

ELECTROCHEMICAL CHARACTERISATION OF PHOTOVOLTAIC THIN FILMS

Katarína Gmucová¹, Vojtech Nádaždy¹, Michal Kaiser¹, Miroslava Tkáčová²

¹Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic

² Institute of Nuclear and Physical Engineering, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

E-mail: katarina.gmucova@savba.sk

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1. Introduction

In past years a significant effort has been paid to the design, synthesis, and characterisation of low band gap polymers and oligomers. The knowledge in the band gap structure of the newly synthesised organic semiconductor is a determining factor for its application in photovoltaic and optoelectronic technologies. The optimization of band gap is critical because it determines the effectiveness with which solar radiation is absorbed in photovoltaic devices, as well as and the colour of the emitted light in the optoelectronic devices. The detail understanding of defect states in prepared thin films is of high importance due to their strong influence on the device functionality.

HOMO and LUMO energies are theoretically determined using Density Functional Theory method [1] and experimentally using electrochemical or optical methods [2, 3]. In case of poor electrochemical responses, e.g., for molecules less stable for electrochemical reduction, the LUMO positions are sometimes determined from the HOMO and band gap and the latter is estimated from the edge of electronic absorption spectra [4].

It is well known, that the electronic properties of organic semiconductors are strongly influenced by trap states in the forbidden gap. Organic photovoltaic materials are multiple trap-level systems with a seemingly continuous distribution of electronic states throughout the bandgap [5]. The identification, characterization and mitigation of defect states is important for pushing the organic photovoltaic materials towards a more ideal, with increased efficiency, reproducibility and stability.

Up to now, little is still known about the defects nature, their position in the forbidden gap, chemical composition, mitigation, etc. In this paper we present a study of applicability of various electrochemical methods in the characterisation of an organic semiconductor band gap structure, P3HT is chosen as a prototypal material.

2. Experimental results and discussion

The electrochemical experiments were performed in three-electrode cell compartment, 0.1 M solution of TBAPF6 in acetonitrile was used as supporting electrolyte. The P3HT thin film was spin-coated on the ITO disc working electrode, the potential was measured vs. reference Ag/AgCl electrode, and Pt wire was used as a counter electrode. The electrochemical analyser, comprising voltammetric and volt coulometric methods, was used for the characterization of the prepared structures. Cyclic voltammetry was performed with scan rate of 100 mV/s, voltammetric and volt coulometric measurements were performed with scan

rate of 6 mV/s. The period of excitation pulses for the volt coulometric measurement was set to 280 ms, the excitation pulse duration to 100 ms, and the excitation pulse amplitude was set to -200 mV. Two, three, four or five channel filtering scheme was used, the sampling events of transient charge and the weighting coefficients were set utilizing high-order filtering scheme [6]. The electrochemical data obtained as a function of "Potential vs. Ag/AgCl" were recalculated towards a function of "Energy vs. vacuum". Thin films were prepared in glovebox by spin-coating (spinning speed of 30 rps) from 1 wt % solution of P3HT in chloroform or in dichlorobenzene and annealed at 110°C.

The possibility to observe the fine structure of HOMO using electrochemical methods is demonstrated in Fig. 1. The electrochemical method probe the surface of organic semiconductor, therefore it is necessary to prevent from oxygen and moisture influence on the sample under investigation. An expressive influence of the ambient atmosphere is shown in Fig. 1, too. The HOMO and LUMO levels are in the literature evaluated either from the onset or from the peak. Although the onset values are argued to be ill-defined, such approach is widely used. This is mainly based on the detailed quantum chemical calculations which shown a linear correlation between ionization potential and oxidation potential and also between electron affinity and reduction potentials. They also indicated that these values refer to the first oxidation and reduction potentials (for removing or adding one electron), which corresponds to the onset values of the electrochemical process [7]. One of the drawbacks for using the onset method is that the onset of oxidation or reduction varies with scan rate. Therefore, such approach is correct only at very slow scan rates where all of the material amount can be reduced or oxidized. This requirement is fulfilled for both the steady-state voltammetry and volt coulometry, however, the onset in volt coulometry is influenced by the used filtering scheme.

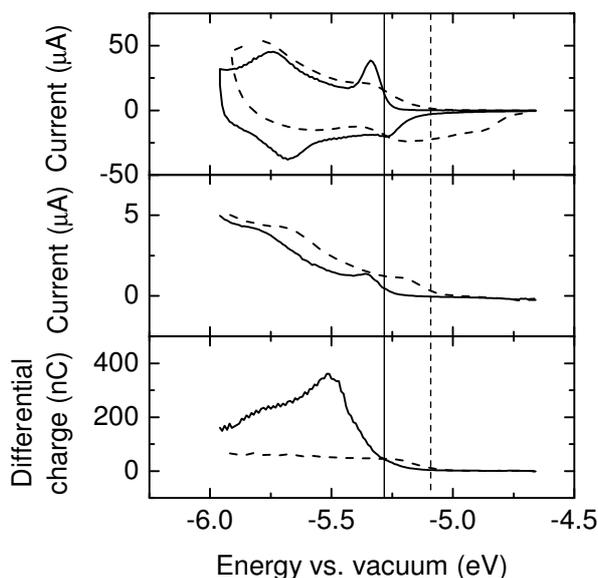


Fig. 1: Cyclic voltammetry, steady-state voltammetry and volt coulometry of P3HT film prepared from chloroform solution: full line obtained in glovebox, dash line in air. Vertical full and dash lines are set at the estimated positions of HOMO levels in an inert atmosphere and in air, respectively.

As a next step we studied the possibility of using electrochemical method to detect the defects in P3HT band gap. Volt coulometric data and the derivative form of voltammetric data obtained under white LED illumination on both the fresh samples and samples exposed for two days to air are shown in Fig. 2. In dark, defect states were not observed. As a hypothesis for such a behaviour we suggest a model similar to blend photovoltaic devices. The defects formed

in P3HT film in a wet oxygen atmosphere (oxygen, hydrogen, and hydroxyl related) are molecular impurities in the P3HT matrix. If the amount of formed defects in the film is sufficient to be considered as a blend of two or more compounds, we can adopt the model of energy level alignment described in [8]. Absorption of photon generates exciton, a neutral electron-hole quasiparticle. The self-localized polaronic states, formed by the separation of electron-hole pair, are then measured by the electrochemical methods.

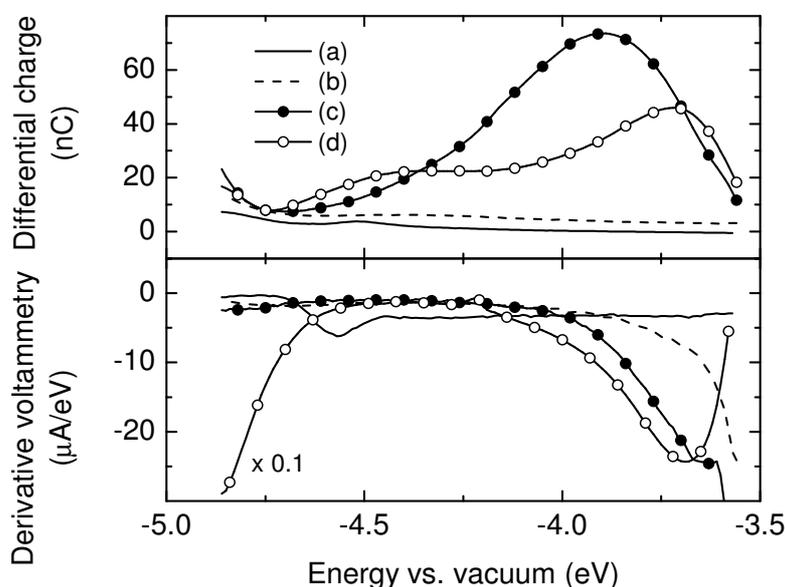


Fig. 2: Voltcoulometric responses (three channel filtering scheme at 15 ms, 75 ms, and 135 ms) and derivative voltammetry obtained in air under illumination with white LED; (a) fresh P3HT film spin-coated from chloroform solution, (b) P3HT film spin-coated from chloroform and exposed to air for two days, (c) fresh P3HT film spin-coated from dichlorobenzene solution, (d) P3HT film spin-coated from dichlorobenzene and exposed to air for two days.

Here, it should be noted that while voltammetry is a method giving direct information on the concentration profile of redox species, i.e., defect states, voltcoulometric signal maxima are influenced by the filtering scheme applied on the charge transfer process of specific kinetic, dependent on the reaction rate constant. Thus, based on the data depicted in the lower part of Fig. 2, we can conclude that P3HT films prepared by spin coating from dichlorobenzene solution are more prone to form defects under ambient atmosphere than those prepared from chloroform solution.

Voltcoulometry, as a method utilising the high-order filtering scheme, provides an opportunity to distinguish between different processes on the basis of their kinetics. Applying various sampling schemes on the transient charge data we can favour specific processes and obtain voltcoulometric responses reflecting a fine structure of the continuous distribution of electronic states throughout the bandgap. Such a situation is depicted in Fig. 3. Voltcoulometric responses obtained with various sampling schemes, representing 2-channel, 3-channel, 4-channel and 5-channel filter applied within the same interval (from 15 ms to 135 ms), are shown in the left part of the figure, and voltcoulometric responses of 3-channel filter applied on different parts of the transient chronocoulometric responses are shown in the right part of the figure. Here, at least three different distributions of electronic states should be found. The peak at -3.7 eV vs. vacuum can be ascribed to the $(\text{H}_2\text{O})_2\text{-O}_2$ complex described in [9].

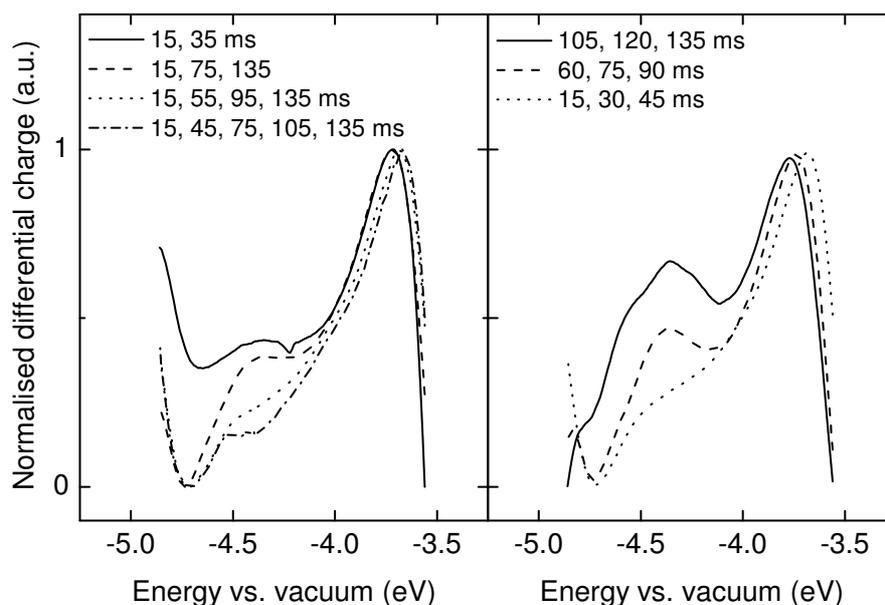


Fig. 3: Voltcoulometric responses obtained for various sampling schemes on P3HT film spin-coated from dichlorobenzene solution.

3. Conclusion

The used electrochemical methods are able to provide valuable information on the organic semiconductor forbidden gap structure, complementary usage of the above mentioned techniques enables better understanding and identification of processes in the measured samples.

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