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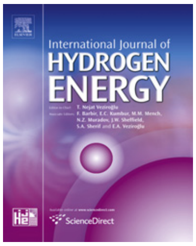

# Catalytic enhancement of hydrogen evolution reaction on copper in the presence of benzylamine

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ABSTRACT

Benzylamine catalytic effect on the cathodic hydrogen evolution in acid aqueous solution has been studied on copper electrode. Experimental results obtained by voltammetric techniques emphasize that the presence of benzylamine in 1 M sulfuric acid solution enhances the hydrogen evolution reaction (HER). In such a solution, benzylamine is protonated and exists as benzylammonium cation. Kinetic parameters of HER have been determined, observing a significant increase of the exchange current in the presence of benzylamine. Also, a decrease of the cathodic transfer coefficient has been noticed. Activation energy for HER has been computed on the basis of the Arrhenius plots. In the presence of benzylamine the activation energy was 33.0 kJ $mol^{-1}$, whereas without benzylamine a greater value was obtained: 94.6 kJ $mol^{-1}$. The catalytic effect of benzylamine was confirmed by electrochemical impedance spectroscopy. The considerable diminution of the double layer capacity is a valid proof of the strong adsorption of benzylamine at the Cu – sulfuric acid solution interface, while the reduction of the charge transfer resistance is a symptom of the enhancement of HER. *Ab initio* molecular modeling of benzylammonium ion showed that, due to a high value of the dipole moment, the molecules are oriented in the most favorable position for the charge transfer reaction, i.e., with the protonated amino group facing toward the electrode.

## 1. Introduction

The cathodic hydrogen evolution reaction (HER) still incites great interest, since water electrolysis has proven to be one of the most "clean" methods to produce hydrogen. Until now, the reduction of the operating voltage and consequently of the hydrogen production costs has been achieved either by catalytic enhancement of both hydrogen evolution reaction and oxygen evolution reaction, or by operating the electrolysis at high temperatures and pressures and by using an electrolyte with good conductivity. Development of ion exchange membranes for electrochemical reactors gave a new impulse to the researches focused on minimizing the energy consumption for hydrogen production. Catalytic enhancement of the HER is one of the best available ways to increase the efficiency of the water electrolysis process, which can be achieved on one hand by using electroactive materials and modified electrodes for HER, and on the other hand, by introducing additives in the electrolyte solution as proton carriers.

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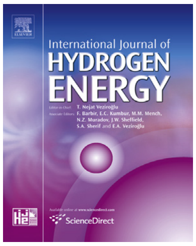

# Enhancement of hydrogen evolution reaction on platinum cathode by proton carriers

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ABSTRACT

The catalytic effect of aniline and benzylamine has been investigated for hydrogen evolution reaction on platinum electrode in sulfuric acid aqueous solution using voltammetric methods and electrochemical impedance spectroscopy. Kinetic parameters which characterize the hydrogen evolution reaction (cathodic transfer coefficient, exchange current density) have been determined using Tafel plots. It has been found that the addition of amines leads to an increase of the exchange current density, explained by an increased concentration of protons available at the interface. The catalytic effect of benzylamine and aniline is strongly correlated to their molecular parameters, such as dipole moment and molecular surface coverage. Also, apparent activation energies for hydrogen evolution reaction from solutions with and without addition of aromatic amines have been calculated. Electrochemical impedance spectroscopy results confirm an overall enhancement of hydrogen evolution in the presence of amines, as indicated by the lower values of charge transfer and adsorption resistances and by the decrease of characteristic time constants.

## 1. Introduction

The plenary affirmation of hydrogen as energy carrier focused the researches to more economic and environmentally friendly ways to produce hydrogen. Among the industrial methods for hydrogen production a notable place is occupied by the electrochemical process, on the one hand, due to the technical advantages as: stability in control of process parameters and reliable operation, on the other hand, due to the operating possibilities in large variations of energy supply, characteristic for the renewable sources like photovoltaic cells, wind turbines and wave energy converters [1–4]. The electrochemical procedure is based on water electrolysis process. The major disadvantage of this method is obviously the high energy consumption for electrolysis [5]. Consequently, the interest of researchers has been targeted to the catalytic enhancement of the cathodic hydrogen evolution reaction (HER). The investigation of cathodes with catalytic activity for HER has led to significant scientific and technical results. Electroactive cathodes based on platinum metals were realized by depositing a thin film on common metals, so that, cathodes costs for water electrolysis were substantially reduced [6–11]. Due to the prohibitive prices of platinum and platinum group metals the HER has been studied as well on other metals and alloys, oxide films or modified electrodes [12–22]. Skeleton non-noble metals, e.g. Ni, have demonstrated good catalytic properties in order to be used as electrode materials for water electrolysis [23–28].

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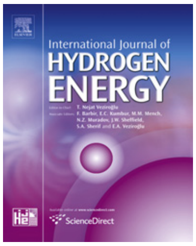

# Aromatic amines as *proton carriers* for catalytic enhancement of hydrogen evolution reaction on copper in acid solutions

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ABSTRACT

The catalytic effect of some aromatic amines towards hydrogen evolution reaction on copper in diluted sulfuric acid solution has been studied. Since amines facilitate the transport of protons from the solution bulk to the interface in the cathodic hydrogen evolution reaction, they are known as *proton carriers*. The catalytic effect of aniline, *N*-methylaniline, *N*-ethylaniline, *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, *o*-toluidine, *m*-toluidine and *p*-toluidine has been highlighted by linear sweep voltammetry. The kinetic parameters for the hydrogen evolution reaction (cathodic transfer coefficient 1-$\alpha$ and exchange current density $i_o$) in the presence of the studied aromatic amines were derived from the Tafel plots. It has been found that the catalytic effect of amines is active even at low concentration. Thus, in 0.5 mol $L^{-1}$ $H_2SO_4$ solution the exchange current density increases by two orders of magnitude, from $2.01 \cdot 10^{-5}$ A $m^{-2}$ in the absence of aniline to $2.85 \cdot 10^{-3}$ A $m^{-2}$ in the presence of $10^{-4}$ mol $L^{-1}$ aniline. The influence of amines concentration on the catalytic effect is described in detail for the case of *m*-toluidine. The results obtained by voltammetry have been compared with electrochemical impedance spectroscopy data. Furthermore, the kinetic parameters for the hydrogen evolution reaction have been determined as a function of temperature and amines concentration.

## 1. Introduction

The perspective that hydrogen will become one of the most important energy carriers in the future stimulates the researches in this field, on the one hand to discover economic methods to produce hydrogen, on the other hand to improve the existing technologies. A special emphasis is placed on methods that can use renewable energy resources. Among them, a leading role is occupied by electrochemical hydrogen generation, due to its advantages: stability of process parameters control, operational safety, environmental friendliness and, above all, the ability to operate even at large fluctuations in energy supply, typical for renewable sources such as wind, wave and photovoltaics. The major disadvantage of the electrochemical process is obviously the high electricity consumption in the electrolysis process, which is why further investigations are focused on ways to enhance hydrogen evolution reaction.

Several systematic studies performed over the years by many researchers have emphasized that platinum group metals are excellent catalysts for hydrogen evolution reaction (HER) [1,2]. Due to prohibitive prices, they are not used as commercial cathodes for water electrolysis, whereas the costs of hydrogen electrochemical reactors would be overgrown.

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# Effect of temperature on the electrochemical synthesis and properties of polyaniline films

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ABSTRACT

The effect of temperature on the electrochemical oxidative polymerization of aniline and on the electrochemical properties of the resulting polyaniline (PANI) film was studied. The electrochemical deposition of PANI has been carried out on platinum at different temperatures. Three different films (PANI-25, PANI-40 and PANI-60) have been prepared at 25, 40 and 60 °C by electrochemical polymerization and characterized by cyclic voltammetry and electrochemical impedance spectroscopy. Increasing the synthesis temperature leads to an increase of the polyaniline films thickness from 0.4 to 0.9 μm and, respectively, 1.1 μm, associated with an increase of the films capacitances from $3 \times 10^{-2}$ F cm$^{-2}$ to $7 \times 10^{-2}$ F cm$^{-2}$ and $10 \times 10^{-2}$ F cm$^{-2}$. The impedance measurements showed that only PANI-25 and PANI-40 exist in the conductive state over a large potential window, while PANI-60 has an intermediate behavior at low and high electrode potentials.

## 1. Introduction

Among conductive polymers, polyaniline (PANI) [1,2] has been widely studied in the last decades due to its simple synthesis, stability in ambient environment, unique electrochemical properties and possibility of deposition on various substrates [3]. PANI is frequently used in electrochemical devices because of its easy preparation, good chemical stability and the possibility of behaving like an insulator, a semiconductor or a metal, through chemical doping or dedoping process. There are several ways to influence the structure and properties of the resulting polyaniline film, such as electrical conductivity, processability and solubility. One of the synthesis parameter that can be varied for both chemical and electrochemical polymerization of aniline is temperature. Several studies have been conducted at low temperatures [4–6] since it has been reported that polyaniline obtained at sub-zero temperatures should exhibit a higher conductivity. However, high conductivity polyaniline can be prepared by the chemical oxidative polymerization of aniline at temperatures above room temperature with an optimum between 50 and 60 °C [7]. It has been reported that the effect of thermal treatment on the conductivity of electrochemically prepared polyaniline films is an increase of the conductivity at moderately high temperatures up to 70 °C [8] or even 100 °C [9]. At elevated temperatures a marked decrease of the conductivity is observed generally due to molecular structure changes such as deprotonation, oxidation, chain scission and cross-linking reactions [10–13]. Studies on the thermal stability of polyaniline films have shown that 80 °C is the minimum temperature at which a noticeable decrease on the electrochemical activity was observed [14]. Nevertheless, the rate of the electrochemical polymerization increases with temperature. In case of the electrochemical polymerization of substituted anilines a 4.2% per degree increase of the polymer rate formation is obtained [15] although ortho-coupling and degradation reactions are also favored by temperature.

The aim of this study is to investigate the effect of moderately high temperatures on the electrochemical synthesis of polyaniline and to determine the electrochemical properties of PANI films obtained at different temperatures. Cyclic voltammetry has been applied to study the redox reactions of PANI films deposited on platinum and to evaluate the films pseudocapacitances. Electrochemical impedance spectroscopy has been proven to be a valuable method in the study of electroactive polyaniline films [16–20] and it was the method of choice for studying electrical resistance, double layer capacitance and pseudocapacitance of polyaniline films.

## 2. Experimental

Aniline was freshly distilled under reduced pressure and stored in dark at low temperature. Double distilled water and analytical grade sulfuric acid were used to prepare the electrolyte solutions.

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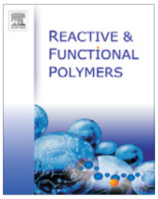

# Impedimetric detection of dopamine on poly(3-aminophenylboronic acid) modified skeleton nickel electrodes

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ABSTRACT

Detection of biologic compounds in particular dopamine is usually based on the complexation between boronic acid groups and diols. For this reason the development of new sensors based on direct monitoring of boronic acid–diol complexation is attractive. A measurable electric response due to a change in the dopamine concentration can be achieved on electrodes modified with boronic groups. In this work a modified electrode has been obtained by electropolymerization of 3-aminophenylboronic acid in aqueous solutions on a preformed polyaniline layer electrochemically deposited on smooth and skeleton nickel electrodes. The modified electrodes have been tested as impedimetric sensors for the detection of dopamine in aqueous phosphate buffer at pH = 7.4. Both sensors gave a linear response for dopamine concentrations between $10^{-5}$ and $10^{-10}$ mol $L^{-1}$. Poly(3-aminophenylboronic acid) modified skeleton nickel electrode has the advantage of an increased specific surface area, that lead to a high density of boronic acid groups and hence to a better sensitivity.

## 1. Introduction

Electrochemical sensors based on conducting polymers offer some advantages and possibilities to detect biological compounds. One of the most intensively investigated conducting polymers is polyaniline (PANI) due to its facile synthesis, excellent stability in different solutions, good electronic properties, and strong biomolecular interactions [1]. Various sensors and biosensors, such as enzyme sensors, DNA sensors and immunosensors based on PANI are reported [2,3]. The emeraldine salt (ES) form is the only conducting state among the three oxidation states of PANI and it is obtained in acidic conditions (pH = 2.5–3.0). The pH sensitivity is unfavorable for application in biosensors, because most bioassays must be performed in neutral or slightly acidic conditions. In order to overcome this disadvantage, functionalization strategies were adopted. In some studies *N*-substituted anilines were used instead of aniline and it was found that the alkyl chain, which is covalently bonded to the nitrogen atom, prevents the formation of the emeraldine base (EB) form, and finally the obtained polymer is not pH sensitive [4]. Another derivative of PANI, self-doped PANI, which is usually known as sulfonated PAI, shows redox activity even in solutions with neutral pH [5]. Sulfonated PANI was used in amperometric biosensors [6]. It has also been demonstrated that blends of PANI that included negatively charged co-components such as sulfonic acid or polyacrylic acids exhibit redox activity in neutral aqueous solutions [7]. The polymerization of monomers containing a boron moiety leads to poly(aniline boronic acid) PABA [8] a polymer which exhibits redox activity also in solutions with neutral pH. PABA was used in the detection of fluoride [9], iodide [10], saccharides [11,12], butylamine [13] and dopamine [14] based on the analyte interactions with the boronic acid functionality. Composite materials for the detection of DA have been developed, based on PABA obtained by template electrochemical polymerization [15]. Also acryloyl derivatives of 3-aminophenylboronic acid have been used to obtain copolymers in form of hydrogels with sensitivity towards glucose detection [16–18]. Most of the papers investigate the electropolymerization of aminophenylboronic acid (ABA) on noble electrodes (platinum or gold) and most of the developed sensors are either amperometric or potentiometric sensors.

In this work a method has been developed for the preparation of a sensitive electrode based on PABA for the detection of dopamine. The method consists in the electrochemical deposition of two layers of conducting polymers, first a polyaniline layer and then a sensitive PABA layer. This approach has been already used for the preparation of an amperometric protein sensor, obtained by the application of two separate polymer layers, one of polypyrole and one of poly-aminophenylboronic acid on screen-printed platinum electrodes [19]. In our work, the polymer films have been

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# Synthesis of polyaniline nanostructures by electrochemical deposition on niobium

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## ABSTRACT

Nanostructured polyaniline films have been electrochemically synthesized on passivated niobium substrate by potentiodynamic method in 0.5 and 1 mol $L^{-1}$ $H_2SO_4$ solution and different aniline/acid molar ratios. The niobium oxide particles formed during passivation induce the nucleation of polyaniline nanofibers via adsorbed phenazine nucleates. The infrared spectra of polyaniline nanofibers showed the presence of vibrations attributed to phenazine-units in the polymer chain which support the phenazine nucleates theory for polyaniline nanofiber growth. The morphology of polyaniline is also influenced by acid concentration and a branched structure consisting of polyaniline nanofibers with a mean diameter of 70 nm is observed for 1 mol $L^{-1}$ sulfuric acid solution. The shape of the impedance spectra is controlled by charge transport through ion diffusion, with higher diffusion resistances for granular polyaniline. The capacitance increases with the polymer layer thickness and has higher values for nanofibrilar than for granular polyaniline.

## 1. Introduction

Nanostructured conducting polymers, especially polyaniline (Pani) have been intensively studied in the last years due to their potential applications in micro- and nanoelectronics and for the construction of sensors, biosensors and biomedical devices [1,2]. It is expected that nanostructured polyaniline will show net superior properties compared to amorphous polyaniline, or even unique properties. Several studies have recently shown that going down to nano-level dimensions, together with a marked increase of the specific surface area, can bring further improvement of several other properties like conductivity, processability and sensing properties. Several methods have been proposed to synthesize polyaniline nanostructures. Most of them are chemical oxidative methods which include the use of insoluble hard templates such as zeolites or polymer membranes with controlled pore size or soluble soft templates such as macromolecules, surfactants [3] or nanofibers such as $Mn_2O_3$ that acts as both guiding template and oxidant [4]. Alternative synthesis methods include nanoseeding which is usually done with other nanostructured organic or inorganic materials like carbon nanotubes [5,6], polyaniline [7], graphene oxide [8] vanadium oxide nanofibers [5]. Attempts have been made to develop template free synthesis methods including chemical interfacial polymerization [9–13]. Chemical synthesis can be also applied as template free method to produce polyaniline nanostructures by changing the reaction conditions, e.g. the monomer/oxidant ratio [14] and the rate of oxidant addition [15], by using milder oxidants [16–18] or by the homo- or co-polymerization of aniline dimers [19].

Despite the net advantage of chemical method in producing large scale quantities of polyaniline, the electrochemical method in turn allows a more rigorous control of synthesis parameters and offers a very convenient way to study the electrochemical properties of polyaniline nanofibers. Nanostructured conducting homo- or copolymers of polyaniline have been obtained by template free electrochemical methods such as cyclic voltammetry [20–22], galvanostatic [23,24] or potentiostatic [25] methods, pulse galvanostatic or potentiostatic methods [26,27]. The results point out that the nanofibrilar morphology might be an intrinsic property of electrochemically synthesized polyaniline [25], however it is strongly affected by synthesis conditions. One of the factors reported to influence the morphology [28], as well as the diameter and length of nanofibers [23] is the scan rate in potentiodynamic methods.

It is generally accepted that the substrate plays a special role in the formation and growth of polyaniline nanofibers, however there are only scarce studies regarding the effect of electrode material on the formation and growth of electrochemically deposited

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# Scan Rate Dependent Morphology of Polyaniline Films Electrochemically Deposited on Nickel

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The effect of scan rate on the morphology and properties of polyaniline has been investigated for samples deposited electrochemically on nickel from sulfuric acid solution. A nanofibrilar network structure has been obtained for low scan rates (10, 25 and 50 mV $s^{-1}$) whereas for the highest scan rate (100 mV $s^{-1}$) the structure was more compact, the nanofibrils aggregated and their features were not very obvious. Both diameter and length of nanofibers are scan rate dependent, decreasing from 140 to 90 nm and from 1.35 to 0.72 μm when the scan rate is increased from 10 to 50 mV $s^{-1}$. The nanofiber network tends to be more compact and with less free-volume as the scan rate is increased. Generally, high specific capacitances and low charge transfer resistance values are obtained for all nanofibrilar polyaniline films as compared to the compact structure. The optimum scan rate for deposition was found to be 25 mV $s^{-1}$, leading to the highest specific capacitance and lowest charge transfer resistance.

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**Keywords:** Polyaniline nanofibers, scan rate, nickel, electrochemical impedance spectroscopy

## 1. INTRODUCTION

Polyaniline is an intrinsic conducting polymer that has been intensively investigated due to its versatile use in a large number of practical applications, i.e. the fabrication of electrochemical storage devices, sensors, biosensors, anticorrosive coatings. Polyaniline can be obtained by either chemical or electrochemical oxidative polymerization. Chemical polymerization has the advantage of producing large scale quantities of polymer, but electrochemical polymerization allows a more rigorous control of synthesis parameters and is useful when polymer film electrodes are needed. The synthesis method and processing conditions play an important role in tailoring polymer properties, i.e. morphology and as a

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**PAPER**

# The stabilization of charged states at phenazine-like units in polyaniline under p-doping: an *in situ* ATR-FTIR spectroelectrochemical study

**Andrea Kellenberger,[ab] Evgenia Dmitrieva[a] and Lothar Dunsch*[a]**

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The structure and stabilization of charged states during p-doping of polyaniline (PANI) were studied by *in situ* ATR-FTIR spectroelectrochemistry. The role of phenazine-like units in several copolymers of aniline and a phenazine derivative (3,7-diamino-5-phenylphenazinium chloride, phenosafranine) was investigated by spectroelectrochemistry. PANI and three copolymers with different aniline to phenosafranine ratio were electrochemically prepared. FTIR spectra of as-prepared polymers as well as *in situ* FTIR spectra during the oxidation of the polymers give evidence of the presence of phenazine-like units in the structure of electrochemically prepared PANI, as shown by vibrations of the phenazine rings. New bands corresponding to the in-plane and out-of-plane C–H vibration of 1,2,4-trisubstituted benzene nuclei in the phenazine skeleton are found at 1033, 957, 880, 766 and 681 $\text{cm}^{-1}$. The potential dependence of IR bands observed during oxidation of the polymers was compared to that of the ESR intensity and the absorption data and points to the diamagnetic species like π-dimers formed at higher oxidation level of PANI. This charged state is shown to be fixed at the link of the phenazine-like units with the linear segments of PANI.

## Introduction

The chemical structure of PANI is often given as a linear model with three oxidation states of the polymer: the completely reduced form having only benzenoid rings (leucoemeraldine base), the fully oxidized form with only quinoidic nitrogen (pernigraniline base), and the half-oxidized form (emeraldine base) (Fig. 1). Based on these structures the well accepted polaron–bipolaron model for conducting polymers is interpreted as follows: the polaron is the singly oxidized form of a polymer segment with spin $s = \frac{1}{2}$ and the bipolaron is a doubly oxidized form which is diamagnetic.[1] Brédas *et al.* studied the redox states of oligothiophenes with different chain lengths. For a long oligomer or an infinite polymer a new charged state "two polarons on a single chain" is energetically favoured and characterized by two absorption peaks in the UV/vis/NIR spectra.[2] More recently the equilibrium and kinetics of systems with either polarons and bipolarons or polarons and polaron pairs as charged states were compared by Paasch *et al.*[3]

It is well accepted in the scientific community that PANI consists preferably of a linear arrangement of the monomer.[4] Since the early works of Willstätter and Moore[5] and Green and Woodhead[6] for chemically synthesized PANI and the later works on electrochemically prepared PANI[7] it is obvious that phenazine rings have to be considered as a part of the polymer chain (Fig. 2a). The presence of substituted phenazine structural units, formed by the intramolecular cyclization of branched PANI chains, has been identified by the appearance of characteristic FTIR bands at 1623, 1414, 1208, 1144, 1136, 1108 $\text{cm}^{-1}$ and Raman bands at 1645–1630, 1420–1400, 1380–1365, ∼575, and ∼415 $\text{cm}^{-1}$.[8–10] Do Nascimento *et al.* demonstrated that the cross-linking units in PANI nanofibers are phenazine- and/or oxazine-like structures, which show Raman bands at *ca.* 1640, 1380 and 578 $\text{cm}^{-1}$.[11–13] Therefore, phenazine units play an important role in defining the structure, morphology and properties of PANI.

In the present work the role of phenazine-like units in the formation and stabilization of charged states in PANI is studied using *in situ* FTIR spectroelectrochemistry. The p-doping behaviour of PANI is compared with that of several copolymers containing both phenazine derivative (phenosafranine) and aniline units as well as with polyphenosafranine (PPS) (Fig. 2b). The copolymers with increasing portions of phenosafranine are denoted as PANI-PPS1, PANI-PPS2 and PANI-PPS3, respectively (see experimental part).

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# Structure Dependence of Charged States in “Linear” Polyaniline as Studied by In Situ ATR-FTIR Spectroelectrochemistry

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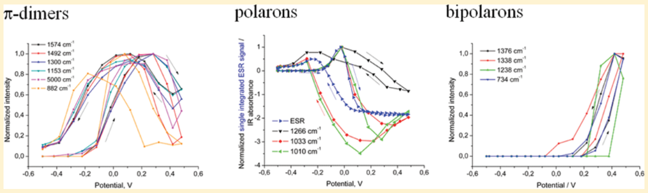
**ABSTRACT:** The electrochemical doping of emeraldine salt and emeraldine bases with different weight average molecular weights was studied by in situ Fourier transform infrared (FTIR) spectroelectrochemistry using attenuated total reflection (ATR) technique. The formation and stabilization of charge carriers in polyaniline during p-doping was followed in dependence of the chain branching. The potential dependence of the IR bands during the oxidation of the polymer clearly demonstrates the formation of the different charged polymer structures ($\pi$-dimers, polarons, and bipolarons). It is shown that IR bands usually attributed to a semiquinoid polaron lattice correspond in fact to doubly charged species, $\pi$-dimers, which are face-to-face complexes of two polarons. Bands corresponding exclusively to polarons have been identified at 1266, 1033, and 1010 cm$^{-1}$, suggesting that polarons are predominantly stabilized on the linear segments near the polymer branches by phenazine.



## INTRODUCTION

The chemical structure of polyaniline (PANI) is often given by a linear model with three oxidation states of the polymer: the completely reduced leucoemeraldine, the intermediate emeraldine, and the fully oxidized pernigraniline base.[1] Switching between the different oxidation states of PANI can be realized by chemical or electrochemical doping/dedoping. In a typical cyclic voltammogram of PANI, the first redox peak has been attributed to the transformation of leucoemeraldine into emeraldine, and the second main peak to the further oxidation of emeraldine to fully oxidized pernigraniline form.[2] Considering a linear PANI structure, the well-accepted polaron−bipolaron model for conducting polymers is interpreted as follows: the polaron (radical cation) is the singly oxidized form of a polymer segment with spin $s = 1/2$ and two optical transitions; the bipolaron (dication) is a doubly oxidized form, which is diamagnetic and has one optical transition.[3,4] Miller and co-workers suggested a *polaron-$\pi$-dimer model* in addition to bipolarons in oxidized polythiophene.[5] The $\pi$-dimer is considered as a face-to-face complex of two radical cations interacting through their $\pi$-orbitals. However, $\pi$-dimers formed during p-doping of conducting polymers are also reported for polypyrole[6] or PANI.[7] Our group has previously shown that the most important intermediate formed during aniline polymerization, the p-aminodiphenylamine, forms a $\pi$-dimer of two radical cations under oxidation in acidified organic solvents.[8]

Fourier transform infrared (FTIR) spectroscopy as a powerful tool for identifying types of chemical bonds in a molecule by the molecular “fingerprint” is used in combination with electrochemistry for detailed structural information on the intermediates and products in a charge transfer reaction. Attenuated total reflection (ATR) technique is especially useful for IR measurements of solids (films, polymers and powders), semisolids (pastes, creams, gels), and liquids as well as dark colored materials. By in situ ATR-FTIR spectroelectrochemistry, structural changes in the polymer film during its doping can be followed.[9−11]

During the first oxidation peak of electrochemically prepared PANI, the IR bands at 1564, 1481, 1304, 1250, and 1144 cm$^{-1}$ were attributed to a semiquinoid polaron lattice structure.[12,13] The second oxidation step results in the formation of quinoid structures with vibrations at 1625, 1569, 1376, 1341, and 846 cm$^{-1}$. The IR band at 1250 cm$^{-1}$ is often attributed to the polaron lattice structure[14] based on its analogy in Raman spectroscopic studies, giving a Raman band at around 1253 cm$^{-1}$ attributed to the $C-N^{\bullet+}$ stretching mode in the semiquinone radical cations.[15,16] The broad absorption band centered at about 5000 cm$^{-1}$ was interpreted as the intermediate oxidized metallic form of PANI.[17,18] Most studies on the electronic structure of PANI have used the linear structure model for interpretations in which PANI consists of a linear arrangement of the monomers. However, early works have shown that phenazine rings have to be considered as a part of the polymer chain for both chemically and electrochemically prepared PANI.[19−23] Such branches occur by aniline coupling reaction in the ortho-position of the quinoid structures - a reaction well-known in organic chemistry. The following intramolecular cyclization results in the formation of

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# *In Situ* ESR/UV−vis−NIR and ATR-FTIR Spectroelectrochemical Studies on the p-Doping of Copolymers of 3-Methylthiophene and 3-Hexylthiophene

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A combined spectroelectrochemical study by ESR/UV−vis−NIR as well as FTIR spectroscopy on the influence of the copolymer composition on the stabilization of charges upon electrochemical p-doping is presented. As compared to the parent homopolymers 3-hexylthiophene (**3-HeTh**) and 3-methylthiophene (**3-MeTh**) which seems to be irregular, FTIR studies of the copolymer of both monomers (**copMeHeTh**) point to a regioregular structure. The *in situ* ESR and UV−vis−NIR spectroelectrochemistry at higher doping levels of the polymeric materials proves bipolarons and polaron pairs as stable charged states in poly(3-hexylthiophene) as well as the copolymer **copMeHeTh.** During the p-doping of poly(3-methylthiophene) bipolarons are the dominating species at higher doping levels. It is demonstrated that only the simultaneous use of both the ESR and the UV−vis−NIR spectroscopy enables the differentiation of polarons (paramagnetic) and polaron pairs (diamagnetic) in a conducting polymer.

## Introduction

Conjugated polymers, such as poly(3-alkylthiophenes) (**PATh**s), have been extensively studied owing to their high stability of both their doped and undoped states as well as their structural versatility. The variation of the monomer structure by alkyl-side modification results in a broad modulation of the polymer morphology as well as electronic and electrochemical properties of the conjugated polymers. All these properties have led to significant developments in applications such as electric conductors, electrode materials, organic semiconductors, sensors, electrochromic devices, and transistors.[1] Moreover, polythiophenes have been often considered as a model for the study of charge transport in conducting polymers with a degenerate or nondegenerate ground state.[2]

Among the poly(3-alkylthiophene) precursors are 3-methylthiophene (**3-MeTh**) and 3-hexylthiophene (**3-HeTh**) monomers which are very useful in copolymerization reactions as starting materials together with other thiophene derivatives. The copolymerization reaction of two monomer units is used to combine desirable properties of two polymers like desired electrochromic properties and high electrical conductivities. It has been recognized that the copolymerization of 3-alkylthiophene derivatives leads to a higher thermal stability of doped **PATh**s[3] which is a tremendous problem for their application.[4] To achieve this aim, random copolymers of **3-MeTh** and 3-octylthiophene have been prepared.[3] The thermal undoping is significantly suppressed, and this effect has been attributed to the statistical decrease of the side-chain interactions. The effect of the copolymerization between **3-MeTh** and **3-HeTh** has also been discussed in terms of a new material which still has excellent solubility together with high electrical conductivity, even higher than the conductivity of poly(3-hexylthiophene).[5] This observation is attributed to the presence of **3-MeTh** moieties since this monomer shows an exceedingly high conductivity among the polythiophenes.[6] It was also found that the resultant copolymer has a good stretchability.

In this contribution an *in situ* ESR UV−vis−NIR and a FTIR spectroelectrochemical study of the copolymer (**copMeHeTh**) from 3-methylthiophene and 3-hexylthiophene on ITO electrodes is performed. The use of several *in situ* spectroelectrochemical techniques results in the direct detection of both the paramagnetic and diamagnetic species formed during electrochemical doping of such a copolymer. The structure of the copolymer is studied by *in situ* FTIR spectroelectrochemistry. This study is devoted to the description of the influence of the random distribution of the long side alkyl chain of the **3-HeTh** in the formation and stability of the charge carriers during the p-doping of the copolymer **copMeHeTh** using *in situ* ESR/UV−vis spectroelectrochemistry. These results are compared with those from the spectroelectrochemical study of the p-doping of the corresponding homopolymers poly(3-methylthiophene) (**p-3-MeTh**) and poly(3-hexylthiophene) (**p-3-HeTh**). To the best of our knowledge, there are no reports concerning the *in situ* ESR/UV−vis−NIR spectroelectrochemical study of the charge carriers involved in the mechanism of the electrochemical oxidation of the copolymer from **3-MeTh** and **3-HeTh**. The simultaneous use of ESR and optical spectroscopies does allow us to differentiate the nature of the charge carriers electrogenerated during the p-doping and to get the individual spectra of each intermediate.

## Experimental Section

**Chemicals.** Acetonitrile (ACN, puriss., absolute, ≥99.5% GC, $w(H_2O) \leq 0.001\%$) purchased from Fluka and ferrocene (p.a., ≥98%) from Merck were used as received. Acetonitrile was stored over molecular sieves. Tetrabutylammonium hexafluorophosphate ($n$-$Bu_4NPF_6$, puriss., electrochemical grade, ≥99.0% CHN) from Fluka was dried under reduced pressure at 80 °C for 24 h before use. All solutions were deaerated with nitrogen

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