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REPORT OF DOCTORAL THESIS

Charge transport in organic semiconductors monitored by impedance spectroscopy, Doctoral Thesis of Mr. Pavel Chulkin, Silesian University of Technology

The PhD Thesis, "Charge transport in organic semiconductors monitored by impedance spectroscopy " focus an actual and very interesting field of work in electrical behavior of organic semiconductors, with special application to Organic Light Emitting Diodes (OLEDs) and polymers, widely accepted as of high importance but really not explored. The employment of small signal analysis to study the electrical characteristics of semiconductors, it's been done for several years, but every time but it always appeared to be particularly complicated and with not always satisfactory results. In particular, injection, transport and recombination of electric charges can be assessed and understood in relation to the physical operating conditions of the devices, thus being an equally excellent technique for improving device merit figures through the obtained feedback. When used to study organic semiconductors, the technique has proved extremely important for developing physical models associated with device behaviors, in a generally more interesting way than for inorganic ones. Thus, it is indeed important, current and of total interest the general topic of the present thesis. Overall, the thesis is well written, conceptualized and easy to read and understand the results, discussions and conclusions. Apart from minor spelling errors that are not important, the document contains no major flaws that could compromise presentation and discussion.

The thesis starts with a brief introduction that focus the main idea behind the work and points in a concise idea the subject of the proposed work. It is simple to understand how the main idea (impedance spectroscopy to study the electrical charge transport in – specifically – organic semiconductors).

The state of art is presented in the first chapter. Here, is interesting (and very well done) the schematic representation of the thesis work in the "interconnected research areas". In the first part, the development of the basic models for charge transport in semiconductors are shown, with the fundamental theory that will be developed, with a specific approach to the organic semiconductors. Not much presented in deep but very well discussed and – more important – contains all the necessary ideas. Electrical carrier recombination and electroluminescence concepts, as well the basic principles of OLEDs are introduced, followed by the impedance spectroscopy technic explanation. The detailed explanations and the approach (relatively new) to determinate de electrical carrier mobility are precise. The chapter finalizes with the application of electrochemistry technique to investigate organic

materials. All the required information is clearly present. As a less well done part in this chapter, is the relatively small amount of a more explained state of the art containing what the more important has been published in this filed. Nevertheless, some related information are given across the entire document.

Chapter 2 contains all the information regarding the experimental setup used for device fabrication and the framework for experimental data treatment. All these descriptions are of importance for the readers to know the real experimental conditions and the approach followed to data analysis. It is well described and contains all the necessary information, including for someone working in this field to reproduce the work done.

The first main part of the work is described in Chapter 3. One of the most serious issue related with OLEDs development is precisely the charge transport across the device layers. Not is only the basis for the device structure development as also determines the final efficiency, as the transport, recombination and confinement of charges in the active layer conditions the OLED figures of merit. The fundamental basis of this chapter is the electrical charge density and mobility obtained by the impedance spectroscopy method. Besides the models development, the specific applications to real data obtained from devices, with a very interesting agreement, is, in fact, a real novelty. Particularly important – because not much explored in literature with so deep investigation – the effect of the organic layers thickness. In my opinion, this part is the most important in this chapter that, with precise and detailed data and related models, opens new possibilities of future research towards device improvements. Finally, the brief and important data from the study about OLED stability, although simples, open the possibility for new approaches in this particular topic.

Chapter 4 contains the remaining part of the work. Conductive polymers are the basis for all organic devices (not only polymer LEDs – PLEDs – but also in OLEDs – as hosts for emitters – and polymeric organic photovoltaics). The study of the electrical charges behavior and the constrains for achieving a perfect transport across the organic polymer matrix, is one of the most investigated filed in organic devices development. Moreover, the interaction of the polymers with surrounding layers – organic or metal – may be, in some situations, critical for the device optimization. In the basic electrochemical study, common polymers are investigated, namely PANI and PEDOT. The approach followed in the work, embodied the theoretical description of models associated with the treatment of experimental data, which is, in my opinion correct. The final model obtained for impedance of conductive polymer films is noticeable as well the – correct – strategy for data treatment approach in order to obtain the relevant physical parameters. The experimental data conveniently fitted to the previous developed models, particularly the concentration of ions as a function of the electrode potential, gives rise to a new concept of application of impedance spectroscopy for organic semiconducting materials far beyond just what in this work was studied. It should be noted that some results obtained are in fact new and are without doubt a prime novelty, namely the charge concentration

in cited polymers as well the estimation of the respective diffusion coefficients. These results will be evident for the application of such conductive polymers in any device.

Conclusions are precise and objective enough to clearly show not only the main work, its importance but also the novelty in this very important and interesting research filed. It should be noted that nothing has been said about future work, although it is not absolutely necessary.

As a general idea, this work is clearly important and introduces new approaches for use of impedance spectroscopy as a tool for explore new physical phenomena in organic semiconductors, in a research field every day as more important. In my opinion, we are in the presence of an excellent work where, not only an experimental part was made but also – more important – the related physical models was developed. The importance for future will be surely guaranteed.

Less well done, I would point out two questions: 1) some lack of state of the art as it is every time interesting to show to the reader the departing point in the research field and because in the final, can enhance the obtained results and 2) a more detailed description related with some possible constrains when trying to – eventually – define the limitations of the developed models.

Finally, the excellent publications made based in this work, is obviously one of the most important consequences for the validity and importance for the research field, adding suitable new and valuable approaches, that the scientific community has recognized value.

Thus, considering the overall thesis document, including the organization, writing and concept, the novelty of the work and the related publications, **I recommend that the thesis "*Charge transport in organic semiconductors monitored by impedance spectroscopy*" should be accept as it is, ready for exam.**

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