and 0.216 cm thick MMA–co–EGDMA (70/30 w/w) membranes with a mass fraction of PPy in the composites of approximately 11–16 %. SEM micrographs suggested that the prepared composites were not homogeneous with respect to PPy. The pores at the surface were almost completely closed by PPy but not inside the membrane. However, the electrical conductivities of the order of 10^{-2} S cm^{-1} were obtained for MMA–co–EGDMA–PPy composites prepared from 0.065 cm thick MMA–co–EGDMA (65/35 w/w) membranes with a mass fraction of PPy in the composites of approximately 7–11 %. The higher electrical conductivities are most probably due to the small thickness of the membranes used in this case. Namely, it can be supposed that the higher electrical conductivities of the thinner composites arises from a more homogeneous distribution of PPy throughout the sample compared to the thick ones. Also, the composites prepared with MMA–co–EGDMA (65/35 w/w) membranes had better mechanical properties, since the composites broke spontaneously during the Py polymerization. The concentration and time of polymerization had no significant effect on the electrical conductivity of MMA–co–EGDMA–PPy composites under the given conditions.

Electrochemical properties and application of PPy

At the end of the electrochemical synthesis, according to Eq.(1), PPy is in its p–doped (oxidized) state. However, the polymer can easily be reduced to the neutral state by virtue of the reversible doping – undoping electrochemical process which involves only a fraction of the charge used for the total polymerization synthesis:

$$[(PPy)^{y+} (A^-)_y]_n + nye^- \overset{doping}{\underset{undoping}{\Leftrightarrow}} (PPy)_n + nyA^-. \qquad (10)$$
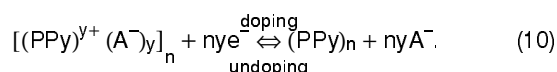
The reversibility and characteristics of process (10) make PPy a very attractive material for application as positive electrodes in rechargeable lithium batteries. Assuming that the diffusion of counterions A^- from the electrolyte to the PPy electrode surface and the charge transfer reaction are fast, the kinetics of the PPy p–doping (charging) and undoping (discharging) reaction are likely to be controlled by the diffusion of the doping anions A^- through the polymer structure. Under these circumstances, the surface morphology and primary structure of PPy film electrodes become a crucial factor in determining their electrochemical properties (cyclability and charging – discharging efficiency).

The electrochemical properties of PPy film electrodes, prepared in the presence of ClO_4^- and p–toluene sulphonate (TsO^-) as counterions, were

examined in lithium cells based on LiClO₄/DME–PC electrolytes [10, 15, 17]. Typical cyclic voltammograms of two PPy film electrodes are presented in Figs 8 and 9.

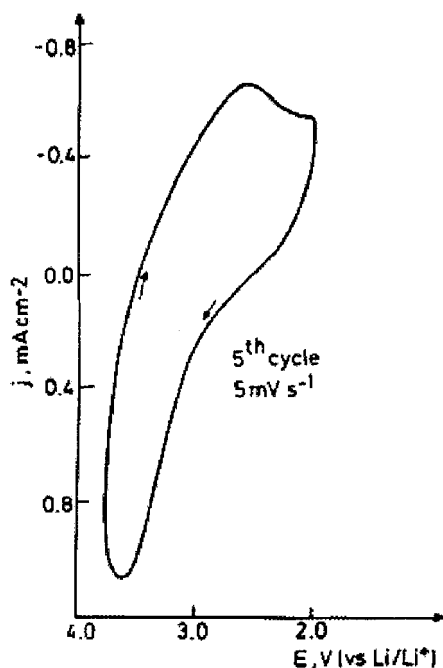*Figure 8. A typical cyclic voltammogram of PPy film (20 μm) in 0.1M LiClO₄/PC at 25°C. The PPy was synthesized at 0°C in 0.1M LiClO₄ + 0.5M Py in PC with 3 vol.% of water at a current density of 2 mA cm⁻².*
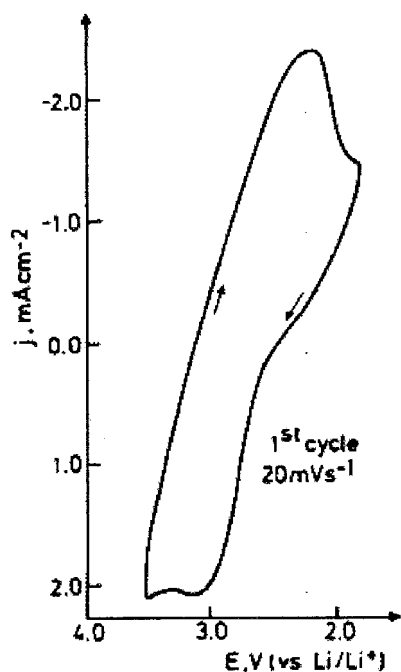

Figure 9. A typical cyclic voltammogram of a PPy film (20 mm) in 0.1M LiClO₄/DME–PC (30/70 v/v) at 25°C. The PPy was synthesized at 0°C in 0.1M tetrabutylammonium p–toluene sulphonate (TBATos) in PC with 6 vol.% of water at a current density of 4 mA cm⁻².

The scan rate and the potential interval during the cycling experiments were selected to obtain a complete reduction of the polymer electrode within the stability range of the electrolyte. Although it has been shown [23] that sharp voltammetric peaks, found with thin and ultrathin PPy layers, flatten for layers thicker than some tens of μm and finally disappear for layers thicker than some tens of μm, we found that the anodic and cathodic peaks for a 20 μm thick PPy film electrode, prepared in the presence of TsO⁻ counterions (PPy/TsO⁻), are quite well defined (Fig.9). According to the cyclovoltammetric curves, the PPy/TsO⁻ film electrode has a higher charging – discharging efficiency than the one prepared in the presence of ClO₄⁻ counterions (PPy/ClO₄⁻). The reduction of the PPy/ClO₄⁻ electrode is more difficult and a slower scan rate is required to undope the PPy film. The superior electrochemical behaviour of the PPy /TsO⁻ electrode can be ascribed to its much more developed surface (shown by SEM micrographs [10]) and to the easier diffusion of ClO₄⁻ ions during the doping – undoping (charging – discharging) reaction (10) through the channels formed during the electrodeposition of the PPy film in the presence of the larger TsO⁻ ions.

Corrosion Studies

In this article, the results of corrosion studies of mild steel with an epoxy coating, mild steel covered with a polypyrrole coating and mild steel covered with a polypyrrole–epoxy combination are presented.

Fig. 10 shows the open circuit potential vs. time dependence for the three investigated samples. The sample with the polypyrrole coating, kept a positive potential value, close to the redox potential of polypyrrole, but after 1 hour it had reached a potential value close to corrosion potential of mild steel. It is interesting that in our previous works [19, 24], for electrodes with polypyrrole coatings obtained by electrodeposition, the plateau of the redox potential lasted for 300 seconds.

The sample with the epoxy coating reached, in a short time period, the value of the corrosion potential of
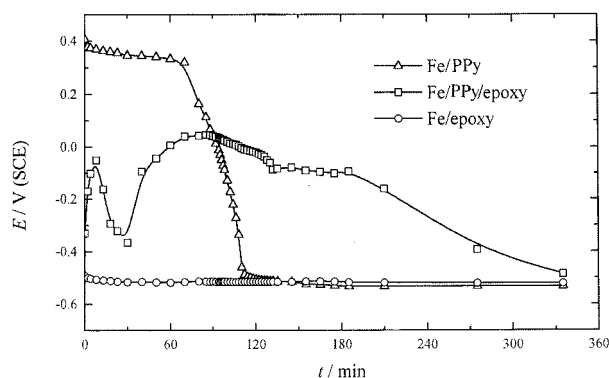

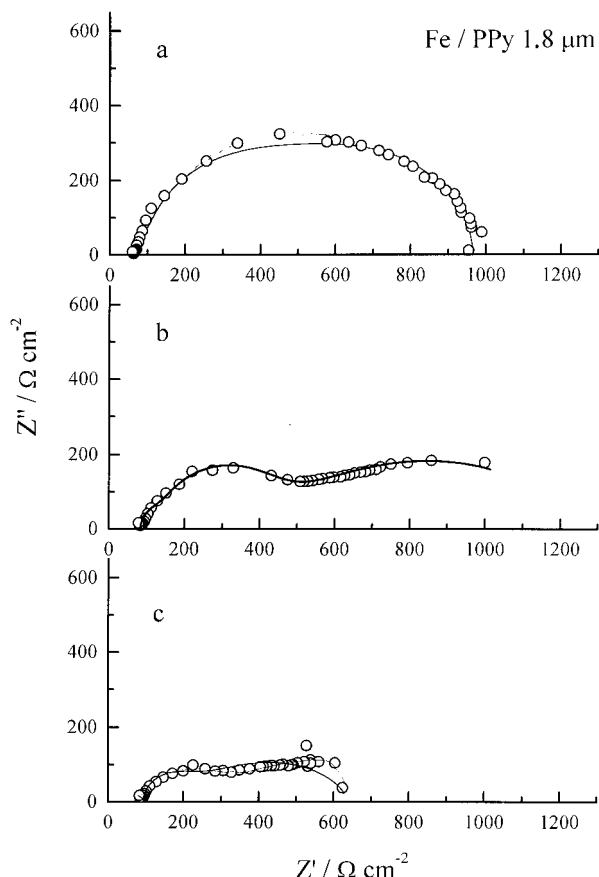*Figure 10. Corrosion potential vs time curves for mild steel electrodes with various protective coatings.*

Figure 11. Electrochemical impedance spectra for a mild steel electrode with a 1.8 μm thick polypyrrole coating for different times a–1, b–28 and c–46 days in 0.1 M H_2SO_4 solution, (o)–experimental data and (—) results of the fitting procedure.

mild steel, which is indicative of the high porosity of this coating.

In contrast to the sample with the polypyrrole coating, the sample with the polypyrrole epoxy blend

exhibited unusual behavior. The initial value of the corrosion potential amounted to about –0.3 V (SCE), after some period of time this value increased to about 0 V (SCE), and then decreased to about –0.4 V (SCE), after which it increased again to about 0.1 V (SCE), and then finally it started slowly to establish the value close to the corrosion potential of mild steel in about 360 minutes. This unusual behavior could be related to the development of pores in the epoxy coating and polypyrrole film, during which the corrosion potential was established, by to a process of dedoping of the polypyrrole through the pores of the epoxy coating and iron dissolution through the pores of the polypyrrole film and epoxy coating.

Fig. 11 shows the impedance spectra vs. time for Fe/PPy in 1.0 mol dm^{-3} H_2SO_4 solution. The total impedance of the coating increases during 40 days, which is in accordance with previous results [19]. The impedance spectra have been analyzed by an equivalent circuit, presented in Fig 12b, based on the physical model given in Fig. 12a [19]. The given model is based on the assumption that during the process of the establishment of the corrosion potential a reaction of dedoping of the polypyrrole coating is operable, and that the corrosion rate after the establishment of the corrosion potential is associated with the cathodic reaction of dedoping of the polypyrrole coating and the anodic reaction of iron dissolution in the pores of the coating[19].

In the proposed electrical equivalent circuit, R_f is the sum of the film resistance and the electrolyte resistance, R_{mp} is the charge transfer resistance at the metal/polymer interface, C_{mp} is the capacity of the metal /polymer interface, R_p is related to the pore resistance, while C_p ia the capacity of the pores. The impedance of the electrochemical corrosion of iron is presented by R_{Fe} and by the capacity of the polypyrrole film C_f which is in
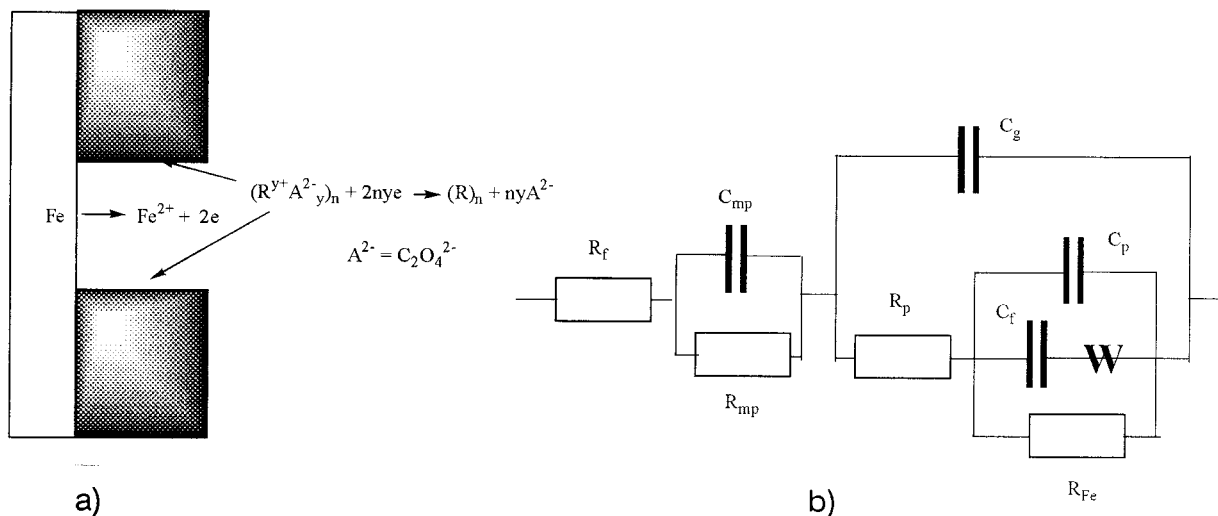

Figure 12. a) Physical model of the corrosion of mild steel with a polypyrrole coating and b) the electrical equivalent circuit for the given model.
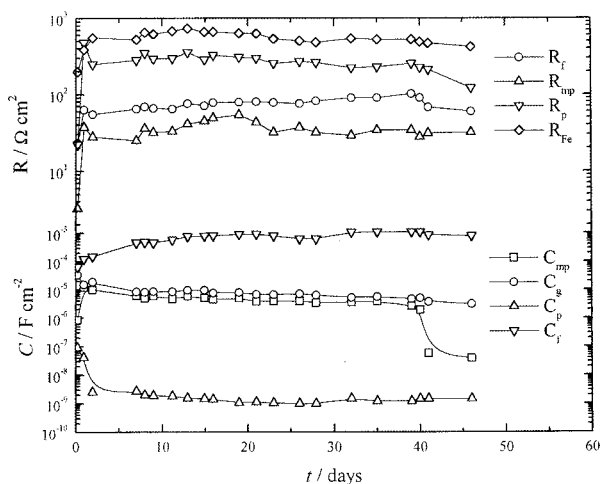
Figure 13. Time dependence of the electrical parameters for Fe/pPy.

series with the Warburg impedance W, which arises from the fact that the reaction of dedoping of polypyrrole is under diffusion control.

The values of the electrical circuit parameters were obtained by fitting the experimental data of the impedance of Fe/PPy in 0.1 M H_2SO_4 with the electrical equivalent circuit given above. The capacity and resistance changes with time are displyed in Fig. 13.

It can be seen that during the first two days the values for R_p, R_f, R_{mp}, and R_{Fe} showed a significant increase, after which their values remained practically the same. After 42 days, ohmic pore resistance R_p had decreased significantly, which is a result of the increase in the pore dimensions. The increase in the value of R_f is
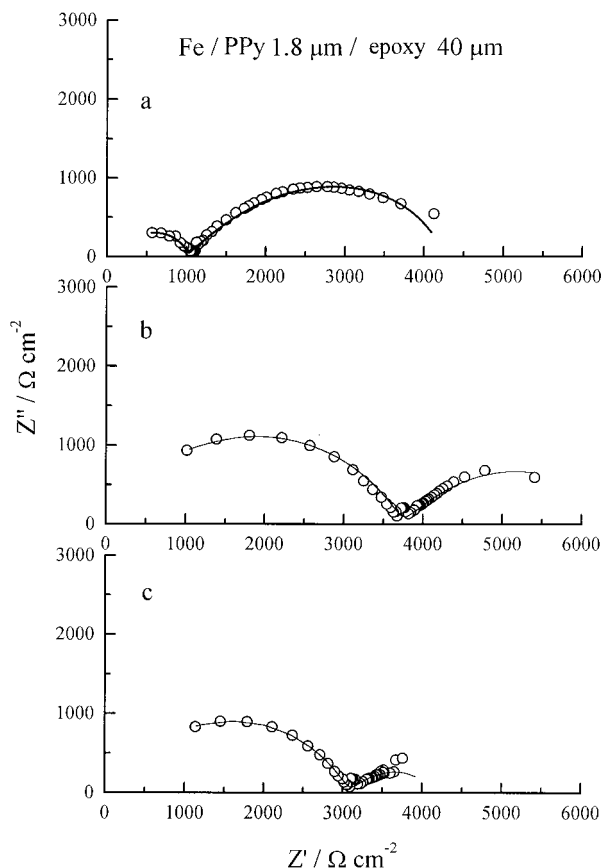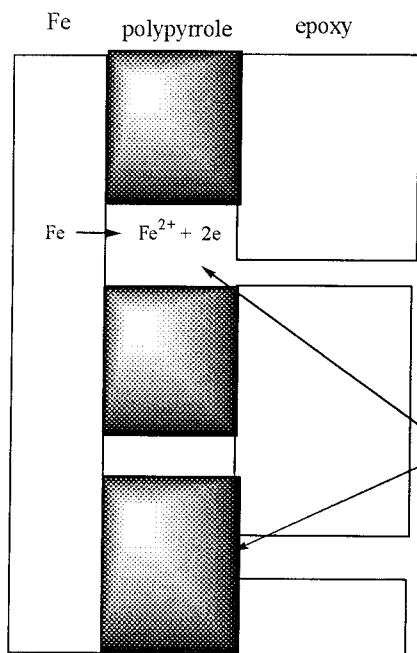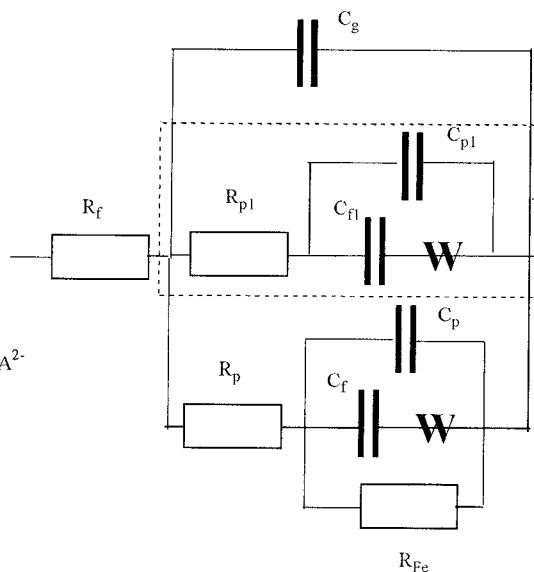

Figure 14. Electrochemical impedance spectra for mild steel with polypyrrole epoxy coating in 0.1 M H_2SO_4 solution for different times of exposure a–1, b–13 and c–46 days. (o–experimental data and (—) results of the fitting procedure.

$$(R^{y+}A^{2-}_y)_n + 2nye \longrightarrow (R)_n + nyA^{2-}$$

$$A^{2-} = C_2O_4^{2-}$$

Figure 15. a) Physical model for the corrosion of mild steel with a polypyrrole epoxy coating b) electrical equivalent circuit for the given model.

a consequence of an increase in the degree of reduction of the film with time, after which it started to decrease (acting as a usual coating). The values of the capacities did not change significantly, only the values for c_{mp} increased cliring the first two days after which the value first remained constant, and, finally, it increased rapidly. This phenomena is associated with the degradation of the metal–polymer interlayer.

Fig. 14 shows time development of the electrochemical impedance spectra, together with fitted values (presented as solid lines in the same figure) for the Fe/PPy/epoxy sample.

The impedance behavior shows that this system is not just a simple combination of the behavior of polypyrrole and epoxy. Two semicircles were observed in the impedance complex plane. The high frequency semicircle armss from a response of the epoxy paint, while the lower frequence semicircle can be related to the corrosion reaction. Figs. 15a and 15.b reflect the occurrence of three parallel reactions: the anodic dissolution of iron through the polypyrrole epoxy pores, which allows direct contact with electrolyte, and two cathodic reactions, the reduction of polypyrrole and dedoping of polypyrrole in pores of the epoxy coating (the equivalent circuit consisted of elements with 1 in index, framed by dashed lines). Because of the high complexity of the proposed electrical equivalent circuit, it has been assumed that the process of dedoping of polypyrrole in the pores of the epoxy paint were completed during the initial period and that the following reaction take place through the pores of the epoxy paint and polypyrrole coating, so that the steel is in direct contact with the electrolyte. By fitting the experimental data of the electrochemical impedance for the electrode with Fe/PPy/epoxy in 0.1 M H_2SO_4, the electrical impedance parameters were obtained. The time dependence of the capacitances, together with the ohmic resistances are presented in Fig. 16.
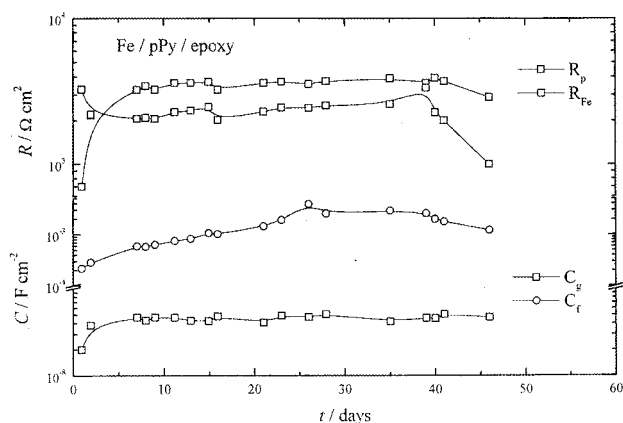
The ohmic resistance of the pores R_p, similar to the polypyrrole coating, increased during the first 7 days, and then after 15 days it started to decrease slowly. This decrease is either related to the degradation of the epoxy paint, or to the end of the development of the pores. After this, R_P did not change significantly. After 40 days the values for R_P decreased significantly, which is related to the enhance ment of the pore dimensions and to the destruction of the coating. On the other hand, the charge transfer resistance R_{Fe} exhibited a completely different behavior compared to the polypyrrol coating. During the first 6 days R_{Fe} decreased with time. This could be related to the complete dedoping of the polypyrroll in the pores of the epoxy paint. During this period, the epoxy–polypyrrole pore system was acting as a classical paint, due to the slow diffusion of oxalate anions from the bulk of polypyrrole towards the pores. After 6 days, R_{Fe} started to increase, which indicates a leveling of the concentration gradients in the pore walls and in the bulk of the polypyrrole.

The capacity of the coating did not vary significantly with time, while the capacity of the polypyrrole film, C_f, increased a little, probably as a result of pore development in the epoxy paint, after which it started to decrease, indicating, a lowering of the polypyrrole dedoping rate.

Fig. 17 summarizes the dependances of the corrosion current densities of the protected samples on time. As can be seen the electrode with the polypyrrole epoxy blend coating exhibited the maximum corrosion stability, while the electrode with the polypyrrole coating, and the electrode with the epoxy paint have similar values of the rate of corrosion. As can also be seen from Fig. 17, the corrosion current density for the polypyrrole epoxy blend is the lowest, with a reduction of the corrosion rate of mild steel by a factor of 20. For the epoxy paint and polypyrrols coating, the corrosion rate is reduced by a factor of 5.
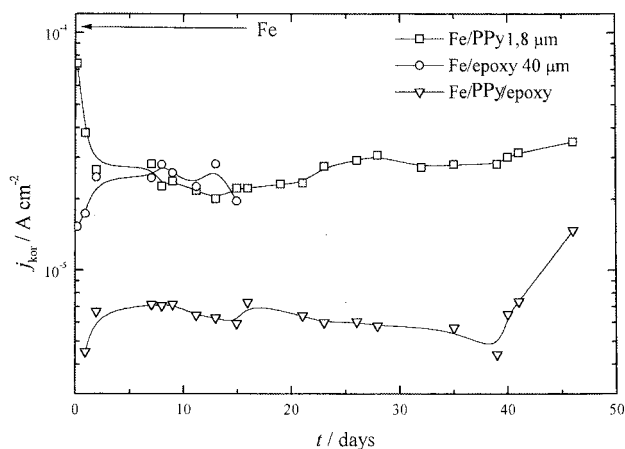

Figure 16. Time dependence of some electrical parameters for the Fe/PPy/epoxy system.

Figure 17. Dependence of the corrosion current densities for the three examined simples on time.

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IZVOD

SINTEZA I ELEKTROHEMIJSKA SVOJSTVA POLIPIROLA, POLIANILINA I POLI–3–METILTIOFENA

(Pregledni rad)

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U okviru ovoga rada prikazani su rezultati dobijeni izučavanjem elektrohemijski inicirane polimerizacije pirola i hemijski inicirane oksidativne polimerizacije pirola, anilina i 3–metiltiofena sa $FeCl_3$, kao i elektrohemijskih svojstava sintetizovanih elektroprovodnih polimera. Razvijen je novi reaktor za sintezu polipirola pri konstantnoj koncentraciji inicijatora – $K_3Fe(CN)_6$ i po prvi put određene odgovarajuće konstante polimerizacije pirola. Pokazano je da polipirol i polianilin mogu da se primenjuju kao elektrodni materijali za obnavljajuće izvore električne struje i da tanki slojevi ovih polimera mogu uspešno da se koriste za zaštitu gvožđa od korozije.

Ključne reči: pirol • anilin • 3–metiltiofen • elektrohemijska i hemijska polimerizacija • svojstva polipirola • polianilina i poli–3–metiltiofena • korozija • elektrohemijska impedanca •

Key words: Pyrrole • Aniline • 3—methyl thiophene • Electrochemical and chemical polymerization • Polypyrrole • Polyaniline • Poly 3—methyl thiophene properties • Corrosion • Electrochemical impedance •