

Spectroelectrochemical characterization of doped P3HT for application in neuromorphic computing

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Abstract

Neuromorphic computing appears as a solution for the current von Neumann architecture dilemmas, such as the von Neumann bottleneck and the difficulty in recognizing complex patterns. Among various types of neuromorphic technologies, electrochemical devices present advantages such as biocompatibility, low-energy consumption and unprecedented non-volatile memories levels. However, the technology still lacks long-term stability and, more importantly, material variability. Here we propose the characterization of doped poly(3-hexylthiophene) (P3HT) with various types of electrolytes, to attest its applicability as active layer for neuromorphic units. Cyclic voltammetry and UV/Vis spectroscopy were the main techniques employed in the current stage of the project, and early results show that Hansen's RED served as a good prediction for P3HT's response under different electrolytes. The best performance i.e. reversible doping was achieved utilizing LiClO₄ in acetonitrile as the electrolyte.

Keywords: P3HT; organic electronics; cyclic voltammetry

Introduction

Despite the increasing performance of the modern computing architectures, the field still struggles with the von Neumann bottleneck and, more recently, with the recognition of complex patterns – normally

applied in artificial intelligent (AI) algorithms [1]. Neuromorphic computing (NC) was proposed to overcome these problems by proposing electronic devices meant to mimic the brain's neural architecture. The basic NC unit is, therefore, inspired by the functioning of neuronal cells, and among several technologies [2], the electrochemical neuromorphic device (ND) presents great advantages such as biocompatibility, low energy consumption and precision in achieving memory states. However, one of its state-of-the-art devices, the well-known Electrochemical Non-volatile Organic Device (ENODE), lacks long-term stability and reproducibility [3]. In addition, its materials library is limited to poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) derivatives and aqueous electrolytes, thus stressing the importance of investigating alternative materials.

Here we propose the characterization of poly(3-hexylthiophene) (P3HT) by a set of electrochemical and optical techniques in order to evaluate the material's applicability in ND. So far cyclic voltammetry (CV) and UV/Vis spectroscopy were used to evaluate the device properties, however additional techniques, such as quartz crystal microbalance and x-ray photoelectron spectroscopy will be added to the analyses pool in the near future.

Experimental Procedure

For CV measurements (VersaStat II - Princeton Applied Research), 120 nm thick P3HT films were spin-casted from a dichlorobenzene (DCB) solution on indium tin oxide (ITO) substrates (with active area of 0.5 cm²). In the experimental setup, platinum plate worked as the counter electrode while Ag/AgCl pellet worked as a reference electrode. Four electrolytes were evaluated in the current stage: 0.1M LiCl in ultrapure water (up-H₂O); 0.1M LiClO₄ also in up-H₂O; 0.1M LiClO₄ in cyclohexanone (CHx); and 0.1M LiClO₄ in acetonitrile (ACN). Scan rate for the CV was kept at 5mV/s for all measurements. Open circuit potential was defined by the equipment. UV/Vis spectroscopy was performed in situ.

Results and Discussion

Up-H₂O, ACN and CHx were chosen as solvents for electrolytes due to their Hansen relative energy difference (RED) (compared to P3HT R₀). While CHx has an RED of 0.966, ACN has an RED of 3.939 and water has an RED of 10.262 [4].

For the CV analyses, the 5th cycle-run of each sample is presented in Figure 1.

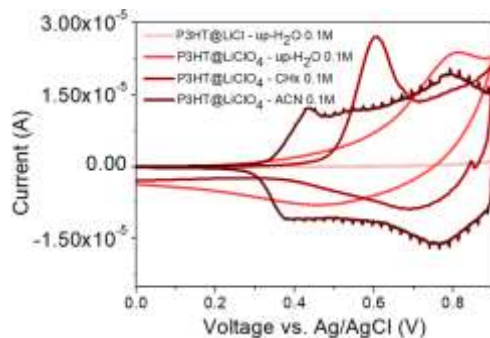


Figure 1 - CV measurements from 0 V to 0.9 V of P3HT in: LiCl in up-H₂O 0.1M; LiClO₄ in up-H₂O 0.1M; LiClO₄ in CHx 0.1M; and LiClO₄ in ACN 0.1M.

The CV curves presented in Figure 1 exhibit peaks in both oxidation and reduction runs, except for the sample tested in 0.1M LiCl in up-H₂O. The presence of peaks in both sides of the curves denotes a degree of doping reversibility [5].

The sample tested in 0.1M LiClO₄ in ACN shows similar peaks in oxidation and reduction runs (Figure 1), suggesting a strong tendency of doping/dedoping reversibility [5].

The doping reversibility of the samples is confirmed by UV/Vis spectroscopy, which ran simultaneously with the CV. Figure 2 presents the absorption shifts of P3HT (520 nm) and absorption shifts of its polaron formation (800 nm) [6].

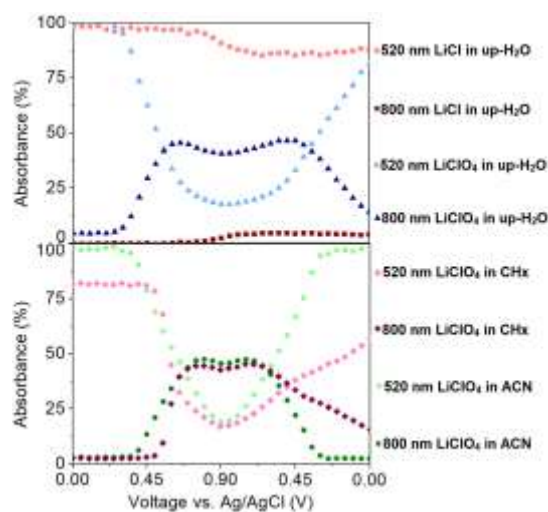


Figure 2 – UV/Vis spectra of 520 nm and 800 nm for P3HT film in a) LiCl in up-H₂O 0.1M, LiClO₄ in up-H₂O 0.1M, b) LiClO₄ in CHx 0.1M and LiClO₄ in ACN 0.1M.

The UV/Vis spectra of P3HT in 0.1M LiCl in up-H₂O presents a very small absorbance shift for 800 nm (Figure 2a), suggesting that no electrochemical reactions took place during characterization. This result corroborates with the absence of peaks in the CV curves of this sample (Figure 1).

As for LiClO₄ also in up-H₂O (Figure 2a), absorbance shifts can be seen for 520 nm and 800 nm. The absorbance values do not return completely to their initial values, configuring a quasi-reversibility of the doping process.

Comparing only the aqueous electrolytes, one concludes that the chemical group ClO₄⁻ is able to dope and interact with P3HT while Cl⁻ itself is not. Interestingly, smaller anions tend to hold water molecules

tighter than bigger anions, creating bigger solvation shells [7]. Since P3HT is a hydrophobic material the Cl^- group hardly swells the bulk of P3HT film.

As for the CHx solvent, absorbance shifts occur for both wavelengths (Figure 2b) followed by an attempt to return to their initial values. This phenomenon allied with the CV curve presented in Figure 1 suggests a quasi-reversible doping-dedoping process in this electrolyte [5]. Interestingly, samples analyzed using LiClO_4 as solute in CHx and up- H_2O yield similar absorption shift patterns.

Finally, in the UV/Vis spectra of P3HT using $\text{LiClO}_4\text{-ACN}$ (Figure 2b), the measurement baselines basically return to their initial positions after voltage withdrawal. This behavior corroborates with the CV curve and confirms the strong tendency of doping/dedoping reversibility.

Comparing all samples using LiClO_4 , and considering their RED's, it is possible to conclude that both low and high RED's solvent (<1 and >10 respectively) yield a quasi-reversible doping/dedoping process. Meanwhile, a medium RED, such as ACN's (~ 5), present better doping reversibility, indicating that solvents in this RED range are the best choice for a stabler neuromorphic device using P3HT films.

Conclusions

Hansen RED parameter served as a good prediction of P3HT's response during spectroelectrochemical analyses. While CHx and water electrolytes do not promote total doping reversibility ($\text{RED}<1$ and $\text{RED}>10$ respectively), ACN is able to do so ($\text{RED}\sim 5$). Due to the tight hydration shell, smaller anions are not the best choice when working with aqueous solvent (polar) electrolyte and hydrophobic polymers. Moving forward, we plan on using quartz crystal microbalance and x-ray photoelectron spectroscopy to further understand the doping mechanisms in P3HT under different electrolytes: while the

former will allow us to calculate the amount of ionic species that swells the polymer film under certain voltage condition, the latter gives us the possibility of measuring the polymer's Fermi-level upon doping. This is crucial to evaluate the doping degree and, therefore, to understand the fundamentals on ion-polymer interaction.

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