

Revising the kinetics of aniline electropolymerization under controlled potential conditions

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The kinetics of electropolymerization of aniline under controlled potential conditions has been studied with the use of controlled potential electrolysis and UV-Vis spectroelectrochemical techniques. At a high electrode potential, the occurrence of electrochemical degradation of polyaniline formed has been analyzed to proceed parallelly to electropolymerization. Based on this, an empirical relation describing the kinetics of aniline electropolymerization has been supplemented with a term related to the degradation process:

$$R = k \cdot [P] \cdot [M] + k' \cdot [M] - k_d \cdot [P],$$

where R is the rate of electropolymerization of aniline, $[M]$ is monomer (aniline) concentration in polymerization solution, $[P]$ is polyaniline concentration at the electrode surface, k and k' are rate constants for electropolymerization of aniline at an electrode covered with polyaniline and at a bare electrode, respectively, and k_d is the first order degradation rate constant for polyaniline.

Key words: polyaniline, electropolymerization, degradation, kinetics

INTRODUCTION

Since the discovery of electrically conducting polymers more than 20 years ago these novel materials are finding increasing use in various fields of science and technology [1–3]. For diverse uses of these materials, the deposition of conducting polymer layers onto different surfaces is of primary interest. Apart from polymer processing and chemical oxidative deposition [4], electrochemical (anodic) polymerization of the corresponding monomers is of great importance in obtaining conducting and electroactive coatings onto metal surface. Two basic techniques are widely used in obtaining conducting polymer coatings at metal or other conducting surfaces. These are the potential cycling procedure and electrolysis at a controlled electrode potential. In both cases the electropolymerization starts at a high positive electrode potential, where highly reactive species such as radical cations are formed due to electrochemical oxidation of monomer molecules.

The electropolymerization process is well known for its autoaccelerating character which has been a subject of a few investigations during the past decade. For electropolymerization of aniline, Wei et al. expressed the rate of polymer formation as a sum of two terms by the following empirical equation [5]:

$$R = k \cdot [P] \cdot [M] + k' \cdot [M], \quad (1)$$

where R represents the rate of polymer formation, k is an empirical rate constant for electropolymerization at a polymer covered electrode, k' is a rate constant before polymer is formed on the electrode (*i.e.* the rate constant for a bare electrode), $[M]$ is the monomer (aniline) concentration, and $[P]$ is the polymer (polyaniline) concentration at the electrode surface.

Both empirical rate constants k and k' depend on many variables such as electrode potential, scan rate and switching potential (for electropolymerization by potential cycling), temperature, acidity of the polymerization solution, etc. Therefore, albeit the absolute values of these constants are of little

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interest, the ratio of the constants reflects the auto-accelerating character of the electropolymerization process. In accordance with Eq. (1), autoacceleration should proceed at $k \gg k'$, *i.e.* when the rate of electropolymerization at a surface covered with a polymer layer exceeds greatly the rate at a bare substrate surface. For a variety of experimental conditions used, Wei et al. found the ratio $k/k' = 1.8 \cdot 10^{-4}$ [5]. This means that the rate for polymerization of aniline at a polyaniline-coated electrode exceeds the polymerization rate at a bare electrode approximately by four orders of magnitude.

Somewhat later, Wu and Yang analyzed the kinetics of electropolymerization of aniline and its derivatives, *o*- and *m*-toluidines (*o*- and *m*-methylanilines) at a RuO₂ coated titanium electrode in 1.0 M HCl solution within the frame of the same kinetic model, and obtained the ratio k/k' to vary between $3.5 \cdot 10^{-6}$ and $5.4 \cdot 10^{-6}$ for these three monomers [6]. At a thermally prepared platinum coated titanium electrode, the ratio k/k' of $6.64 \cdot 10^{-6}$ for aniline and $3.23 \cdot 10^{-6}$ and $3.15 \cdot 10^{-6}$ for *o*- and *m*-toluidines, respectively, were obtained in 1.0 M HCl solution [7]. The same tendencies were observed for autoaccelerating chemical polymerization of aniline in aqueous acidic solutions as well. With the use of ammonium persulfate as an oxidizing agent, the following empirical kinetic equation was derived [8]:

$$-\frac{d[AN]}{dt} = k \cdot [AN] \cdot [APS] + k' \cdot [AN] \cdot [P] \quad (2)$$

where $[AN]$, $[APS]$, and $[P]$ are the concentrations of aniline monomer, ammonium peroxydisulfate, and polyaniline, respectively.

In general, the ratio k/k' of 10^{-2} – 10^{-3} was obtained [8] in accordance with the autoaccelerating character of chemical oxidative polymerization.

On the other hand, it is well known that polyaniline undergoes degradation processes in an acidic solution at a high electrode potential [9]. With the use of UV-Vis spectroelectrochemical techniques, first order degradation rate constants ranging from $8.40 \cdot 10^{-6}$ to $2.93 \cdot 10^{-3} \text{ s}^{-1}$ were determined for polyaniline deposited at an ITO glass electrode, within the potential window of 0.85 to 1.20 V vs. RHE (*i.e.* 0.65 to 1.00 vs. the Ag / AgCl reference electrode), respectively [10]. For polyaniline deposited on a platinum electrode, first-order degradation rate constants ranging from $2.87 \cdot 10^{-5}$ to $3.11 \cdot 10^{-3} \text{ s}^{-1}$ were found for electrode potentials ranging from 0.3 to 0.9 V vs. Ag / AgCl [11]. Similar results were obtained also for poly(styrene sulfonate) doped polyaniline deposited at a platinum electrode [12]. The upper limit of the degradation rate constant of *ca.* $3 \cdot 10^{-3} \text{ s}^{-1}$, obtained at a high electrode potential of 0.9 or 1.0 V vs. Ag / AgCl, corresponds to fast degradation process of a polymer film with the half-period of *ca.* 3 min. Therefore, since electropoly-

merization of aniline proceeds at a high electrode potential reaching or exceeding 0.9 V, intense degradation processes should proceed in parallel to electropolymerization. Thus, the degradation of polyaniline should influence considerably the observed kinetics of the electropolymerization process.

The present work has been aimed to study the net kinetics of aniline electropolymerization at a controlled electrode potential with the use of electrochemical and UV-Vis spectroelectrochemical techniques.

EXPERIMENTAL

Aniline was distilled before use. Electropolymerization solution contained 0.5 M of sulfuric acid and 0.05 M of aniline.

A PI-50-1 potentiostat, arranged with a PR-8 model programmer, was used in electrochemical experiments. Electrochemical experiments were performed in a three-electrode cell containing a platinum wire working electrode, 5 mm in length and 0.5 mm in diameter, a platinum wire counterelectrode and a saturated Ag / AgCl reference electrode. UV-Vis spectra were recorded with a Shimadzu model UV-2101 spectrometer. Spectroelectrochemical experiments were done in a 1-cm path length quartz cuvette arranged with an indium-doped tin oxide coated optically transparent glass electrode installed perpendicularly to the light path, a platinum wire counterelectrode, and a relative hydrogen reference electrode filled with 0.5 M solution of sulfuric acid and connected to a spectroelectrochemical cell by a

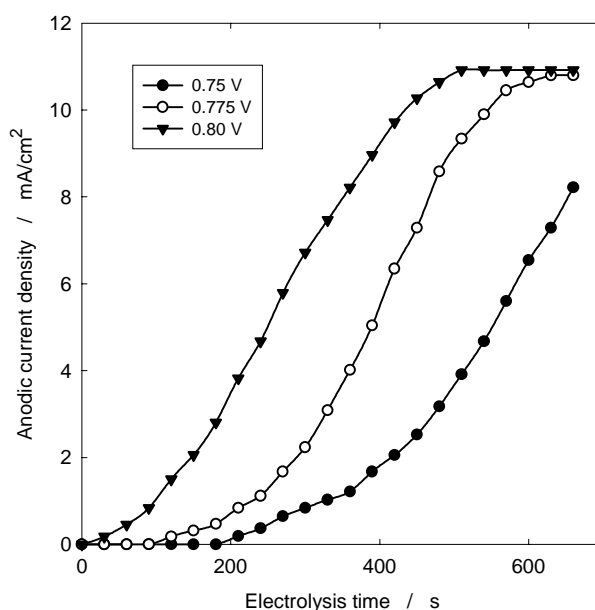


Fig. 1. Time dependence of anodic current for platinum electrode, obtained after applying a controlled potential (as indicated) performed in electropolymerization solution containing 0.5 M of sulfuric acid and 0.05 M of aniline

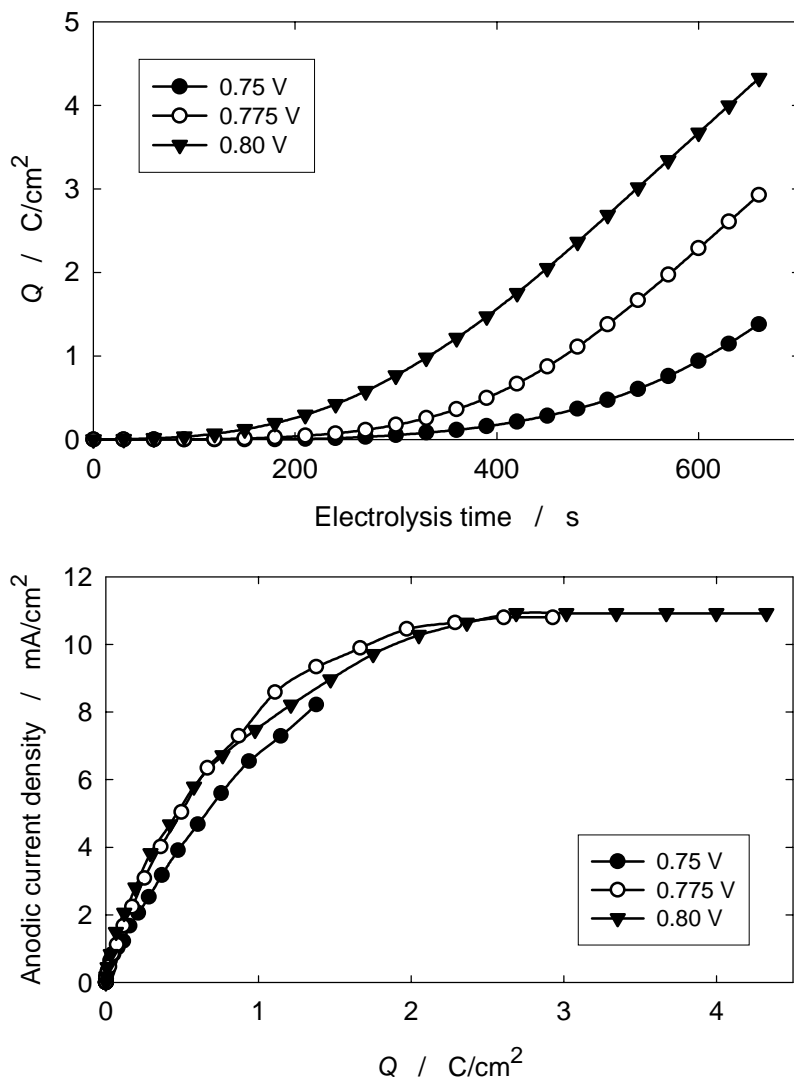


Fig. 2. Top: time dependence of anodic charge, passed during electropolymerization of aniline at a controlled potential (as indicated). Bottom: dependence of anodic current on electric charge passed during electropolymerization of aniline at a controlled potential (as indicated)

salt bridge. All potential values given below relate to a saturated Ag / AgCl electrode.

RESULTS AND DISCUSSION

Figure 1 shows the growth of anodic current for electropolymerization of aniline at the different electrode potentials applied. In Fig. 1 the autoaccelerating character of the electropolymerization process is well seen: after a definite initiation time, the oxidation current grows until it reaches a maximum. The initiation time depends greatly on the potential applied. For the experimental conditions used, the initiation time varied from more than 400 s for the applied potential of 0.725 V to almost zero at a potential exceeding 0.85 V. The shape of the current-time dependencies obtained can be approximated by a simple 3-parameter sigmoidal equation:

$$I = \frac{I_{\max}}{1 + \exp\left(-\frac{t - t_{1/2}}{a}\right)}, \quad (3)$$

where I and I_{\max} are the anodic current and the maximum anodic current reached, t and $t_{1/2}$ are the reaction time and the reaction time corresponding to a half of the maximum current, respectively, and a is an empirical coefficient.

Treatment of experimental data according to Eq. (3) yields nearly coinciding values of $I_{\max} = (11.5 \pm 0.48)$ mA/cm² for all polymerization potentials used. Taking into account that the anodic current corresponds to a the total rate of all electrooxidation processes taking place, it may be concluded that, after a definite time, the intensity of these processes reaches its maximum which does not depend on the electrode potential applied. Within the frame of the model proposed [5], this means that the maximum rate of electropolymerization corresponds to a total coverage of the electrode surface with polyaniline. However, in contrast to this model [5], the direct ascription of a maximum current to the rate of electropolymerization is doubtful, since intense electrochemical degradation of the polymer layer should proceed, in parallel to electropolymerization process, at a relatively high electrode potentials used for electropolymerization. From the data presented in

[11] it could be deduced that, for the working potential ranging from 0.75 to 0.80 V, the first order degradation rate constant for polyaniline at a platinum electrode varies between $5.0 \cdot 10^{-4}$ and $8.5 \cdot 10^{-4}$ s⁻¹, corresponding to a half-period of degradation of ca. 2700 to 810 s, respectively. Thus, intense degradation of the polymer formed should proceed parallelly to electropolymerization, taking into account that the time scale of experiments (Fig. 1) is well comparable with the half-period of degradation.

Treatment of the data obtained according to Eq. (3) also yields $t_{1/2}$ values, i.e. the characteristic time intervals when the anodic current reaches a half of its maximum. The values for $t_{1/2}$ of (587 ± 11) , (402 ± 2) , and (268 ± 3) s were obtained for electropolymerization potentials of 0.75, 0.775, and 0.80 V, respectively. This shows a strong dependence of the initial polymerization rate on the electrode poten-

tial: a relatively small increase of the electropolymerization potential (from 0.75 to 0.80 V) causes a great acceleration of the polymerization process, resulting in a more than twofold decrease of $t_{1/2}$.

Integration of the data of Fig. 1 leads to the dependence of a total electric charge passed during electrolysis on electrolysis time shown in Fig. 2 (top). One can see that, for all electrode potentials applied, the electric charge grows nearly exponentially up to a definite value, ca. 1.2 to 1.5 C/cm², whereas the further growth bears a linear character. Following the known model [5], it could be supposed that the initial exponential growth reflects a gradual coverage of electrode surface with polyaniline which accelerates the growth process. After the entire electrode surface is covered with polyaniline, the growth proceeds at a constant rate, resulting in a linear increase of electric charge depending on reaction time. To approve this assumption, the anodic current has been plotted as a function of electric charge passed before, as depicted in Fig. 2 (bottom). The latter dependence can be treated within the frame of a hyperbolic equation:

$$I = \frac{I_{\max} \cdot Q}{Q_{1/2} + Q}, \quad (4)$$

where I and I_{\max} are the anodic current and its maximum value, respectively, Q is the electric charge passed, and $Q_{1/2}$ means the electric charge for which a half of anodic current is attained.

It follows from Eq. (4) that, at a low coverage of electrode surface with polymer, *i.e.* at $Q < Q_{1/2}$, the rate of electropolymerization or, more precisely, the anodic current grows linearly with the surface coverage (at the early stage of electropolymerization, the surface coverage could be assumed to be directly proportional to the anodic charge passed before). A nearly linear dependence of I on Q for low Q values, as is seen in Fig. 2 (bottom), confirms the model proposed [5], taking into account that the rate of electropolymerization at a polyaniline-coated electrode surface exceeds by a few orders of magnitude the rate for a bare electrode [5–7]. Adversely, as follows from Eq. (4), the polymer growth rate does not depend on electrode coverage at a full covered

electrode, *i.e.* at $Q \gg Q_{1/2}$. This is also well seen in Fig. 2 (bottom). Therefore, neglecting the electropolymerization rate for a bare electrode, it could be assumed that $Q_{1/2}$ corresponds to a half-coverage of electrode surface. Treatment of experimental data according to Eq. (4) yields the values for $Q_{1/2}$ of (0.84 ± 0.05) and (0.75 ± 0.04) C/cm², for operating potentials of 0.775 and 0.80 V, respectively. These nearly coinciding values obtained also support the known model in that the rate of polymerization is directly proportional to the relative surface area of the electrode, covered with a final polymer.

The data presented above relate to anodic current or its derivative value – electric charge. These values clearly relate to the rate of electropolymerization and the quantity of polyaniline deposited onto the electrode. However, since polyaniline undergoes an intense electrochemical degradation at the electropolymerization potentials applied [10–12], it

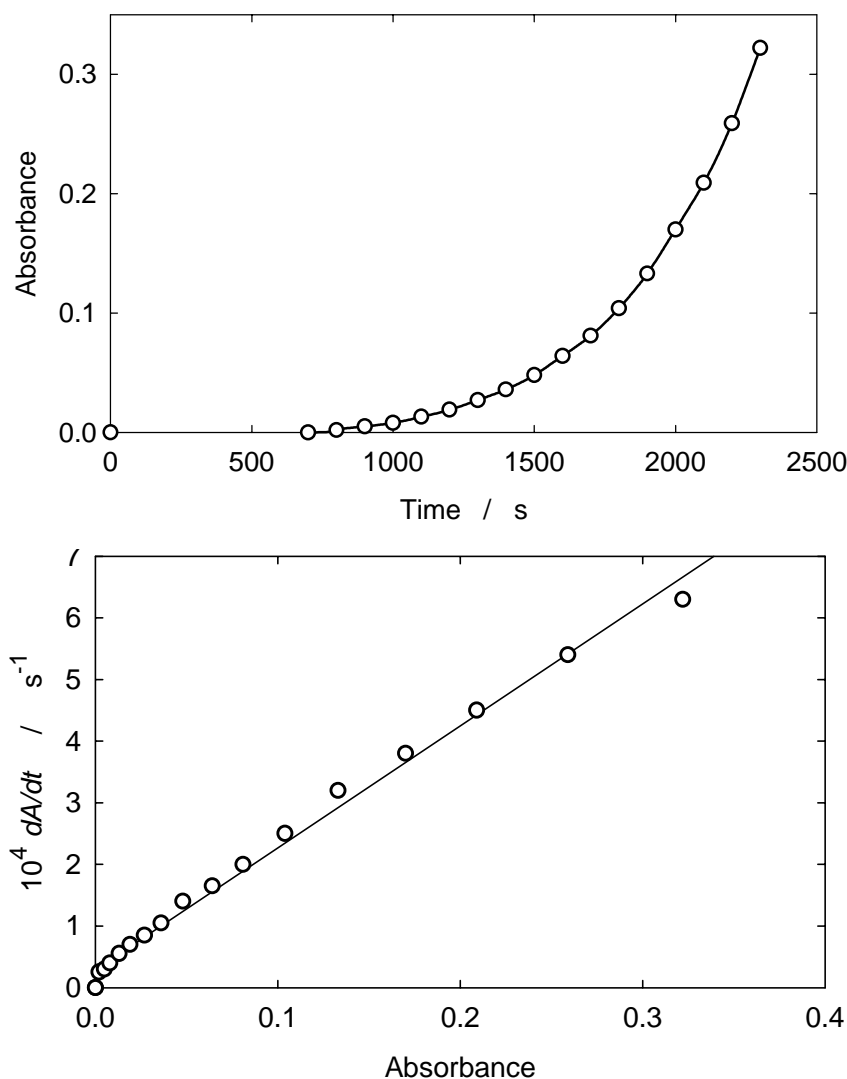


Fig. 3. Top: time dependence of optical absorbance recorded at 750 nm, obtained after applying a controlled potential of 0.75 V in electropolymerization solution.

Bottom: dependence of the growth rate of optical absorbance on absorbance at 750 nm

is clear that part of the anodic electric charge is consumed in these destruction processes. Therefore, an overall rate of electropolymerization, expressed as in Eq. (1), should contain at least two kinetic components, one being related to electropolymerization and another one to destruction processes. However, a particular part of electric charge, consumed for electrochemical destruction, cannot be estimated based on $I-t$ or $Q-t$ transients only.

In order to estimate both these components, UV-Vis spectroelectrochemical experiments were performed for electropolymerization of aniline at an optically transparent electrode. In contrast to the total electric charge passed during electrolysis, the optical absorbance and its growth during electrolysis relate only to the polyaniline content deposited onto the electrode. In our experiments, we used a constant wavelength of 750 nm at which the maximum absorbance of polyaniline is observed, whereas low molecular mass products of polyaniline destruction like quinones and quinoneimines do not absorb in this spectral region. Figure 3 (top) shows the kinetics of aniline electropolymerization at a relatively low electrode potential (0.75 V), at which autoaccelerating character of this process is well seen. Similarly as for current-time and charge-time transients, both the initial absorbance growth rate and the initiation time for absorbance-time transients depend greatly on the polymerization potential applied. Particularly, a lower initiation time is observed for a higher operating potential. Figure 3 (bottom) shows the dependence of the rate of absorbance growth on the absorbance reached before. It follows that at low absorbance values the growth rate of absorbance increases nearly linearly with increasing absorbance. Obviously, since the absorbance is directly proportional to the amount of polyaniline deposited, this means that the electropolymerization rate is directly proportional to relative surface coverage. For a higher degree of surface coverage, however, a deviation from linearity is observed.

Some different features are exhibited by absorbance-time transients obtained at higher electrode

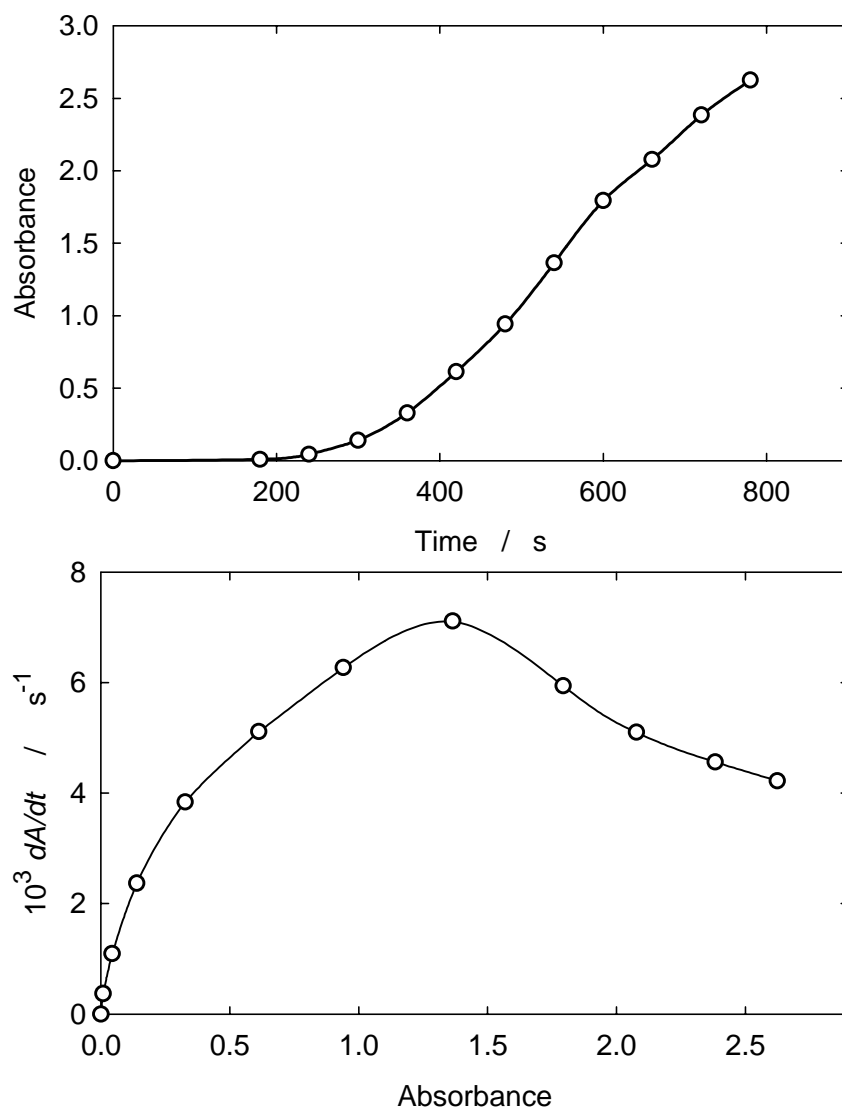


Fig. 4. Same as in Fig. 3, obtained at a controlled potential of 0.90 V

potentials, as shown in Fig. 4 (top). When plotted against the absorbance reached, the profiles for absorbance growth rate possess a well expressed maximum, as shown in Fig. 4 (bottom). This is in contrast with the corresponding dependencies of the anodic current on electric charge, depicted in Fig. 2 (bottom), when a constant maximum current is reached at high charges. Both anodic current density in Fig. 2 (bottom) and absorbance growth rate in Fig. 4 (bottom) are measures of the net process rate, however, optical absorbance depicted at the X axis of Fig. 4 (bottom) is an integral measure for the polyaniline deposited at electrode during electrolysis, whereas the electric charge in Fig. 2 (bottom) is presumably a sum of the charges consumed for electropolymerization and for electrochemical degradation of the polymer layer deposited. Therefore, it may be assumed that a decrease of absorbance growth rate observed at high absorbance and thus a high surface coverage as shown in Fig. 4 (bottom) are caused by the processes of electrochemical

degradation, proceeding parallelly to electropolymerization. At a lower optical absorbance, and thus at a lower quantity of polyaniline deposited, the absorbance growth rate increases with increasing electrode coverage, in accordance with the known model, however, at a high electrode coverage with electrodeposited polymer degradation processes become more intense, causing a pronounced decrease in absorbance growth rate.

In absence of polymer degradation, the dependence of dA/dt on A should follow, on analogy to the current-charge transient given by Eq. 4, a simple hyperbolic function:

$$dA/dt = \frac{(dA/dt)_{\max} \cdot A}{A_{1/2} + A}, \quad (5)$$

where (dA/dt) and $(dA/dt)_{\max}$ are the absorbance growth rate and its maximum value, respectively, A is optical absorbance, and $A_{1/2}$ is the optical absorbance that corresponds to a half of the maximum growth rate.

However, taking into account the degradation processes that proceed following a first order reaction scheme [10–12] and thus are directly related to the amount of polyaniline deposited, *i.e.* to optical absorbance, Eq. (5) could be modified into a full kinetic equation as follows:

$$dA/dt = \frac{(dA/dt)_{\max} \cdot A}{A_{1/2} + A} - k_d \cdot A, \quad (6)$$

where k_d is the first order degradation rate constant.

The degradation rate constant in Eq. (6) should depend, similarly as the other rate constants k and k' used in the initial kinetic expression, Eq. (1), on many variables such as the electrode potential or the acidity of the solution. Following this scheme, the degradation rate constant k_d could be obtained from the data presented in Fig. 4 (bottom) and compared with the known value obtained by a direct measurement performed under the same or closely related conditions. By treating the experimental data of Fig. 4 (bottom) the value of $k_d = (4.5 \pm \pm 1.1) \cdot 10^{-3} \text{ s}^{-1}$ was obtained. From direct UV-Vis spectroscopic measurements, a first order degradation rate constant for polyaniline of $(1.12 \pm 0.2) \cdot 10^{-3} \text{ s}^{-1}$ has been obtained earlier for an electrode potential of 1.10 V *vs.* RHE, *i.e.* 0.90 V *vs.* Ag / AgCl reference [10]. The value of the degradation rate constant obtained here appears to be a few times higher than that reported in [10]. A possible reason for this is that the rate constant obtained in the present work relates to a freshly formed or just forming polymer which consists obviously of relatively short polymer chains, whereas the data of [10] relate to a separately deposited polyaniline which differs in the degree of polymerization and in polymer film morphology.

CONCLUSIONS

In conclusion, taking into account the electrochemical degradation processes to proceed at a high electrode potential used in the electropolymerization procedure, the known empirical kinetic equation for the growth rate of polyaniline can be supplemented with a term related to the degradation process. The final form of this equation should be as follows:

$$R = k \cdot [P] \cdot [M] + k' \cdot [M] - k_d \cdot [P]. \quad (7)$$

The first two terms have the same value as in Eq. (1) [5] and reflect the growth rate at the electrode covered and uncovered with polyaniline, respectively, whereas the third term reflects the electrochemical degradation processes taking place parallelly to electropolymerization. The degradation rate constant k_d , similarly as both rate constants related to polymer growth, k and k' , depends on many variables, the dependence on electrode potential being most important. This dependence has been revealed and analyzed earlier [10–12].

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**ANILINO ELEKTROPOLIMERIZACIJOS TYRIMAS
KONTROLIUOJAMO POTENCIALO SĄLYGOMIS**

S a n t r a u k a

Anilino elektropolimerizacijos kontroliuojamo potencialo sąlygomis kinetika buvo tirta taikant kontroliuojamo potencialo elektrolizės ir spektroelektrochemijos metodus. Gautieji duomenys analizuoti atsižvelgus á galimà polianilino elektrocheminá skilimà esant aukštam elektrodo potencia-

lui. Remiantis tuo, pasiūlyta empirinë lygtis, aprašanti anilino elektropolimerizacijos kinetikà:

$$R = k \cdot [P] \cdot [M] + k' \cdot [M] - k_d \cdot [P];$$

čia R – elektropolimerizacijos greitis, $[M]$ – monomero (anilino) koncentracija tirpale, $[P]$ – elektrodo paviršiaus uždymas polianilinu, k ir k' – anilino elektropolimerizacijos ant padengto ir nepadengto polianilinu paviršiaus greièio konstantos (atitinkamai), k_d – polianilino elektrocheminio skilimo pirmojo laipsnio greièio konstanta.