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New Processes and Materials Based on Electrochemical Concepts at the Microscopic Level  
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## Control of thickness of PEDOT electrodeposits on Glass/ITO electrodes from organic solutions and its use as anode in organic solar cells

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### Abstract

Poly-ethylenedioxythiophene (PEDOT) was electropolymerized from the monomer EDOT in acetonitrile (ACN) containing  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$ ,  $\text{BF}_4^-$  or  $\text{PF}_6^-$  ions as supporting electrolyte. The electrode used was transparent electrodes (Glass/ITO) in order to generate the anode of an organic solar cell (OSC). Potentiodynamic and potentiostatic electropolymerization techniques were used to make the conducting polymer deposits (E-PEDOT), which were obtained as a thin film onto the ITO surface. It was possible to control the thickness of the electrodeposited films in the range of 15 to 200 nm measured by AFM. With the thinner films (until 100 nm), it was observed that its absorbance at 700 nm was linearly dependent with their thickness and it was possible to obtain an equation that was used to measure the films thickness of future experiments. The E-PEDOT films were successfully used for constructing OSC's and the efficiency values found were equivalent or slightly superior to those found with the classical PEDOT:PSS anode.

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Keywords: Organic Solar Cell; Electrodeposits; PEDOT; Electropolymerization; Hole transport layer

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## 1. Introduction

The discovery of conductive polymers in 1977 by Shirakawa, MacDiarmid y Heeger<sup>1</sup> was the beginning of a new era of technologically important polymers, whose enormous quantity of applications make them win the Nobel Prize in 2000. Among the important applications can be highlighted the organic solar cells (OSC's). These devices are quite new in the photovoltaic arena and have reached until now over 10% of efficiency in less than 15 years of existence.<sup>2</sup> The main advantage of OSC's vs. the inorganic (Si) solar cells is their cost, which is lower, and the much simpler preparation conditions to make them.<sup>3</sup> The inner structure of the OSC's contains a glass substrate, a transparent electrode generally Indium Tin Oxide (ITO) working as anode, a layer of 40-60 nm of conducting polymer polyethylenedioxythiophene (PEDOT) serving as hole transport layer, an active layer which is a mixture of an electron donating and an electron acceptor compound and finally the circuit is closed with a metal layer serving as cathode (Figure 1). Several mixtures of donating-acceptor systems have been proposed; one of them which was used in this work is the poly-[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylen-vinylene] (MEH:PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-[6,6]-methane-fullerene PCBM).<sup>4</sup>

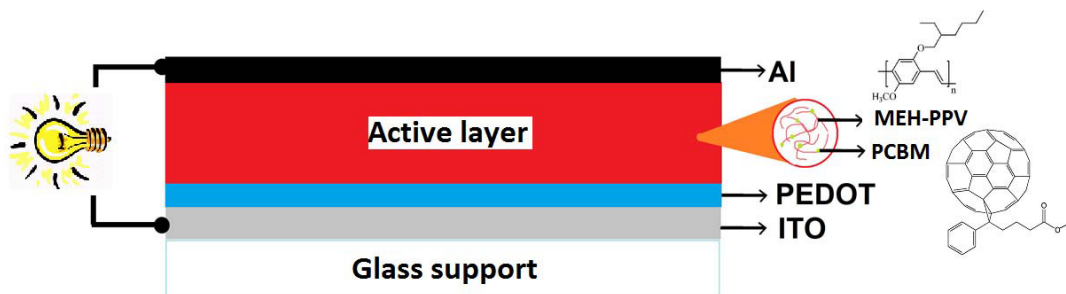


Fig. 1. Scheme of a typical OSC

Classical method for deposit the thin layer of PEDOT is spin casting from the aqueous PEDOT:PSS suspension, and electrochemical methods have been underestimated to make these films in the OPVC's field. Electrochemistry can be used efficiently to generate conducting polymers directly from the corresponding monomer.<sup>5</sup> The polymerization mechanism follows an oxidative pathway where the cation-radical intermediates dimerize to obtain the oligomers and polymers that are deposited on the electrode used for the oxidation process. The quantity of conducting polymer deposited on the electrode can be easily controlled with the parameters that are used in the electrochemical experiment. Particularly for PEDOT is well known that electropolymerized films (E-PEDOT) have high conductivity, but there are few reports of using in OPVC's these films of PEDOT obtained by means of an electrochemical technique.<sup>6</sup> Thus, our interest was to use two electrochemical techniques (Potentiodynamic or cyclic voltammetry and Potentiostatic or chronoamperometry) in different electrolyte solutions to obtain Glass/ITO/E-PEDOT films and to construct OPVC's with this anode composition.

## 2. Experimental

### 2.1. Materials

Glass/ITO electrodes were acquired with KINTEC Company and they have a resistivity of 10 ohm/m<sup>2</sup>, polished grade, (25x10x1.1 mm). EDOT (PM = 142.15 g/mol, d = 1.334 g/cm<sup>3</sup>), anhydrous acetonitrile (ACN, 99.8 % purity), PEDOT:PSS (conductive grade, dispersion in H<sub>2</sub>O 1.3 % w/w), MEH-PPV (Mn = 70000 - 100000 g/mol, mp > 300°C) and the Wood's metal (Eutectic alloy 50 % Bi, 26.7 % Pb, 13.3 % Sn y 10 % Cd, grains, mp ~ 75°C) were bought to ALDRICH Co. Electrolyte salts of tetrabutylammonium perchlorate (TBAP, ≥ 99 %, PM = 341.92 g/mol), hexafluorofosfate (TBAF, ≥ 99 %, PM = 387.43 g/mol) and tetrafluoroborate (TBAB, puriss, PM = 329.28

g/mol) were FLUKA. PCBM ( $\geq 99.5\%$ , PM = 910.9 g/mol) was from SES Research. No further purification was carried out.

## 2.2. Electrodeposition of E-PEDOT films

ITO electrodes were cleaned before its use initially with cotton and an aqueous solution of Triton X-100 (1:100), followed by 10 min of consecutive ultrasonic baths in solutions of Triton X-100 (1:100), deionized water, ethanol, EDTA 1 mM (pH = 13), and finally deionized water. The electrodes were dried at room temperature. The electrodeposit solution (10 ml) consisted in EDOT 5 mM and TBAP (P), TBAF (F) o TBAB (B) 0.1 M. The solution was deoxygenated by a gentle bubbling of  $N_2$  (INFRA, 99.999 %) during 10 minutes. The solution was prepared directly in a 3 electrodes electrochemical cell fitted with WE: ITO (area 1.5 x 1.0 cm), CE: Pt foil (area  $\approx 1.6 \times 1.6$  cm), parallel each other with a distance of 1.5 cm and RE:  $Ag^0/AgNO_3$  ( $AgNO_3$  0.01 M/ TBAP 0.1 M en ACN, 0.47 V vs NHE). All the experiments were carried out under  $N_2$  atmosphere (Figure 2).

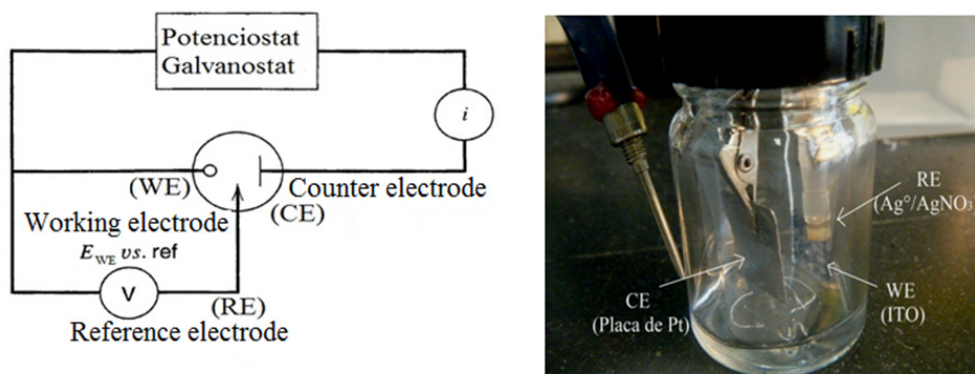


Fig. 2. Electrochemical cell used for the PEDOT electrodeposits. WE: Working electrode; CE: Counter electrode; RE: Reference electrode.

The potential during electrodeposits was controlled using a BAS100W potentiostat using chronoamperometry (CA) or cyclic voltammetry (CV). Once the electro-polymerization occurred, the electrode was rinsed with clean ACN, dried with  $N_2$  and were kept in hermetic vials until its use. PEDOT electrodes obtained by CV were used in the oxidized state, applying a potential pulse of 1.31 V vs  $Ag/Ag^+$  during 30 s in clean electrolyte.

## 2.3. Analysis and characterization of E-PEDOT films.

### 2.3.1. Electrochemical analysis

Electrochemical characterization was carried out in a three electrodes cell containing clean electrolyte with the same salt where the film was obtained (TBAP, TBAF o TBAB 0.1 M) in anhydrous acetonitrile under  $N_2$  atmosphere at 25 °C. WE was: ITO/E-PEDOT: $ClO_4^-$ ,  $PF_6^-$  or  $BF_4^-$  deposit surface  $\approx 1.0 \times 1.0$  cm limited with an scotch type. CE: Pt gauze  $\approx 1.9 \times 1.5$  cm. RE:  $Ag^0/AgNO_3$ .

### 2.3.2. UV-Vis analysis

The ITO/E-PEDOT electrodes were analyzed in a spectrophotometer Thermo Scientific GENESYS 10S UV-Vis, The spectrum was obtained reading in the range 300 to 1100 nm using as blank a new and clean electrode of ITO. An *ad-hoc* plastic holder was constructed from a plastic cell to have reproducible measurements.

### 2.3.3. AFM analysis

Morphology analysis and thickness of the oxidized E-PEDOT were studied with an Atomic Force Microscope JEOL JSPM 4210 or an Asylum MFP 3D Origin Scanning Probe Microscope in tapping mode with a 80 x 80  $\mu m$  scanner. The thickness was obtained by means of transversal cut-off in the central region of the polymer with a scalpel. The height of the polymer step was measured by triplicate in different polymer regions and the reported

value is an average of this points. The AFM images were analyzed with the WinSPM 407 program and processed with WinSPM Data Processing 2.12 program.<sup>7</sup>

### 2.3.4. Organic Solar Cell construction and test

All the OSC constructed with a glass/ITO/E-PEDOT anode were compared with a glass/ITO/PEDOT-PSS anode. This last film was obtained using a Spin coater, Chemat Scientific KW-4A with two rotation steps: a) 300 rpm 4 s and 2230 rpm 60 s. The electrodes were maintained in the oven at 80°C overnight before deposition of the active layer. The active layer was prepared dissolving 5mg of MEH-PPV and 10 mg of PCBM in chloroform with magnetic stirring; prior its deposition was sonicated during 20 min. The active layer was spin coated deposited with the same two rotation steps used for applying PEDOT-PSS. The selected region of analysis was delimited with Scotch magic tape® leaving a free area of 1 cm<sup>2</sup>. Some pellets of Woods metal, which behaves as cathode,<sup>8</sup> were melted on a glass at ca. 80°C; the melted metal was gently placed on the selected area closing the OSC circuit. To characterize the OSC, was used a Xenon lamp Oriel Research Arc Lamp Source 50-200 W, 1.5 inch Series UV-Fused Silica Aspher calibrated with a reference solar cell (Newport-Oriel, Reference Solar Cell and Meter 91150V) to obtain 100 mW/cm<sup>2</sup> (1 sun). The OPVC was fitted parallel to the incident light and the current-voltage curve was obtained with a Keithley Instruments, Source Meter 2400 connected to a personal computer running a Labview software specially designed for this task. From these curves the operational parameters of the OSC's were calculated: open circuit potential ( $V_{OC}$ ), current density in short cut ( $J_{SC}$ ), fill factor (FF) and efficiency ( $\eta$ ).

## 3. Results and Discussion

The EDOT showed an oxidation signal with the same characteristics in the three electrolytes used in ACN, tetrabutylammonium perchlorate (P), hexafluorofosfate (F) o tetrafluoroborate (B) 0.1 M (Figure 3). The peak potential of the oxidation is located at 1.38 V, in the second cycle can be clearly observed an increase of the baseline current indicative that the conducting polymer is growing. With this information the E-PEDOT films were generated on the ITO electrodes.

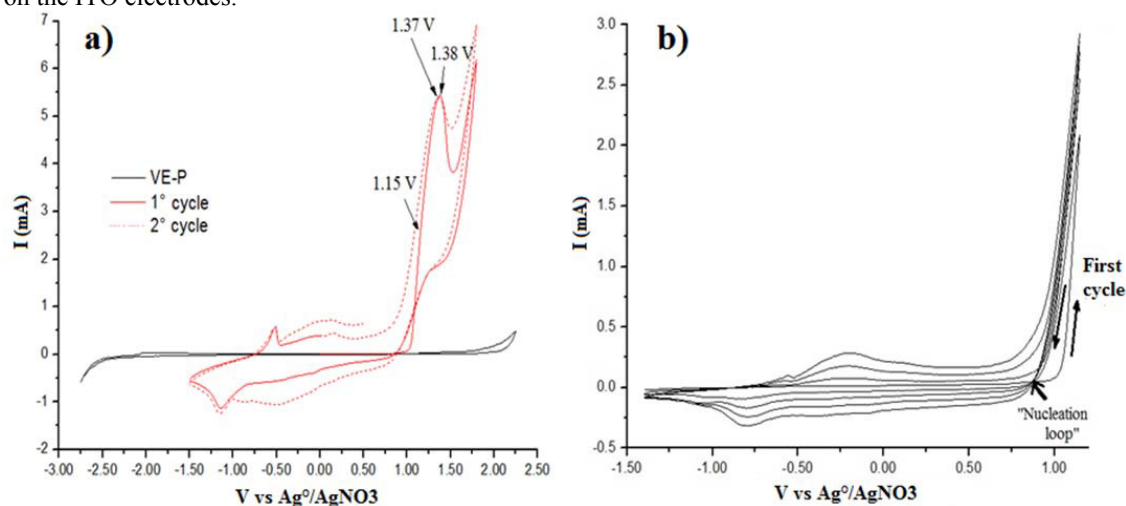


Fig. 3. a) Electrochemical window and oxidation signal of EDOT 5 mM with in ACN, TBAP (P) 0.1 M,  $v = 100$  mV/s, WE: ITO, CE: Pt, RE: Ag/Ag<sup>+</sup>. b) Potentiodynamic electrodeposit ( $E_i = -1.4$ ,  $E_f = 1.31$  V,  $v = 100$  mV/s) of PEDOT on ITO electrodes. EDOT 5 mM with in ACN, TBAP (P) 0.1 M, WE: ITO, CE: Pt, RE: Ag/Ag<sup>+</sup>

The potentiodynamic polymerization using cyclic voltammetry experiments (Figure 3b) shows the classical growth of the base line with the number of cycles, as well as the nucleation loop generally observed during the conducting polymers electrodeposition in the first cycle. In this technique the thickness control parameter are the number of cycles, the scan rate and the inversion potential value ( $E_i$ ). For comparison purposes, it was selected the

same anodic potential value for potentiodynamic and potentiostatic PEDOT deposition experiments and the scan rate was fixed at  $v=100$  mV/s in all the experiments. The sole parameter that was changed to modify the thickness was the number of cycles; higher is the number of cycles the thickness of E-PEDOT films increased. In the potentiostatic growth, the chronoamperogram in TBAP (CA-P) shows a very fast polymerization characterized by a fast growth of the current in the first second and later the current drops due to the diffusion controlled process (Figure 4). As voltage pulse time increased the current drop is larger indicating that the electrode interface ran out of starting material, thus limiting the speed of polymer growth. In this technique during the whole experiment there is polymerization, because the electrode is positive polarized; the thickness control parameters are the time of pulse and the chosen oxidation potential.

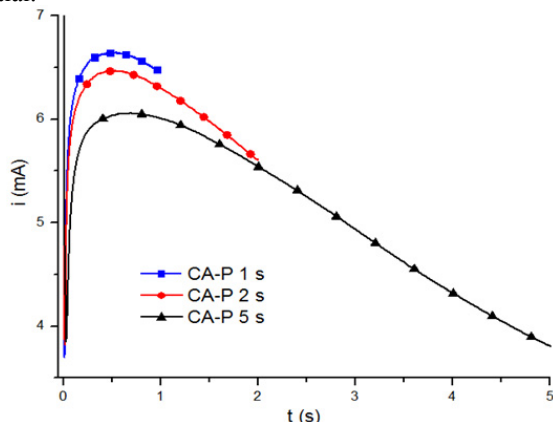


Fig. 4. Potentiostatic (1.31 V) electrodeposits of PEDOT on ITO electrodes. EDOT 5 mM with in ACN, TBAP 0.1 M (P), WE: ITO, CE: Pt, RE: Ag/Ag<sup>+</sup>

The obtained films were analyzed by UV-Vis spectrophotometry in the oxidized state (Figure 5a). Films obtained by chronoamperometry using different potential pulse time are already charged at the desired level but those obtained by cyclic voltammetry required a pulse of potential of 1.31 V during 30 s to be analyzed in the desired oxidized state. The E-PEDOT films showed a sky blue color for the thinner films and a deep blue color for the thicker ones (right to the UV-Vis spectra in figure 5). In the oxidized state, UV-Vis PEDOT spectra depicts very low absorbance in the region of 300-500 nm, but at higher wave lengths the absorbance increase considerably, showing a shoulder with maxima in 700 nm. This value was selected to read the E-PEDOT absorbance value. The first proposal was to find a correlation between the films thickness and the absorbance value. In order to explore this idea, the thickness analysis was carried out by AFM and was correlated with the absorbance obtained for each film. The AFM showed clearly the polymer step and from the transversal section analysis (red line in figure 5b), it was determined the thickness average of the electrodeposited film.

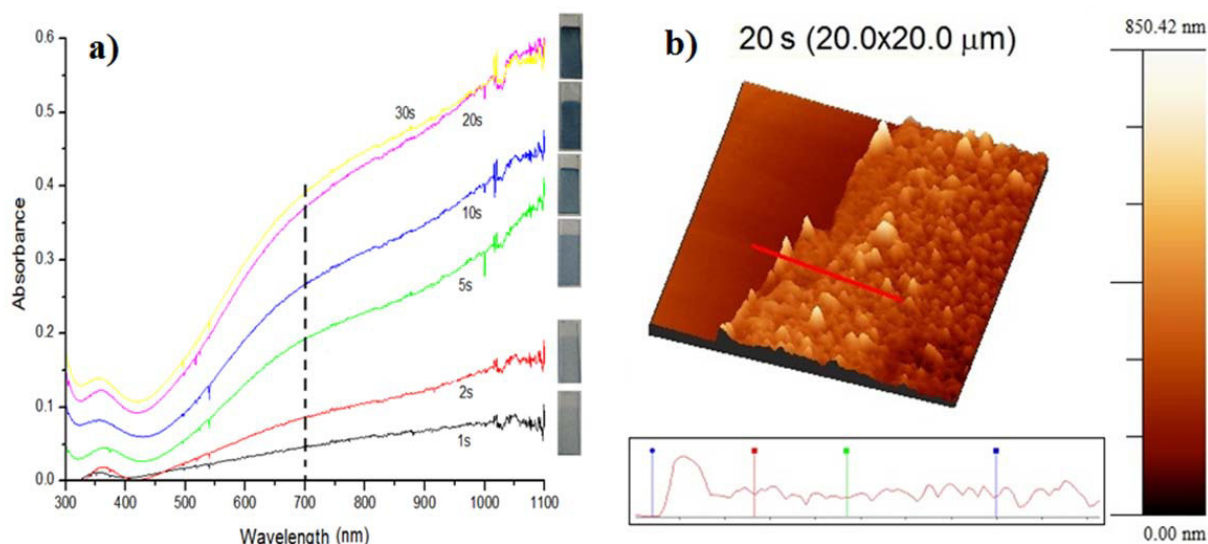


Fig. 5. a) UV-vis spectra of E-PEDOT/CIO<sub>4</sub><sup>-</sup> deposits on ITO electrodes potentiostatically obtained at 1.31 V vs Ag<sup>+</sup>/AgNO<sub>3</sub> using the different pulse time. In the right side can be seen the color of the obtained films. The vertical dashed line indicates the length wave (700 nm) used for reading the absorbance value of the films. b) AFM micrography obtained in tapping mode showing the polymer step and the morphology analysis of a E-PEDOT/CIO<sub>4</sub><sup>-</sup> deposit on ITO electrode obtained by chronoamperometry at 1.31 V vs Ag<sup>+</sup>/AgNO<sub>3</sub>, and 20 s of time pulse.

Figure 6 shows the correlation between absorbance and thickness, where is observed to follow a linear trend at thickness values until 100 nm. The experiments were repeated three times and the confidence bars of these experiments are shown in the figure. It can be concluded that the production of thinner films is much more reproducible than thicker films. The inset curve depicts only the linear region, the linear regression analysis of these points gave the following equation,  $A^{700nm} = -0.0011 + 0.0031 L$  that let us rapidly correlate in the future experiments, the thickness value of the E-PEDOT film by means of the simple absorbance determination of the electrodeposited conducting polymer on ITO.

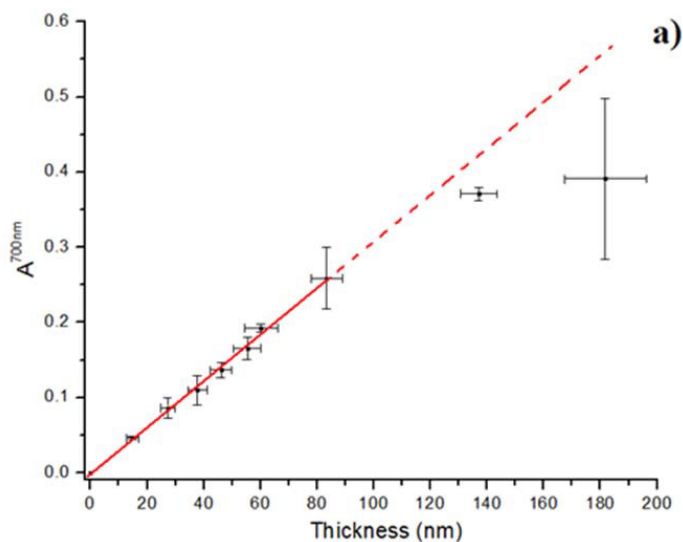


Fig. 6. Correlation between E-PEDOT films absorbance read at 700 nm and the thickness determined by AFM.

This equation showed to be applicable to all the electrolytes used (TBAP, TBAF o TBAB 0.1 M) in anhydrous ACN. The thickness and the absorbance were not modified by the anion that is being used to dope the polymer film in the oxidized state. This control was taken for the films obtained by chronoamperometry (CA) and Cyclic Voltammetry (CV) (Table 1).

Table 1. Comparison of the theoretical (equation 1) and experimental thickness with different electrolytes

Entry	$A_{700\text{nm}}$	Theoretical thickness (nm)	Experimental thickness (nm)
CA-P 4 s	0.150	$49 \pm 4$	$51 \pm 3$
CA-F 5 s	0.149	$49 \pm 4$	$54 \pm 4$
CV-P 8 s	0.161	$52 \pm 4$	$53 \pm 2$
CV-F 4 s	0.167	$54 \pm 4$	$51 \pm 4$

The layer of PEDOT in OSC's must have a thickness between 40-60 nm, values which are inside the linear region of our calibration curve and correlates with absorbance values of 0.1 to 0.2. Generally this layer is generated through the spin coating of an aqueous dispersion of the polymer. In order to solubilize it, the polyelectrolyte polystyrenesulfonate (PSS) is used as counterion. The water remain, the phase separation of the PEDOT and PSS and finally the strong acidic character of the PSS generate serious drawbacks that decrease the efficiency of the OSC's.<sup>9-11</sup> Therefore, electrochemical deposition of E-PEDOT from a neutral and non-aqueous system can be an important improvement in this field. The E-PEDOT deposits were optimized to obtain the best efficiency with an OSC with ITO/E-PEDOT/MEH-PPV/PCBM/Woods metal architecture. These OSC's generate J-V curve depicted in Figure 7. It is observed that the E-PEDOT (CA 0.5mM) generates more voltage that the equivalent cell constructed with PEDOT:PSS therefore the efficiency of the cell increased. The values of the operational parameters of the cells are shown in table 2.

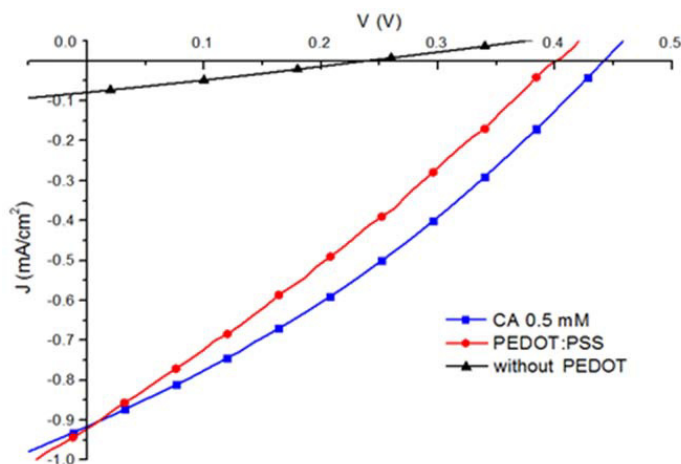


Fig. 7. J-V curve for the OSC's constructed with different anodes using ITO/E-PEDOT/MEH-PPV/PCBM/Woods metal architecture

Table 2. Operational parameter of OSC's with ITO/E-PEDOT/MEH-PPV/PCBM/Woods metal architecture.

Entry	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	η (%)
E-PEDOT CA 0.5 mM	0.45	0.90	0.31	0.13
PEDOT:PSS	0.41	0.90	0.28	0.10
Without PEDOT	0.24	0.08	0.25	0.01

#### 4. Conclusions

The PEDOT was electrochemically deposited on the glass/ITO electrodes controlling adequately the film thickness. The relationship between absorbance and thickness follows a linear trend only for thickness values until 100 nm. The E-PEDOT films were successfully used for constructing OSC's and the efficiency values found were equivalent or slightly superior to those found with the classical PEDOT:PSS anode.

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