

## Research paper

# Mobility of holes and polarons in polyaniline films assessed by frequency-dependent impedance and charge extraction by linearly increasing voltage



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## ABSTRACT

Thin films of semiconducting polyaniline hydrochloride were deposited on glass or silicon substrates. Frequency spectra of impedance measured at several voltages display regions of holes and polarons contributions and enable to evaluate their mobility  $2.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at the electric field of  $1 \times 10^5 \text{ V cm}^{-1}$ . Good agreement of the average value  $2.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  of holes mobility was obtained by another method-charge extraction by linearly increasing voltage (CELIV). A Poole-Frenkel type of electric field dependence of mobility assessed by frequency-dependent impedance points to trapping of the charge carriers. From the value of the work function measured by the Kelvin probe and from the position of HOMO level, the hole concentration  $2.9 \times 10^{18} \text{ cm}^{-3}$  was obtained. Using this concentration together with the mobility measured by the impedance spectroscopy and the CELIV method, the conductivity  $1.2 \times 10^{-5} \text{ S cm}^{-1}$  carried by holes was estimated. Our results widen the work dealing with the mixed electron and proton conductivity of polyaniline films in aqueous solution of acids published in the literature.

## 1. Introduction

Polyaniline (PANI) [1] is an organic semiconductor with three types of charge carriers, namely holes, polarons and ions, which is interesting from the theoretical point of view and brings potential in the field of specific applications. This material in an appropriate form falls into the family of conducting polymers characterized by easy synthesis and high stability. Its suitability for various applications has been demonstrated [2]. In organic electronics, PANI has found the use in photochromic devices, organic field-effect transistors, light-emitting diodes, photoelectric or photoelectrochemical cells [3,4] or Schottky barrier diodes. In the combination with silicon, PANI forms effective heterojunctions [5] used also for gamma-radiation detection [6], or ultraviolet photodetectors [7]. Recently, PANI has found application in fuel cells [8].

In functional semiconductor electronic devices, the carrier mobility represents an extremely important parameter for the elucidation of charge-carrier transport. The most traditional time-of-flight (TOF) [9–12] and electroluminescent transient (ELT) [13,14] methods have some disadvantages. For TOF, thick layers are needed contrary to the requirements for practical devices. In addition, the structural and electrical properties may change with the thickness [15]. ELT is applicable only to light-emitting diodes. Measurement of mobility using field-effect transistors (FET) [16,17] gives no information on bulk

transport [16] and it often encountered the contact problems that complicate the interpretation of electrical characteristics.

In present paper, the method of charge extraction by linearly increasing voltage (CELIV) and admittance spectroscopy has been used. CELIV method was for the first time introduced by Juška group [18,19], and then used for the mobility determination in polymer solar cells [20–22] and in metal-insulator-semiconductor (MIS) structure [23]. In the CELIV experiment, the charge carriers are usually injected by electrodes or generated by a light pulse.

The mentioned methods were based on the concept of charge-carrier transport in the energy bands which is supposed also in the polyaniline salts, i.e. in protonated emeraldine base [4,24] (Fig. 1).

Transport in this *p*-type material is realized by positive quasi-particles-holes in valence band. Other charge-carriers are polarons. The origin of the polarons considered in our article is elucidated in Fig. 1 where the rearrangement of electrons in the formula of emeraldine is shown. The protonated emeraldine (protonation is caused by the addition of protons, supplied by hydrochloric acid to imine nitrogen in polyaniline chains) contains unpaired electrons, stable cations radicals. Two electrons, each from electron pairs on imine nitrogens, are injected into the quinonediimine ring. They provide the third double bond to complete the benzenoid ring. Single unpaired electrons left on nitrogens represent cation radicals in chemical terminology, and polarons in the

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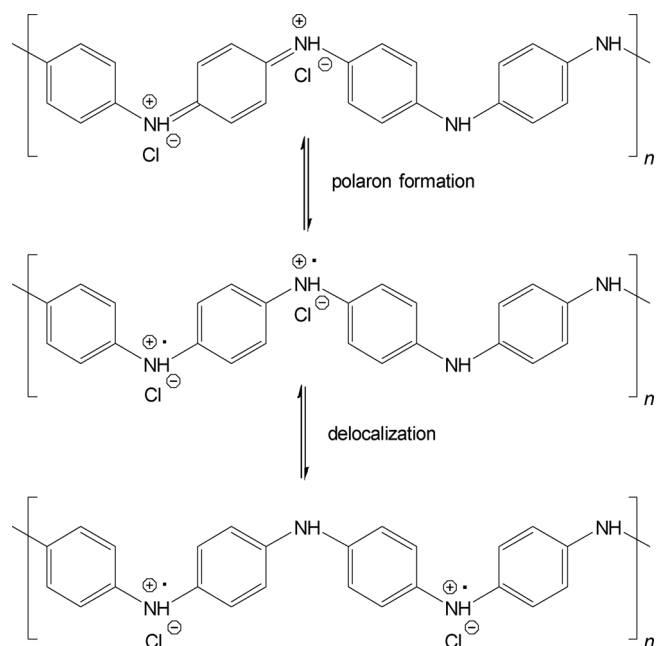


Fig. 1. Two electrons from main-chain double bonds are injected to a quinoneiminoide ring, which converts to a benzenoid one. Two unpaired electrons left on nitrogen atoms produce cation radicals, polarons. These may be delocalized over the polyaniline chain. Adapted from Ref. [1].

domain of physics. These may be delocalized over the polyaniline chain. The presence of unpaired spins can be identified in electron paramagnetic resonance experiments. Origin of the polarons is also shown in [25] in connection with the conductivity of PANI. Further charges contributing to transport are the hydrogen ions.

Many authors have studied conductivity of PANI. The influence of different aqueous acids on the protonation and conductivity is demonstrated in Ref. [25] but without specifying the type of charge carriers. PANI doped with Fe, Ni and La ions was published [26] and it was found that conventional HCl doping gives the highest conductivity. Babu et al. [27] used camphorsulfonic acid in addition to HCl and concluded that the enhanced conductivity is caused by electrons and trapped ions. The electrical conductivity of the doped samples was enhanced about 10 orders of magnitude when compared to non-protonated polyaniline. Mixed electron and proton conductivity of polyaniline films in aqueous solution of acids was reported [28]. It is difficult, however, to compare the conductivity measurement of polyaniline films immersed in the aqueous solution of acid [28] where polyaniline salt is dissociated and the contribution to the ionic conductivity is significant, with present study, where the polyaniline film has been tested in air under ambient humidity and potential dissociation of polyaniline salt is limited. The concentration of protons, pH of the aqueous medium, is also important. At low concentration of protons, high pH values, the deprotonation of polyaniline takes place. This results in the reduction of *electronic (non-ionic)* conductivity. For these reasons, the discussion based on the literature might be difficult for the reader to accept without additional extensive explanation.

The polaron transport depicted in Fig. 1 is the possible one but not necessarily the prevailing mechanism. Otherwise, the conductivity of the polyaniline salt would be of *n*-type which is at variance with the reality. The high conductivity, typically  $5 \text{ S cm}^{-1}$ , measured on PANI samples deposited on glass substrates can be, consequently, ascribed to the protons or holes as charge carriers. The presented results demonstrate that the holes contribution to the conductivity is several orders of magnitude lower compared with proton transport.

## 2. Experimental part

### 2.1. Preparation

Thin polyaniline films were deposited *in situ* on the substrates, (glass or *n*-type Si) immersed in the reaction mixture used for the preparation of PANI [29]. Aniline hydrochloride (20 mmol, 2.59 g) was dissolved in water to 50 mL of solution, and ammonium peroxydisulfate (25 mmol, 5.71 g) was dissolved separately also to 50 mL. Both solutions were mixed at room temperature and poured over the substrate placed in a Petri dish. The concentrations of reactants thus were 0.2 M aniline hydrochloride and 0.25 M ammonium peroxydisulfate. The coated substrates were removed after 2 h and rinsed with 0.2 M hydrochloric acid, followed by acetone, and dried at ambient atmosphere. The protonation occurs by this way. The obtained polyaniline hydrochloride films are green and conducting.

### 2.2. Measurements

Thicknesses of PANI layers, 70–160 nm, were determined by the atomic-force microscopy (AFM). CELIV measurement was performed in the dark and at room temperature. The equipment consisted of an oscilloscope OWN DS 7102 V, a functional generator Agilent 33250A, and a holder with the sample. The Au/PANI/*n*-Si/In structure was used for the measurement by the CELIV method. Its energy level diagram is shown in Fig. 2. The gold or indium electrodes represent ohmic contact to *p*-PANI and *n*-Si, respectively. In principle, the CELIV experiment consists in the application a linearly increasing voltage pulse and in measuring the current response over the time by the oscilloscope. If a negative polarity of the voltage ramp is applied to the gold electrode, the holes are injected into the whole volume of the PANI layer because the dielectric relaxation time is higher or equal to the transit time (relative dielectric permittivity of order of magnitude  $10^6$  was used [30]). For the injection coefficient of holes  $\gamma_p$  it holds

$$\gamma_p = \frac{J_p}{J_n + J_p}$$

where  $J_n$  and  $J_p$  are electron and hole currents, respectively. There is an effective injection of holes into PANI because the holes flowing in the direction from In to Au electrode overcome only 0.9 eV barrier while the potential barrier for electrons is 2.6 eV in the opposite direction.

Consequently,  $J_n \ll J_p$ , and  $\gamma_p \sim 1$ . At the positive polarity of the ramp, the holes are extracted. Measured transient current illustrates the delay of the charge extraction with respect to the voltage pulse and serves for determination of mobility.

Impedance spectroscopy is another powerful method for analysing the charge-carrier transport. Frequency dependence of the complex admittance was examined [31,32] but the frequency dependence of imaginary part of impedance is more convenient technique [33,34]. In present study, this part of complex impedance of PANI/silicon films has been examined as a function of frequency with a precision LCR meter E

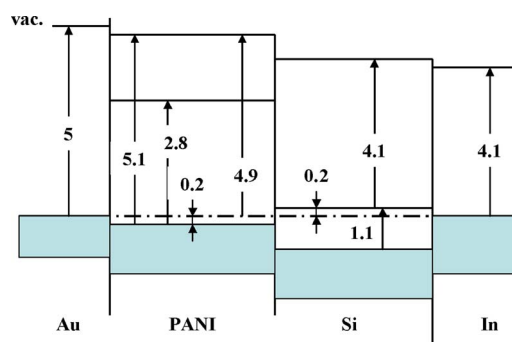


Fig. 2. Energy diagram of Au/PANI/Si/In structure. The values are in eV.

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