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Electrogeneration kinetics of polyaniline in the presence of lithium perchlorate

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Summary

Polyaniline (Pani) was electrogenerated potentiostatically (1 V vs Ag/Ag^+) in acid aqueous medium (2 M HNO_3) in the presence of $LiClO_4$ on Pt electrodes. The kinetic equation of the polymerization process was calculated by means of the electrochemical data of the polymerization charge (Q_{pol}), determined as $R_p = [E]^{0.14} [M]^2$. Furthermore, the number of electrons consumed per monomer unit incorporated in the oxidated polymer was determined. The results show that the electrolyte has practically no effect on the reaction kinetics at the concentrations tested, but that it is, moreover, the triggering factor for fewer electrons to be incorporated into the polymer chain.

Introduction

The great interest aroused by polyaniline (Pani) as a conducting polymer is due to several benefits this material offers, the first of these being the fact that aniline is a relatively cheap compound whose polymerization does not pose major problems, neither chemically nor electrochemically. In addition, the polymer, when doped, presents with a high conductivity, apart from being easy to process and stable, both thermally and environmentally. Thanks to these special properties, Pani is a much appreciated polymer in a host of electrochemical applications, such as cells, sensors, electrochromic windows and anti-corrosion metal-coating [1-4].

The possibility of applying Pani in the field of lithium cells is an issue of major interest in the scientific debate, as evidenced in the great number of publications on the topic [5-11]. Most of these using Pani-based cathodes and anodes based on lithium or compounds into which lithium has been incorporated. Although Pani is doped, as a general rule, in an acid medium without the need of adding a salt to act as an electrolyte, in this research the kinetic study of the electropolymerization reaction of aniline was conducted in the presence of a lithium salt, to the purpose of gaining insight into the influence exerted by that salt on the reaction through the determination of the empirical kinetic equation, calculated from the electrochemical data.

Experimental

Aniline (Aldrich) was vacuum-distilled (43°, 3mm Hg) prior to use. Lithium perchlorate ($LiClO_4$) (Aldrich) was used without previous purification. The acid solutions were prepared with deionized water in a Milli-Q Reagent System fed by a Milli-R04 Water Prufication System and nitric acid (HNO_3) (Panreac).

Electropolymerization was conducted in a METROHM single chamber electrochemical cell with three electrodes. The working electrode consisted of Pt foil (1 cm^2); the counter-electrode was stainless steel (4 cm^2) and the reference electrode Ag/AgCl. The distance between the working electrode and the counter-electrode was maintained at 12 cm, thanks to a support device manufactured in the laboratory. Prior to electrogeneration the Pt electrodes were treated under reductor flame in order to eliminate any residual organic matter.

Potentiostatic electropolymerization (1V) was implemented in a PGSTAT 30 Autolab potentiostat-galvanostat at different reaction times (100, 115, 125, 135 and 150 s). All tests were conducted at room temperature, without stirring and in N_2 atmosphere. The aniline concentrations used in the different experiments were 0.075, 0.1, 0.125, 0.15 and 0.175 M, and the $LiClO_4$ concentrations were 0, 0.025, 0.05, 0.075 and 0.1 M. Following each electrodeposition the Pt electrodes were rinsed in acetone and vacuum-dried to constant weight. The weight of the generated polymer was measured on a Sartorius 4504 MP8 microbalance (accuracy 10^{-7} g) by determining the weight differential between the clean and coated Pt electrode. Subsequently the coated electrodes were immersed in the control solution (absence of monomer, 0.05 $LiClO_4$, 2M HNO_3) and were held there at 0 V for 300 s. Then they were subjected to three scans in cyclic voltametry between 0 V and 1.25 V at a rate of 20 mV/s.

Results and Discussion

The kinetic study of aniline electropolymerization was conducted in 2M HNO_3 acid aqueous solutions, maintaining the acid concentration constant in all tests and varying the aniline and $LiClO_4$ concentrations. Therefore the kinetic equation determined with the aid of the electrochemical data only applies to this single acid concentration.

The kinetic equation was calculated on the basis of the polymerization charge (Q_{pol}), i.e. the electric charge consumed in the electrogeneration of the polymer under the different experimental conditions described above. Q_{pol} is determined by integrating the area under the chronoamperograms obtained from each electropolymerization. The plot of Q_{pol} vs reaction time allows to obtain an empirical kinetic equation of the process. Thus, assuming that Q_{pol} is proportionate to the generated polymer weight (p), it may be expressed as a linear relation:

$$Q_{pol} = kN\ p \qquad \textbf{(1)}$$

where kN represents current performance or the electric charge consumed per mass unit. The slope of the straight line derived from (1) can be expressed in the following way:

$$dQ_{pol}/dt = kN\ dp/dt = kN\ R_p \qquad \textbf{(2)}$$

where R_p is the polymerization rate, whose value is expressed in from equation (3):

$$R_p = k\,[E]^a\,[M]^b \qquad \textbf{(3)}$$

Replacing R_p in equation (2) by its expression in equation (3), (2) can be re-written as equation (4):

$$dQ_{pol}/dt = kNk\,[E]^a\,[M]^b = kO\,[E]^a\,[M]^b \qquad \textbf{(4)}$$

and taking the respective logarithms:

$$\log\,(dQ_{pol}/dt) = \log kO + a \log\,[E] + b \log\,[M] \qquad \textbf{(5)}$$

The reaction order for the electrolyte concentration ‘a’ is obtained, maintaining the monomer concentration constant and varying that of the salt. Likewise, exponent ‘b’, i.e. monomer concentration, is calculated varying the aniline concentration and this time maintaining the electrolyte concentration constant. Thus, the logarithmic plot of log (dQ_{pol}/dt) vs log [E] or log [M] yields a straight line from whose slope the respective electrolyte and monomer reaction orders are obtained.

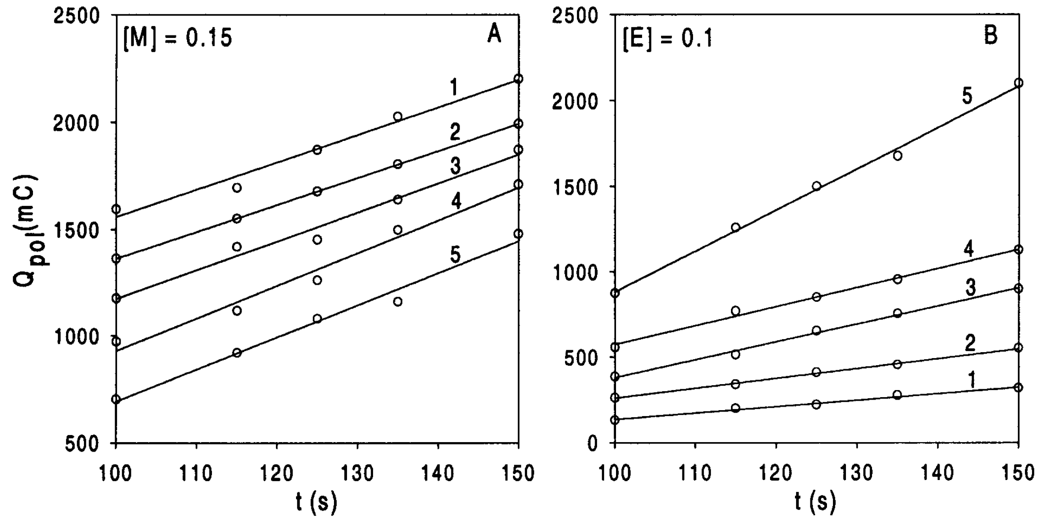

Fig. 1. Polymerization charge as a function of time for (A) [M]=0.15M and different [E]: 1) 0M; 2) 0.025M; 3) 0.05M; 4) 0.075M; 5) 0.1M. (B) [E]=0.1M and different [M]: 1) 0.075M; 2) 0.1M; 3) 0.125M; 4) 0.15M; 5) 0.175M.

Figure 1A shows Q_{pol} variation as a function of reaction time for the different electrolyte concentrations, [M] being constant at 0.15 M. In the first place, Q_{pol} is observed to decrease with increasing salt concentration for one and the same polymerization time. Secondly, the slopes of the straight lines do not show any significant variation as a function of $LiClO_4$ concentration. This means that the polymerization rate R_p remains practically constant and independent of the salt content. Figure 2A shows the plot log R_p vs log [E], yielding again a straight line ($R_p = 0.14\,[E] + 1.33$), whose slope is expressed as exponent ‘a’, i.e. the reaction order of electrolyte concentration, ($a = 0.14$).

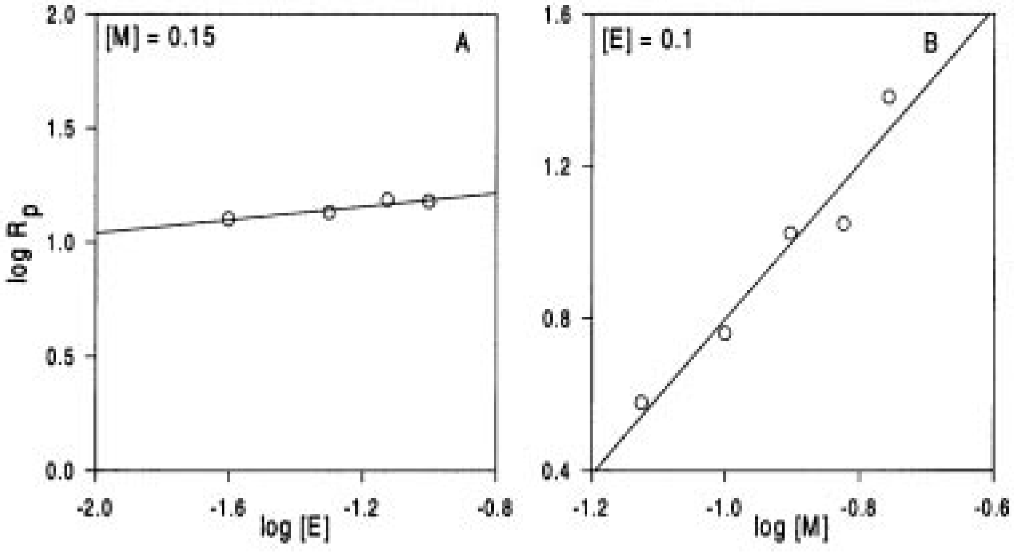

Fig. 2. Log Rp versus log [E] (A) and log Rp versus log [M] (B).

The reaction order ‘b’ referring to monomer concentration is calculated analogously. Figure 1B shows Q_{pol} variation as a function of reaction time for the different aniline concentrations, [E] remaining constant at 0.1 M. In this case the electric charge consumed is the greater, the higher the monomer content for one and the same polymerization time. In addition, the slope of these straight lines becomes progressively steeper with increasing monomer content, most prominently when [M] = 0.175 M. As was to be expected, the polymerization process is the faster, the higher the monomer content. When plotting log R_p vs log [M], a straight line is obtained (log R_p = 2 [M] + 2.84) and hence the reaction order at constant salt is b = 2 (Figure 2B).

Thus the kinetic equation, when utilizing the polymerization charge data can be written as (6):

$$R_p = k\,[E]^{0.14}\,[M]^2 \qquad \textbf{(6)}$$

In the light of equation (6) it is legitimate to state that electrolyte and monomer influence the electropolymerization reaction in different ways.. The high value of ‘b’ is indicative of the fact that the process kinetics is principally governed by monomer concentration. Furthermore the value b=2 coincides with Mohilner's findings [12], who was the first to report that the polymerization reaction of aniline in acid medium depends on the square of the monomer concentration. On the other hand, the value found for exponent ‘a’ points towards a relatively negligible influence of the salt at the experimental concentrations.

Even if the salt is practically not involved in the polymerization mechanism, it does exert an influence on the oxidation-reduction processes of the polymer, i.e. it has effects on the doping characteristics of the film. In this context, relevant information is supplied by the number of electrons consumed per monomer unit (mou) incorporated into the oxidized polymer (n), a parameter which can be expressed as:

$$n = n°e^- / mou = [Q_{pol} / elec.charge \times N_{AV}] / [p / p_{mon}] \qquad \textbf{(7)}$$

where p is the weight of the electrogenerated polymer, and p_{mon} stands for the weight of the monomer unit incorporated $(-C_6H_4NH-)_n$ = 91.127 (g /mol). For applying equation (7) we assume that all the oxidized aniline will be deposited on the electrode.

Theoretically two electrons are needed for the aniline polymerization reaction and, in addition, a certain number of suplementary electrons to oxidize (dope) the polymer. Nevertheless, there exist certain discrepancies in the literature regarding the value of ‘n’. As a matter of fact, this value oscillates between n = 2.16, as found by [13]; n = 2.29 according to [14] and n = 2.6-2.7, the value determined by [15]. In our research different values were found as a function of $LiClO_4$ concentration. Figure 3 shows n-variation as a function of polymerization time, when [M] =0.15M at varying salt content. The value of ‘n’ clearly diminishes inversely proportionate to electrolyte increase. When electropolymerization is conducted in the absence of the salt, the value of ‘n’ positions between 2.6 and 3.0. The number of electrons per monomer unit, however, progressively decreases, when increasing the electrolyte portion up to 1.3. These results may be due to the fact that the anion of the salt, apart from keeping the charge balance, may act as a base capable of proton incorporation from the medium, thus increasing the pH value which will reduce the conducting properties of Pani, defined both as electron transfer and protonation of the nitrogen atoms. This means that the polymer formed is less electroactive, which could be in agreement with the decrease in storing efficiency, i.e. the electric charge stored in the polymer per mass unit, as a function of increasing $LiClO_4$ concentration, as reported in other work [16]. Another possibility could be the formation of soluble products, while the polymer is being deposited. This latter explanation is supported by the appearance of a green cloud around the working electrode, more evident with increasing electrolyte concentration and polymerization times.

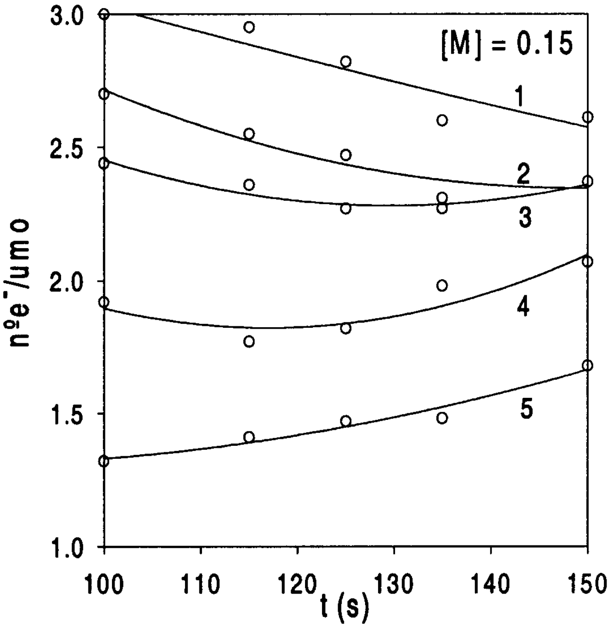

Fig. 3 **Number of electrons per monomer unit as a function of polymerization time [M] = 0.15M and [E]: 1) 0M; 2) 0.025M; 3) 0.05M; 4) 0.075M; 5) 0.1M.**

Conclusions

The results reported on allow for the following conclusions:
- The kinetic equation obtained from the electrochemical data of Pani electropolymerization in an acid aqueous medium (2 M HNO_3) with $LiClO_4$ as electrolyte ($R_p = k\ [E]^{0.14}\ [M]^2$) indicates that the reaction kinetics is principally governed by the aniline concentration, whereas the electrolyte practically does not interfere at the experimental concentrations.
- In the absence of $LiClO_4$ the number of electrons per monomer unit incorporated into the oxidated polymer chain (n), moves between 3.0 and 2.6, as a function of reaction time. $LiClO_4$ addition causes ‘n’ to drop reaching levels of 1.3 due to the fact that the anion of the salt, apart from keeping the charge balance, may act as a base capable of proton incorporation from the medium, thus increasing the pH value and reducing the conducting properties of Pani.

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