11º Encontro Nacional de Química-Física

BOOK OF ABSTRACTS

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FIRST-PRINCIPLES STUDY OF ELETRONIC PROPERTIES OF RADICAL POLYMERS FOR ORGANIC BATTERY APPLICATIONS

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Nowadays, there is an increasing demand for suitable energy storage devices to power the electronic devices used in a society continually oriented to technology and mobility. In order to solve this problem, and allied to environmental concerns, organic radical batteries (ORB) have been considered as possible solution by the electronic industry. In these devices, the electrodes consist on a moiety of a radical polymer and a conductive additive, with well defined electrochemically properties, which gives to ORB interesting performances, like short charging times and stable voltages, with the bonus of good device processability using wet techniques, opening the possibility to build thin and flexible batteries. The suitable electrochemical properties of radical polymers for battery applications arises from the fact that they present an organic radical pendant group with a nitroxide radical which may easily undergo reversible oxidation, forming an oxoammonium cation, or reversible reduction, forming an aminoxyl anion [1] . By suitable molecular design of the pendant group it's possible to optimize the eletrochemical properties of the radical polymer [2], and thus of the electrodes, with the perspective to built an all-ORB. In this communication we will present some of our recent results, obtained by density functional theory (DFT) calculations, in studying the effect of the molecular structure of the pendant group and polymer backbone on the electronic structure and related properties of radical polymers used in ORB. The results obtained can be used as input parameters in mesoscopic models to study the process of charge/discharge of ORB.

[1] K. Oyaizu,H. Nishide. *Adv. Mater.*, **21**, 2339-2344 (2009).

[2] T. Janoschka, M. D. Hager,U. S. Schubert. *Adv. Mater.*, **24**, 6397-6409 (2012).

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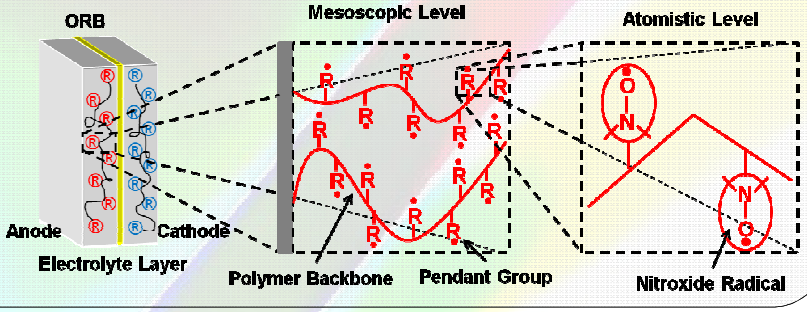
INTRODUCTION

Nowadays, there is an increasing demand for suitable energy storage devices to power the electronic devices used in a society continually oriented to technology and mobility. In order to solve this problem, and allied to environmental concerns, organic radical batteries (ORB) have been considered as possible solution by the electronic industry. In these devices, the electrodes consist on a moiety of a radical polymer and a conductive additive, with well defined electrochemically properties, which gives to ORB interesting performances, like short charging times and stable voltages, with the bonus of good device processability using wet techniques, opening the possibility to build thin and flexible batteries. The suitable electrochemical properties of radical polymers for battery applications, arises from the fact that they present an organic radical pendant group with a nitroxide radical, which may easily undergo reversible oxidation, forming an oxoammonium cation, or reversible reduction, forming an aminoxyl anion.

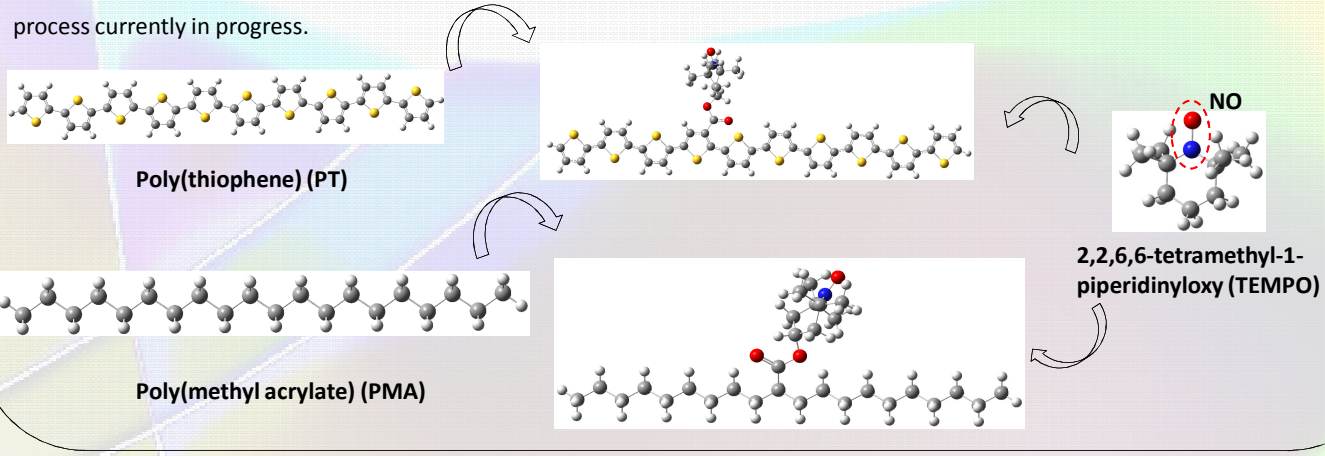
MULTI-SCALE MODEL

The electronic structure and related properties of the radical polymers (i.e. ionization potential, electron affinity, charge localization, specific charge, charge transfer, ...) used in ORB depends on the molecular structure of the pendant group and polymer backbone .



COMPUTATIONAL MODELLING – ATOMISTIC LEVEL

Electronic structures and geometry optimization is realized using density functional theory (DFT) at the B3LYP/6-31(d) level. All the calculations are being carried out with Gaussian 09 program-package. Equilibrium structures of the polymers backbone and the radical molecules where first obtained separately. The radical polymer is obtained by combining both molecules and new optimization process currently in progress.



Poly(thiophene) (PT)

2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)

Poly(methyl acrylate) (PMA)

SOME REASEARCH AIMS

- What is the influence of the polymer backbone and the pendant group on the battery eletrical properties (voltage, specific charge, ...)?
- How charge transfer proccess occurs in different radical polymers and what are the factors that influence this transfer?
- How can we improve ORB performance?

REFERENCES

K. Oyaizu,H. Nishide. *Adv. Mater.*, **21**, 2339-2344 (2009).; T. Janoschka, M. D. Hager,U. S. Schubert. *Adv. Mater.*, **24**, 6397-6409 (2012).

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