

Cyclic potential sweep electro polymerization of aniline and substituted aniline in acidic medium: A kinetic study

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ABSTRACT

The cyclic potential sweep (CPS) was applied to aniline and substituted aniline to study the kinetic aspects and mechanism of polymerization of anilines, the dependence of the deposition rate of aromatic amines (i.e., deposition charge on number of cycles, scan rate and concentration of monomer). In this method, the mass of polymer deposited at electrode is a function of anodic peak current that is recorded during the polymerization. The deposition rates of polymer were thus controlled by the increase in the anodic peak currents at various concentrations of aniline. The second order kinetics was observed for overall electropolymerization reaction.

A kinetic rate expression, $R_p = k' [ANI] + k [PANI] [ANI]$ was obtained for the polymerization, supports the probable mechanism and the structure of the growing polymer formed at the electrode.

Keywords: Cyclic potential sweep, deposition rate, electrochemical polymerization.

INTRODUCTION

Polyaniline (PANI), which is readily obtained by the chemical or electro-chemical polymerization of aniline in aqueous solution and one of the representative conducting polymer. Although, its electronic conductivity is slightly lower than that of other similar material such as polypyrrole and polythiophene. Polyaniline is being an electrically conductive material, having moderately high conductivity upon doping with simple Bronsted acids^{1,2}. It can easily be synthesized by chemical or electrochemical oxidation of aniline²⁻⁴. Polymer film obtained by anodic polymerization of inert electrode is of interest for application to batteries, electrochromic displays (ECD), liquid crystal displays (LCD), electrocatalysis, EC devices for data storage and nano-devices². Recently, polyaniline won a privileged position in the research field⁵⁻¹⁰. It is deposited on an electrode surface by using various methods like use of radio-frequency

plasma¹¹. PANI exhibit different characteristics related to various polymerization parameters. These characteristics depend on the nature of acidity and basicity of the medium, applied current-potential relation and surface area of the electrode, oxidation-reduction system of the polymer etc. In spite of the many studies carried out on polyaniline, several aspects of the system have still been under investigation¹²⁻¹⁸. But very little effort was made to correlate deposition charges to the parameters (i.e., scan rate, switching potential and number of cycles) relevant to the technique. The polyaniline film properties are usually investigated during potentiodynamic /cyclic potential sweeps between -0.2 to 1 V¹⁹. To study the kinetics of PANI formation as well as reduction and reoxidation polymerization system. We applied computer-added potentiostatic pulse measurement, which allow simultaneous recording of current density i and charge density q ²⁰. In the light of above parameters, we have tried to obtain a rate

expression for the electrochemical polymerization of aniline. The study led us to suggest a linear linkage at the *para* position is essential for high structural regularity and bring high electrical conductivity.

EXPERIMENTAL

Polyaniline film deposition of aniline in strongly acid medium was performed at room temperature under oxygen free environment using platinum as working electrode and a SCE (Standard Calomel Electrode) as a reference electrode. Prior to each run the electrode was washed with corresponding solvent and subsequently by distilled water. The electrolyte was prepared by using double distilled water and AR Grade chemicals. Potentiostat/Galvanostat (Model 263A-Princeton Applied Research, USA) was used for electrochemical analysis. Measurement were carried out in cell which was thermostated at 23°C. The aqueous electrolyte was 0.5M H₂SO₄ with 10⁻² M aniline for the PANI formation. The redox measurements were carried out in pure 0.5M H₂SO₄. Cyclic potential sweep method was used for electrodeposition at a sweep rate of (10-100 mVs⁻¹) with starting potential of -0.2 V and a switching potential of 0.7 V up to maximum charges of (0.1-0.33 C cm⁻²) and the current density was measured with an auto-ranging differential amplifier to a corresponding 6.0 μm thickness²¹. Thus, the kinetics of the film formation was investigated during potentiostatic PANI growth in aniline solution. Film produced by this kind of polarization, however, consists of various nuclei of different sizes. The properties of the films are not very reproducible. For this reason, for the measurement of redox process we used the more homogeneous and reproducible films which were grown potentiodynamically by cyclic polarization between -0.2 and 0.7 V at 100 mV/s for 10000s. For these films, a thickness of few micro meter were obtained by using the equation

$$d = \frac{q_{\text{redox}}}{r \cdot x \cdot F} \quad \dots(1)$$

where V is the molar volume of aniline (93.13 cm³/mol), r is the roughness factor (r=1 is assumed), x is the redox charge efficiency (x≈ 0.2) and F is the Faraday's constant¹⁹.

RESULTS AND DISCUSSION

The cyclic voltammogram in blank solution figure 1 shows two main reversible redox systems at 0.2 and 0.7 V, respectively, of comparable integrated charge, in which a total charge of 0.6-0.75 electron per monomeric unit is involved²².

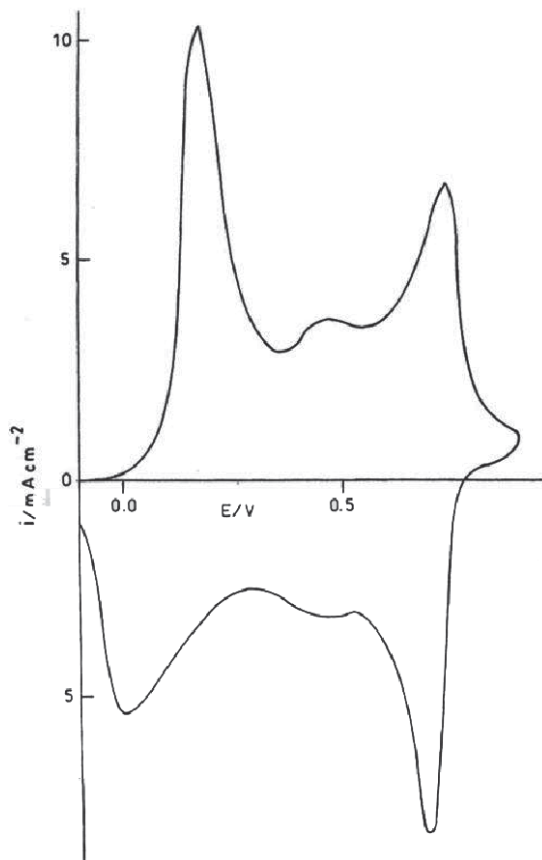
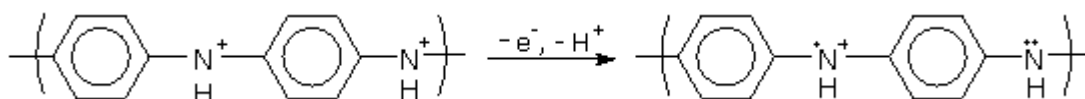


Fig. 1: Cyclic voltammogram for polyaniline-film electrode in 0.5 M sulfuric acid at $v=50 \text{ mVs}^{-1}$

The conducting behavior is very specific only within these potential limits²³. In any case, at potential 0.7 V and in the absence of the monomer, it under goes slow autoacceleration or self-catalysis into a material that is reversibly oxidized and reduced in a single cycle half way between the previous ones²⁴. In the cyclic voltammogram, the two redox systems correspond to two different processes (i.e. oxidation of monomer and self-catalysis or autoacceleration of polymer deposited at the

electrode) the oxidation of monomer occurs at lower potential whereas autoacceleration occurs at higher potential, therefore, the amount of polyaniline formed at the electrode is direct consequence of anodic peak current, hence of great significance for kinetic studies of electrochemical polymerization

of aniline. The anodic peak at ca. 0.2 V vs. SCE has been well understood as the oxidation of polyaniline deposited on the electrode which corresponds to the conversion of amine units to radical cation (Semiquinones)^{6,17}.



At potential less than (0.2 V) neither polymerization of aniline nor other parasitic reactions were observed. The successive potential scans between (10-100 mVs⁻¹) increases the peak current, indicating the buildup of the electroactive polyaniline on the electrode surface. At various increments of the anodic current at ca. 0.2 V vs. SCE during the polymerization, the masses of polyaniline deposited on the electrode were measured. Fig. 2 and Table, shows that anodic current is having direct relationship with the mass of PANI deposited on the electrode, when the current is below ca. 80 mA. However, the rate of polymer formation is a function of anodic current. A negative deviation from the linear behaviour occurs if current is further increased from 80 mA. Mass-current relation was observed at both lower and higher current values. But direct proportionality with

current was seen only at lower current value. So it lead to believe that to monitor the amount of the polymer deposited on the electrode and therefore, to study the rate of PANI formation i.e. the oxidation of aromatic amine leading to PANI deposition on the electrode follows the Faraday's Law. Some kinetic studies involving electropolymerization of aniline using charge as a measure for the amount of polymer formed were found in the literature²⁶⁻²⁸.

Tafel Plot Measurements

The classical method of electrochemical kinetics involves the measurement of log *i* – E curves under conditions of very rapid mass transport so that the electron-transfer process is rate controlling. The log *i* – E values were calculated from the Tafel equation.

Table 1: Kinetic parameters for aniline oxidation at platinum electrode at pH=3.7, conc of aniline=2x10⁻² mol l⁻¹ and temp=23° C.

*(mV/sec)	** (mA)	Mass***
10	26	2.03
20	34	3.45
30	51	5.56
40	66	7.68
50	74	8.72
75	96	10.01
100	131	12.02

*Scan rate, **Peak current, ***Mass of PANI deposited at the Pt.electrode(g) × 1000

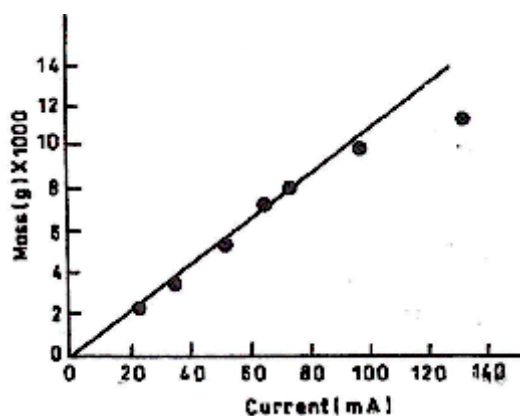


Fig. 2: Mass of polyaniline deposited on the electrode vs anodic peak current at ca. 0.2 V vs SCE.

$$i = dQ/dt = nFAk. C \exp / (\alpha nF/RT) (E-E_0) \dots(2)$$

This technique is essentially suited to relatively slow reactions where mere sophisticated relaxation methods may be needed for rapid processes. From the slope of the straight-line portion of the $\log i - E$ curve, it can easily calculate the product βn_a the product of the anodic transfer coefficient (β) by the number of electrons in the rate controlling step. Details of Tafel plot and other forms of the pertinent equation are given by Delahay 29. Further, from a series of Tafel plots taken with varying bulk concentration of electroactive species (C_{red}^b) one can measure $\log i$ at a constant E_{app} . A plot of $\log i$ vs. $\log C_{red}^b$ give a straight line whose slope indicates the exponent or order of the electrochemical reaction with respect to C_{red}^b . This method has been used widely by Vetter³⁰.

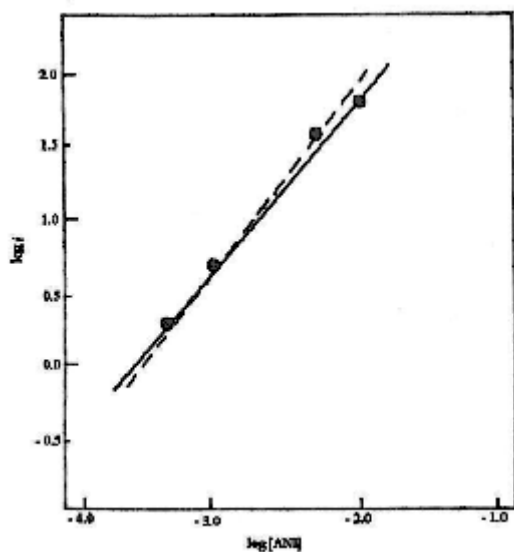


Fig. 3: Reaction order for ANI oxidation by APS: Solid line, slope = 1.1; dotted line, slope = 1.3; current in mA. Conc. (mol l⁻¹)

Tafel measurements were carried out using a pt wire electrode; Linear Tafel regions were obtained for different concentration of aniline. Fig. 3. shows the plot of $\log i$ vs. $\log ANI$ the values for $\log i$ were measured in all cases at 0.7 V vs. SCE. The experimental value of slope is between 1.1 and 1.3 indicating first order kinetics with respect to aniline concentration.

Rate expression

The kinetic studies of electrochemical polymerization of aniline were done on the experimental facts that anodic current obtained increases with potential scan rate and is directly related to the amount of PANI deposited on the electrode. The voltammogram show a couple of redox current peaks, and the anodic and the cathodic peaks lie at 0.2 and 0.7 V vs. SCE, respectively, the peak currents are fairly well proportional to the rate of the potential scan. It is further confirmed by the Fig. 4 that anodic current (therefore, the amount of polymer at electrode) as a function of cycle number, i.e. reaction time, at various concentration of aniline.

At different rates, the amount of polymer formed increases with increase in aniline

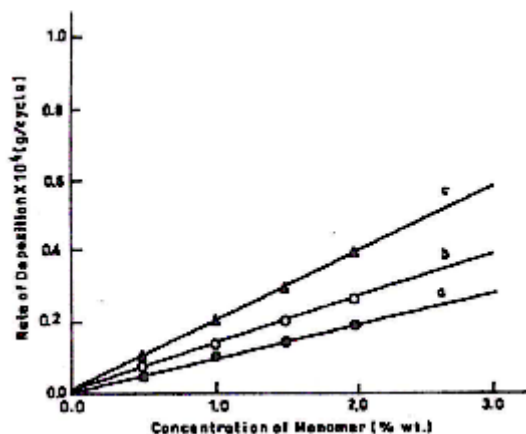


Fig. 4: The rates of polyaniline deposition at various anodic peak current (1.0-5) (mA) vs. monomer concentration

concentration. Higher rate (R_p) corresponds to higher concentration of aniline. At any point of time, the slope of the curves can obtain rate of polymer formation. The rates of electrodeposition of ANI were determined by the slope of the curves against the concentration of aniline at various anodic current values. Since all the plots give straight line passing through origin.

It indicates the first order dependence of R_p on the aniline concentration ANI as expressed in the following equation. 2)odic peaks lie at 0.2 and 0.0

$$R_p = k_{app} [\text{ANI}] R \quad \dots(3)$$

where k_{app} is a set of apparent first order reaction rate which are the slopes of anodic peak current vs. time. The plot k_{app} vs. reaction time is shown in Fig. 5, the gradual increase in k_{app} with reaction time

From the quantitative study of self-catalysis or autoacceleration, the k_{app} values were plotted against the mass of PANI deposited on the platinum electrode. A linear plot is obtained(not shown) with a positive intercept. It indicates mass of PANI deposited is directly proportional to the k_{app} . The intercept corresponds to k' for the initiation or nucleation of aromatic amine and below which there is no PANI deposition. Hence, the nucleation

process is rate determining step for the electro polymerization of aromatic amine.

$$k_{app} = k [\text{PANI}] + k' \quad \dots(4)$$

Thus rate of PANI deposition can be expressed as,

$$R_p = k' [\text{ANI}] + k [\text{PANI}] [\text{ANI}] \quad \dots(5)$$

Both k and k' are dependent on scan rate, switching potential, pH, reaction temperature and anion concentration etc.

Since, *p*-amino diphenylamine is formed as a dimer from the oxidation of aniline. The resulting polymers formed during the course of polymerization have lower oxidation potential than aniline. The overall electropolymerization is a second-order reaction. The eq.5 explains the second-order kinetics for the overall electropolymerization of aniline.

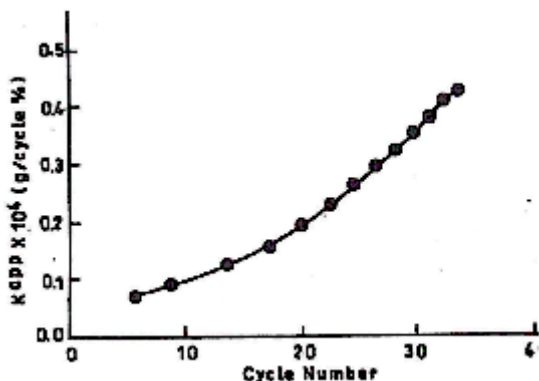


Fig. 5: A plot of K_{app} vs. reaction time (Minutes)

Reaction mechanism

The reaction mechanism of electropolymerization of aniline in a redox reaction, scheme I in figure 6 was proposed by Mohiliner *et al.*⁵ and supported later by Diaz and Logan³ and Noofi *et al.*²⁵. It is observed from these results that a proton-dissociation reaction must be involved in the redox reaction in such a manner that the reaction occurs only in strong acid solutions. Therefore, some modification of the Mohilner's model seems to be desired and scheme II given in figure 6, has been suggested on the basis of the work reported by many researchers

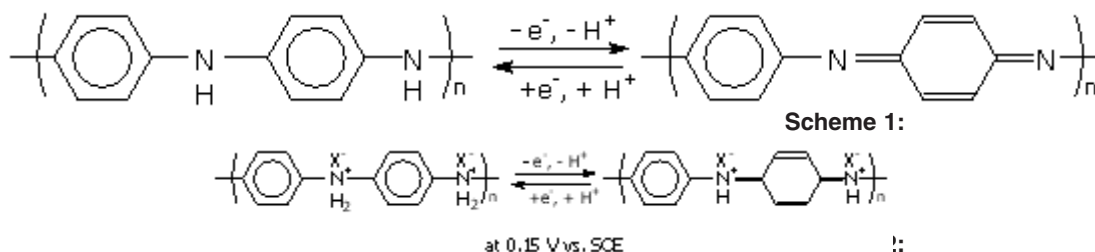


Fig. 6: Reaction scheme of polyaniline films concerning the proton addition elimination. Scheme I is a model proposed by Mohilner *et al* [5] and Scheme II a modified model proposed here. X denotes anionic species of solution. Equilibrium of the proton-dissociation reaction between Scheme I and Scheme II seems to be established at pH = 3~ 4.

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