

CHARGE TRANSFER BASED METHODS FOR DETECTION OF DEFECT STATES IN ORGANIC SEMICONDUCTORS

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1. Introduction

Elucidating the distribution of localized states in organic semiconductors and evaluation of their changes due to technology processing and device operation is prerequisite for taking advantage of the full potential of organic materials in electronics. The aggravating factors in this direction are weak (molecular) coupling and the disordered structure, which both make the spectroscopic methods known from disordered inorganic semiconductors difficult and sometimes impossible to apply. Thus, the need for new methods for organic material characterization is acute and in charge transient methods first attempts have been published [1] [2].

We report on the application of isothermal charge transient spectroscopy (IQTS) in local mode and electrochemical impedance spectroscopy (EIS) to detect defect states in band gap of organic semiconductors. The principle of IQTS is based on the time representation of the charge, induced in the external circuit by a driving voltage pulse, superimposed on the bias voltage applied to the sandwich metal/semiconductor/metal sample. Charge transients may be either due to dielectric relaxations, redistribution of injected charge or due to the release of charges from localized defect states (traps).

EIS is well known technique for the temporal resolution which enables to distinguish slower processes of diffusion and migration from faster redox reactions and charge transfer processes (i.e. double-layer formation). Here, the impedance is represented by the real and imaginary capacitances. As a result, the real capacitance stands for differential capacitance (i.e., dQ/dV) at certain frequency f , while imaginary capacitance illustrates the charge loss (energy dissipation). Therefore, the real capacitance includes the charge from the redox reactions as well as double-layer charging. The imaginary capacitance detects only the charge of redox reactions.

We applied these methods to the prototypical organic oligomer, pentacene, and common polymer, poly(3-hexylthiophene) (P3HT). We observed with both methods defect states in the midgap as well as we detected changes in defect states induced by the exposition of these organic semiconductors to sulphuric acid.

2. Experimental Details

For the IQTS measurements a unique charge-to-voltage converter with the resolution of hundreds of electrons was used [3]. It allows processing the transients from 2 μ s to hundreds of ms in local mode when the usual evaporated top electrode is replaced by the tip of the scanning probe microscope. This arrangement enables to measure the effect of consecutive selected treatments on the same layer. The IQTS is based on the rate window (RW) concept, with swept RW at constant temperature. The charge transients, $Q(t)$, were induced in the external circuit by the rectangular voltage pulse applied to the sample. The transients are transformed to the form of spectrum by combining samples from the charge

transients at time instants according to the formula $\Delta Q(t_1) = Q(t_1) - 1.5Q(2t_1) - 0.5Q(4t_1)$. IQTS measurements were performed with excitation pulses of 100 ms and the period of 1047 ms. To reduce the noise usually 50 transients were collected and averaged. The rate window defined by this filter is $1/t_1$ and it removes the linear component of the response, which is caused by the integration of direct current.

EIS experiments were performed in the three-electrode electrochemical cell with the 0.1 M solution of TBAPF₆ electrolyte in acetonitrile. Organic layers under study deposited on ITO/glass substrate served as working electrode, Pt wire as a counter electrode, and Ag/AgCl wire was used as a reference electrode. Charge exchange between organic layer and solution was detected via measurement of the complex capacitance of this system with the impedance/gain-phase analyzer (Solartron analytical, model 1260) at the frequency of 1 Hz. The imaginary part of the capacitance measured at this frequency corresponds to the charge loss caused by redox reactions taking place between gap states at the surface of the organic semiconductor and electrolyte. Large potential window ($\pm 3V$ with respect to Ag/AgCl reference electrode) of the used TBAPF₆ electrolyte in acetonitrile [4] enables to map localized states acting as redox centers in the whole range of the band gap of organic semiconductors. The amplitude of ac voltage was set to 100 mV and the sweep rate of the superimposed dc voltage ramp was kept at 100 mV/s.

Pentacene and P3HT layers were deposited on ITO/glass substrate. Pentacene layer was grown by thermal evaporation in vacuum with the deposition rate of 0.05nm/s and the thickness of 400 nm. P3HT layer with the thickness of 300 nm was spin coated from 1 wt% chloroform solution of P3HT with the spin rate of 25 rps. After characterization of as prepared organic layers the surface of the samples was exposed to 1M sulphuric acid for 20 min with the aim of forming additional defect states in the band gap.

3. Results and discussion

The results of the spectroscopic measurements of defect states in pentacene layer are shown in Fig. 1. In IQTS spectra (Fig. 1a), the significant peak with the relaxation time constant of 50 ms was detected as a response to the hole injection from ITO electrode (positive potential applied to ITO during excitation pulse). No noticeable IQTS signal was measured due to negative excitation pulses. This fact points out that IQTS peak corresponds to the hole emission from deep levels. The full width at the half maxima of the peak indicates band of defect states rather than a discrete level in the band gap. Location of these defect states in the band gap between highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) determines the activation energy of thermally released holes from defect states to HOMO and it can be evaluated from a set of IQTS spectra taken at different temperatures. This experiment has not been realized yet and it is planned after technical adaptation of the sample holder for setting and stabilization of the temperature. The imaginary capacitance vs. potential applied to ITO electrode with respect to Ag/AgCl reference electrode was measured in the voltage range corresponding to the band gap between HOMO and LUMO (Fig. 1b). The positions of HOMO and LUMO were determined from oxidation and reduction current peaks, respectively, of the cyclic voltammetry [5] (not shown here). Estimated potentials from current peaks of +0.9 V for HOMO and -1.0 V for LUMO give an electrochemical band gap of 1.9 eV, which is in a good agreement to a value of 1.97 eV determined from photoelectric response [6]. Assuming a value of -4.5 eV vs. vacuum level for the reference Ag/AgCl electrode, the band edges for HOMO and LUMO can be estimated at -5.4 eV and -3.5 eV. There is an apparent peak in the imaginary capacitance located around 0 V. Redox reaction at this potential was already reported [7] for the pentacene thin film exposed to acid media and was ascribed to 6,13 dihydropentacene defect. Exposition of the pentacene layer to 1 M sulphuric acid for 20 min led to the increase

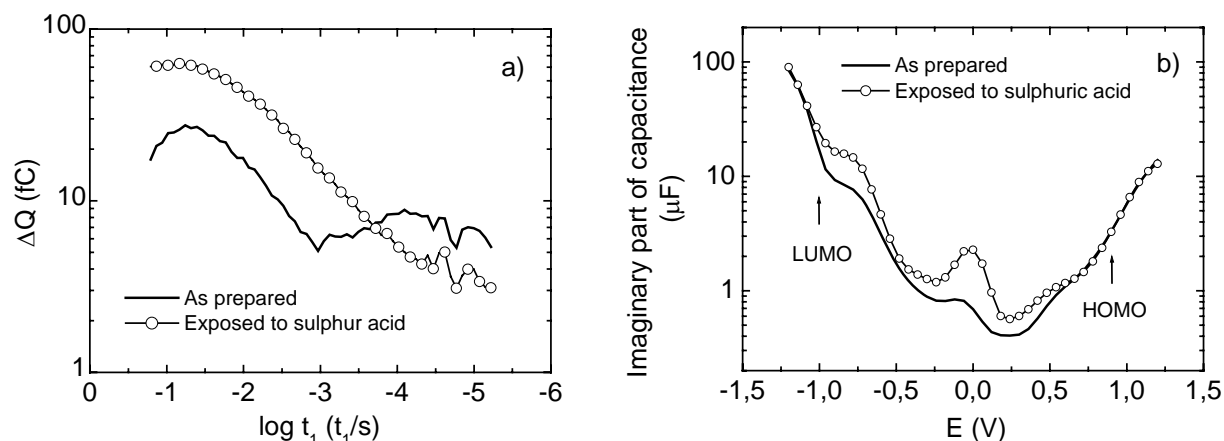


Fig.1: IQTS spectra (a) and imaginary part of the complex capacitance vs. potential applied to ITO electrode with respect to Ag/AgCl reference electrode (b) of the pentacene layer for as prepared (full line) and exposed to 1M sulphuric acid for 20 min (open circles) measured at 295K.

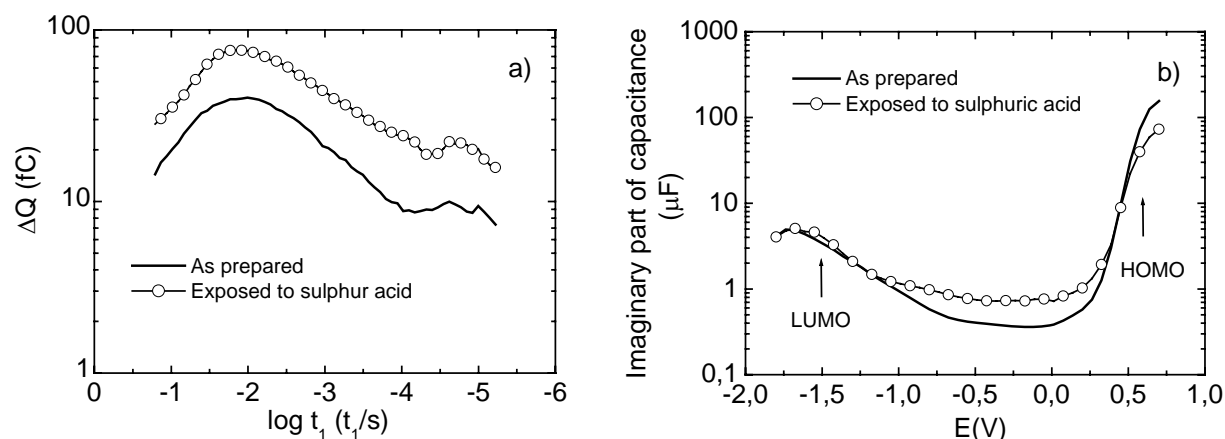


Fig.2: IQTS spectra (a) and imaginary part of the complex capacitance vs. potential applied to ITO electrode with respect to Ag/AgCl reference electrode (b) of the P3HT layer for as prepared (full line) and exposed to 1M sulphuric acid for 20 min (open circles) measured at 295K.

of the peak amplitude in both IQTS and imaginary capacitance spectra by a factor of 2.5. Therefore, we assume that with IQTS and EIS are observed defect states induced probably by dihydropentace defect. The maximum of these defect states is located 0.9 eV above HOMO.

Similarly, the spectroscopic measurements of defect states were carried out on P3HT layer (Fig. 2). As prepared state is characterized by a broad peak with a maximum located at 10 ms. Imaginary capacitance vs. applied voltage shows U-shaped dependence without any notable features most probably due to the amorphous structure of the polymer. The positions of HOMO and LUMO, estimated again with cyclic voltammetry, are at +0.6 V and -1.5 V, respectively. Corresponding band gap of 2.1 eV complies with the values around 2 eV found in previous experiments [8]. Exposition of P3HT layer to sulphuric acid caused nearly uniform increase of both IQTS signal and imaginary capacitance between HOMO and LUMO by a factor of 2. Resembling evolution in measured charge of IQTS and imaginary capacitance of EIS without marked feature implies that sulphuric acid led to the formation of

additional defect states distributed uniformly in the band gap. Present complex of experimental data does not allow to judge on the origin of additionally introduced defects.

4. Conclusion

It was shown that IQTS in local mode and EIS in the measurement mode of complex capacitance are potent tools for detection of defect states and their changes due to an external impact in organic semiconductors. Detection of defect states by IQTS is limited with the capability of electrodes to inject holes or electrons to the organic materials under investigation and with the used equipment, which can measure relaxation processes up to hundreds of ms. Advantage of EIS is the possibility to detect defect states in the whole range of the band gap thanks to a wide potential window of the used TBAPF6 electrolyte in acetonitrile.

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