New view on the origin of high conductivity of polyaniline films protonated by hydrochloric acid

Radka Rutsch, Jiří Toušek, Jana Toušková

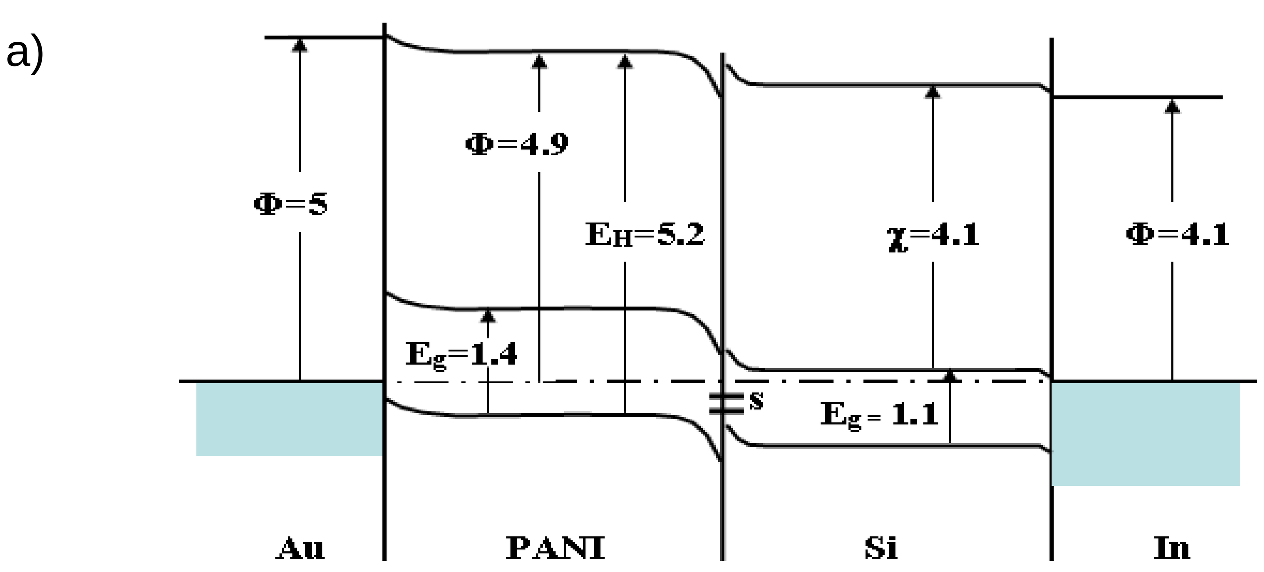
Faculty of Mathematics and Physics, Charles University, 18200 Prague 8, Czech Republic,

Abstract:

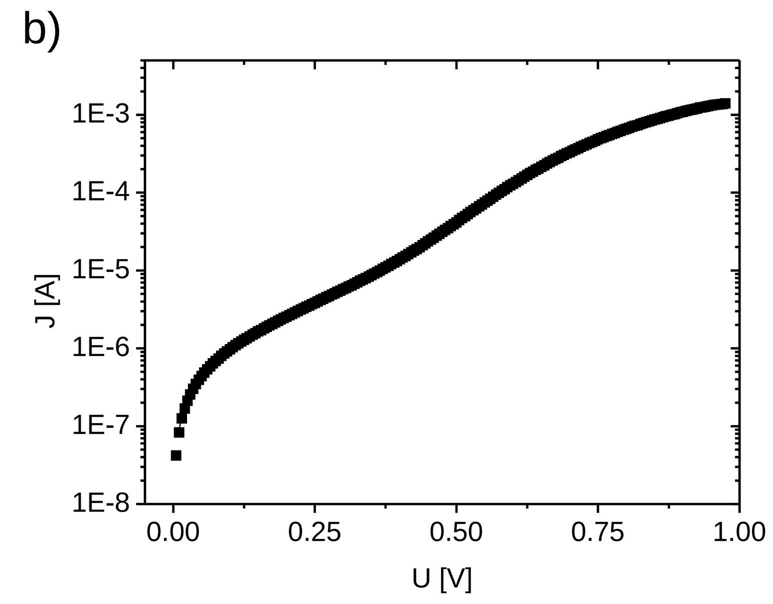
Polyaniline (PANI) is a material known for its high conductivity and also a huge range of obtainable conductivities. In general, three types of charge carriers are considered in PANI salt, namely holes, polarons and protons. Many authors attribute the high conductivity of acid doped PANI to polarons [1-3]. We show that conductivity of polarons might not be necessarily the prevailing mechanism of charge transport. In our research in order to separate contributions from different charge carriers PANI/Si heterojunction was studied. Impedance spectra were measured to distinguish between polaron and hole mobilities. From V-A characteristics on PANI/Si structure contribution of polaron and hole conductivity was calculated. Dielectric spectra of heterojunction were measured to estimate conductivity of ions. Both measurements resulted in values in order of magnitude ~ 10^{-7} S.cm^{-1}. On the contrary conductivity of several S.cm^{-1} on films of PANI on glass substrates were obtained using ohmic gold electrodes. To explain discrepancy between obtained values of conductivity a model utilising redox reaction of hydrogen and chlorine was proposed and diffusion of hydrogen and chlorine molecules in PANI films were studied.

The band diagram of PANI/Si heterojunction

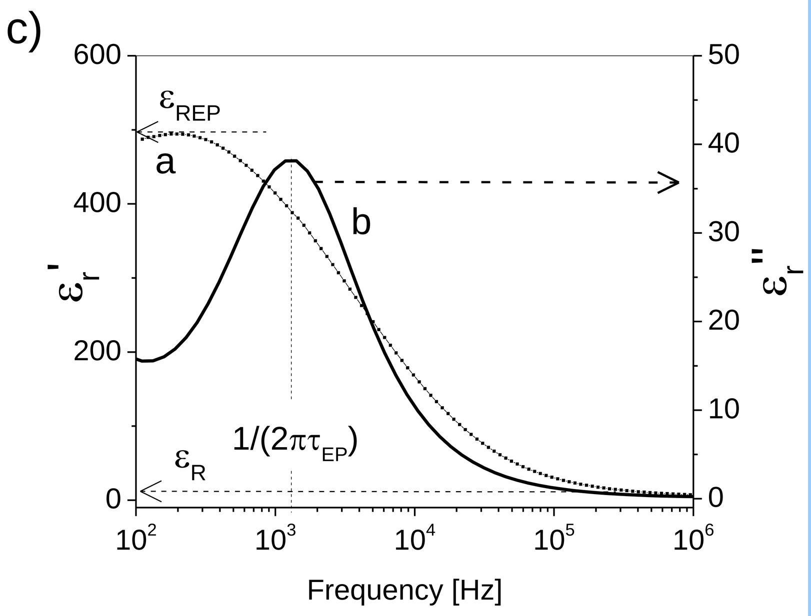
a)



b)



c)



V-A and dielectric measurements:

Conductivity of the holes was extracted from current – voltage characteristic from the series resistance [5]:

$$J = \frac{J_0 J_S \{\exp[e(U - JR_S)/nkT] - \exp[-e(n-1)(U - JR_S)/nkT]\}}{J_0 \exp[-e(n-1)(U - JR_S)/nkT] + J_S} + \frac{U - JR_S}{R_{Sh}},$$

$\sigma_{holes} = 8.0 \times 10^{-7}$ S.cm^{-1} (fig b.).

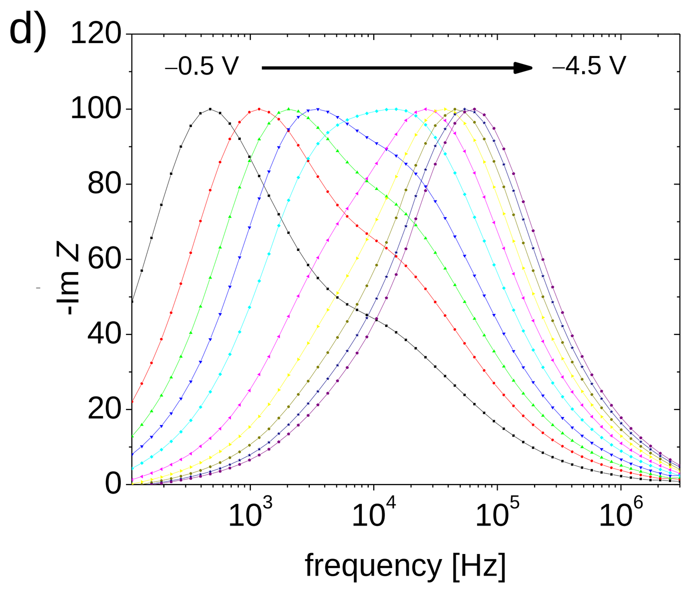
Mobility of protons in the PANI layer was determined by dielectric measurement [4]. The given structure of PANI is not permeable for ions, therefore mobility of protons was calculated by determineing dielectric relaxation time τ_{EP} from the permittivity spectra (fig. c):

$$\mu_{proton} = \frac{ed^2\varepsilon_R}{(4\varepsilon_{REP}\tau_{EP}kT)},$$

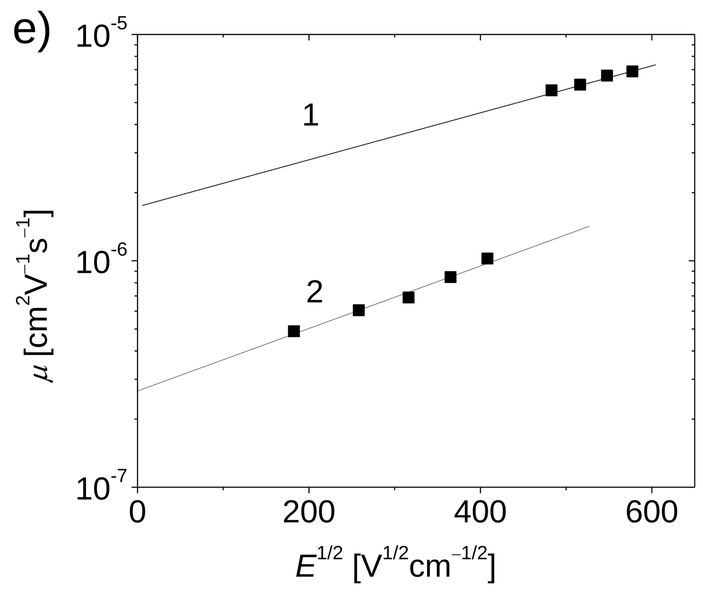
yielding value: $\mu_{proton} = 2.3 \times 10^{-7}$ cm^{2}V^{-1}s^{-1}

The evaluated concentration 7.1×10^{18} cm^{-3} corresponds to DC conductivity of protons: 2.6×10^{-7} S.cm^{-1}.

d)



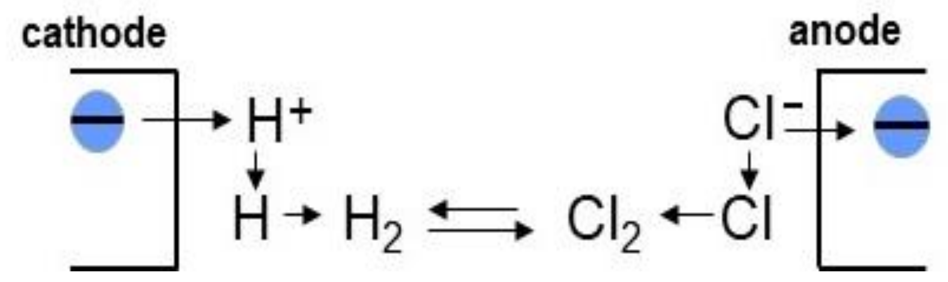
e)



Impedance spectroscopy:

The currents injected from the electrodes are non-stationary space charge limited currents transporting holes and polarons. Peak frequencies ω_{max} gives the carrier transit time $\tau = 1/\omega_{max}$ and shifts to higher values with increasing voltages (fig. d). Voltage dependence of the transit time enables to obtain mobility μ as a function of the electric field E. Assuming moderate dispersion: $\mu = \frac{d}{0{,}44\tau E}$ and by interpolation the mobility for zero voltage was found (fig. e): $\mu_{0holes} = 1.8 \times 10^{-6}$ cm^{2}V^{-1}s^{-1} (curve 1) & $\mu_{0polarons} = 2.7 \times 10^{-7}$ cm^{2}V^{-1}s^{-1} (curve 2).

f)



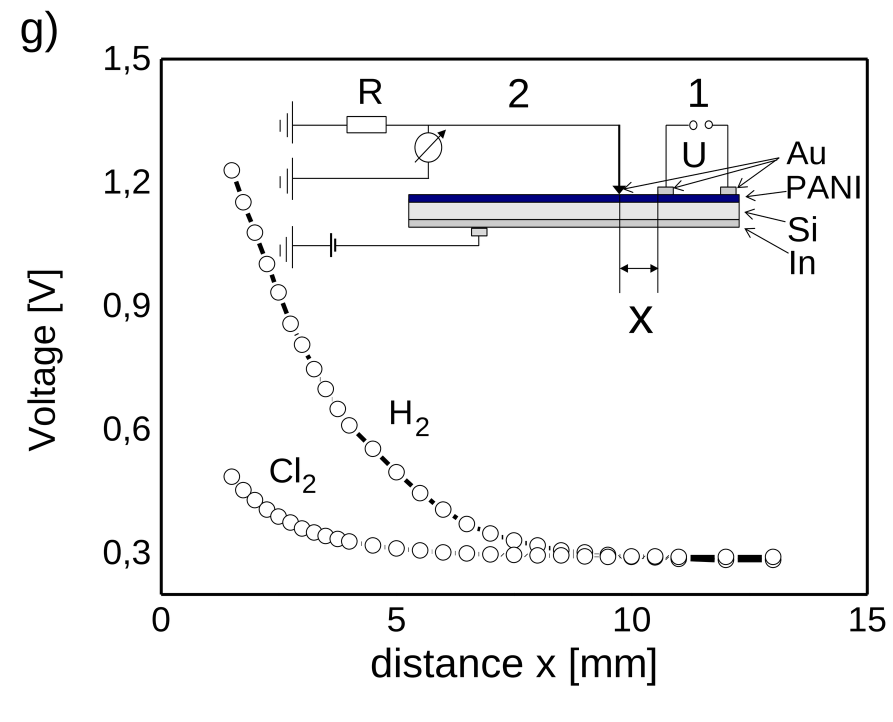
Proposed model:

To explain a huge difference between conductivities measured by ohmic electrode and conductivities of holes, polarons and ions determined by dielectric measurement and V-A characteristic, our model assumes that H^+ and Cl^- ions cause redox reactions at the electrodes: hydrogen ions are reduced at the cathode, chlorine ions are oxidized at the anode. The neutral chlorine and hydrogen molecules diffuse between the electrodes and react with each other transporting electrons in this way. The atoms and molecules are much more mobile than the ions because they are not influenced by the Coulomb forces. The unbounded hydrogen and chlorine are very probably responsible for the high conductivity of the PANI material.

Diffusion measurements:

To demonstrate the diffusion ability of neutral chlorine and hydrogen the equipment shown in fig. g) was built. The circuit (1) generates H and Cl molecules. In circuit (2) their diffusion is registered: voltage drop at resistor R depends on the distance x between the tip of the gold electrode in circuit (2) and gold electrode in circuit (1). The experiment (fig. g)) shows results in order of millimeters for diffusion of H and Cl molecules.

g)



Conclusion:

The conductivity of (1.9-3.5) S.cm^{-1} was measured in protonated PANI with ohmic gold electrodes in the plane of the substrate. The contribution of polarons and holes was determined from Au/PANI/Si/In structure that is not permeable for ions giving values : $\mu_{0holes} = 1.8 \times 10^{-6}$ cm^{2}V^{-1}s^{-1} & $\mu_{0polarons} = 2.7 \times 10^{-7}$ cm^{2}V^{-1}s^{-1}. The current is controlled by thermal emission of holes with a small contribution of diffusion. From the analytical expression of this transport [5] the serial resistance and therefore conductivity of holes with small contribution of polarons were determined: $\sigma = 8.0 \times 10^{-7}$ S.cm^{-1}. Since in the PANI /Si structure ions cause polarization, it is possible to determine their concentration from dielectric spectra:$p = 7.1 \times 10^{18}$ cm^{-3}. Then, from the evaluated mobility $\mu_{proton} = 2.3 \times 10^{-7}$ cm^{2}V^{-1}s^{-1} corresponding conductivity 2.6×10^{-7} S.cm^{-1} was calculated. To explain discrepancy in the conductivity of holes, polarons and ions and conductivity measured on PANI/Au structure we suggested model, where ions have a dual function: they themselves participate in conductivity and generate neutral particles of hydrogen and chlorine by redox reaction at the electrodes. These diffuse between the electrodes and transport charge through reactions with each other. The neutral hydrogen and chlorine particles are not influenced by the Coulomb forces therefore are more mobile than ions.

Literature:

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