

**Review by FX Perrin – Toulon University (France)**

**Student** : Iryna Ivanko

**Thesis Title** : High rate supercapacitors based on conducting poly(3,4-ethylenedioxythiophene)

**Supervisor** : Ing. Elena Tomšik, PhD

**General comment :**

In this thesis work, the link between engineering and methods of synthesis of conductive polymers from the poly(3,4-ethylenedioxythiophene), PEDOT family and the electrical and optical properties of these polymers was studied.

PEDOT was prepared chemically in the presence of oxidant or acid as well as by electrochemistry. The PEDOT thus prepared was used to design two devices, an energy storage and conversion device and a solid-contact ion selective electrode (SC-ISE) sensor. The introduction chapter presents the scientific context of the thesis and a comprehensive review of the current state-of-the-art in the preparation and electrical and optical properties of PEDOT. This bibliographic part is very informative and written in a clear and concise style.

The oxidative polymerization of EDOT in the presence of chloride and structure breaking formate ions was first studied. The hydrated PEDOT films showed promising photoluminescence properties which can be tuned by applying cyclic voltammetry. This change in PL properties was connected with the amorphization and formation of an anisotropic structure during the electrochemical treatment. In a second part, PEDOT films were prepared electrochemically in the presence of formic acid. The Raman and XPS measurements showed electrostatic interactions (H-bonding or coulombic interactions) between formic acid and polymer chains. In the third part of the manuscript, a new method for PEDOT synthesis based on an acid assisted polymerization of EDOT is presented. This method is very promising because of its simplicity (no addition of oxidant or any additive) and the possibility to control the assembly process of the oligomers and their photoluminescence properties. The last part of the work reports the construction of symmetrical supercapacitor and SC-ISE devices based on electroactive PEDOT. The supercapacitor device based on a wet and a dried PEDOT electrode showed higher area energy and power densities compared to the literature data.

To sum up, Iryna Ivanko performed a very rigorous experimental work using sophisticated surface characterization techniques such as Raman spectroscopy, MALDI-ToF technique, X-ray Photoelectron Spectroscopy, NMR and UV-vis analysis, Scanning Electron Microscopy and electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy). This work has resulted in six scientific articles already published in high-impact and internationally reputable journals. The

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manuscript is of high quality and it is well-organized. Even if of course, some questions remain opened, the work by Iryna Ivanko offers a significant and very original contribution that combines fundamental (with a better understanding of the parameters controlling the optical and electronic properties of semi-conductive polymers) and practical aspects (development of supercapacitor and solid-contact ISE devices).

**Questions and subjects for discussion :**

- p21, « the presence of bond water is determined by the presence of a broad exothermic peak at dsc curve,...the narrow one », as the evaporation of water is an endothermic process not an exothermic one, the statement p21 should be clarified.
- Formic acid being a volatile acid, is it certain that the loss of mass observed by TGA below 200°C and the heat flux peak at 100°C in DSC is not partly due to the departure of acid weakly interacting with PEDOT chains ?
- How can the structural changes (amorphization and the formation of an anisotropic structure) induced by the potential sweep be explained knowing that the positive potential limit of the CV was not extended to the region in which the overoxidation of PEDOT takes place ?
- An increase in the crystalline order after CV was reported for the electrochemically synthesized PEDOT film (to be compared with amorphization for films prepared by oxidative polymerization). How can the different effect of potential sweeping be explained on PEDOT films prepared by oxidative polymerization compared to those prepared electrochemically ?
- The anode of the supercapacitor device is prepared by electropolymerization of EDOT in the presence of formic acid followed by soaking the electrode in orthophosphoric acid solution. Would it not be possible to obtain a high  $V_{oc}$  value by preparing the anode directly by electropolymerization in orthophosphoric acid as a supporting electrolyte ?

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