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Optimizing the oxidation level of PEDOT anode in air-PEDOT batteries

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Abstract

We report an air-PEDOT battery where an optimized oxidation level of the PEDOT anode was performed using a simple physical dedoping process, resulting in batteries with high stability in air. Some PEDOT:PSS chains were reduced to their neutral state, preserving their good electrical conductivity, by dipping the PEDOT:PSS films into mixtures of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and dimethyl sulfoxide (DMSO). Because of the neutral PEDOT chains are sensitive to being reoxidized in air, PEI was put on these DMSO-DBU/PEDOT:PSS anodes to ensure their air stability and to maintain their low level of oxidation during the battery operation. The difference in the oxidation level between the dedoped PEDOT:PSS and pristine PEDOT:PSS electrodes produces an open circuit voltage of about 0.80 V almost constant by several days (around 30 days) in air. These batteries present discharge currents of ≈ 2 μA with an electrical load of 0.1 MΩ during 10 hours of operation, output powers of ≈ 1.2 μW, using an electrical load of 265 kΩ, which is in the required range for powering wireless transceiver and sensors.

1. Introduction

Polymers have a great number of interesting properties such as good tenacity, good elongation, ease of processing, low weight, and low cost that make them exceptional for their applications in organic electronics. The excellent conductivity of conjugated polymers opens up new design possibilities in the fields of production, storage and transformation of electrical energy. Additionally, polymer-based devices could be more economical and less polluting, compared with those based in inorganic semiconductors, and a promising technology for flexible electronics. However, the conductive polymers present two main disadvantages for a possible technological application: their insolubility associated to their low processability and their conductivity instability given by their degradation in air. Poly(3,4-ethylenedioxythiophene) doped with the polymeric counteranion poly(styrenesulfonate) (PEDOT:PSS) can be an attractive alternative because of its oxidized state (*p*-doped) ($PEDOT^+$) presents good electrical conductivity, very high electrochemical stability, good air stability and is easy-to-process due to the PSS counterion. The PSS counterion acts as the source for the charge balancing [1,2] and keeps the PEDOT chains dispersed in the aqueous medium. Moreover, some reports show that PEDOT chains can be carried up to a partial reduced state (dedoped, neutral, $PEDOT^0$) by using reducing agents [3-8] resulting in changes in the electrical, thermoelectric, and optical properties [5-9], opening perspectives for new applications.

Between the possible applications of PEDOT:PSS in organic electronics, one of the most interesting is their use in organic battery. In fact, PEDOT has already been used as cathode in metal/air batteries [10,11] and all polymer-air batteries in coplanar configuration have been fabricated with a polyethyleneimine (PEI)/PEDOT:PSS electrode as anode, PEDOT:PSS electrode as cathode and PSSNa as electrolyte. In this last case, it was reported an initial open

circuit voltage (V_{OC}) of ~0.53 V that drops to 0.48 V during the first 50 h of self-discharge in air. In addition, these batteries showed an output power of 0.67 μW using a 265 kΩ electrical load, and an electrical discharge current of 1.7 μA during 1 h, using a load of 0.1 MΩ [7]. The same type of batteries, but in the stacked configuration, was fabricated with the aim of increasing battery capacity, using a screen printing fabrication route that will facilitate large scale manufacturing; these batteries give a V_{OC} of ~0.60 V, displayed a practical specific capacity of 5.5 $mAhg^{-1}$ and an electrical discharge current of 0.6 μA [12]. In all polymer air batteries based in PEDOT:PPS, the use of PEI on the anode is a key factor for the battery operation. PEI has a basic character, reduces the oxidized $PEDOT^{+}$ to its neutral state $PEDOT^{0}$ and keeps this neutral state stable in air through dynamic redox reactions [7]. Even though the electrical current and output power of these all polymer air-PEDOT batteries are very small, they could be used in niche market such as in 10 μW low power RFID chips, in 17 μW at 1.4-1.6 V operational amplifier, in 20 μW at 0.9 V GMR-switch or for the update of a 5 μW cm^{-2} e-ink display [13]

In order to provide a large V_{OC} in these PEDOT:PSS based batteries, the oxidation level of both electrodes must be different as much as possible. However, a complete dedoping of PEDOT:PSS chains, i.e neutral PEDOT chains, leads to a loss of electrical conductivity of the electrode. Thus, the oxidation level of both electrodes must be optimized, preserving their good electrical conductivity. Previously, we reported a reduction of PEDOT:PSS chains to its neutral state by a simple and physical process consisting in the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, $C_9H_{16}N_2$) to the aqueous PEDOT:PSS dispersion.[14]. DBU is generally used as reagent and catalyst in organic synthesis.[15-18]. The advantages of this base compared with other ones are their commercial availability and relatively low cost [15]. In the present work, we report a simple dedoping process based in dipping the PEDOT:PSS films into DBU mixed with

dimethyl sulfoxide (DMSO). DMSO is a polar organic solvent used to enhance the conductivity of PEDOT:PSS films [19-24] due to a partial phase separation of the PSS excess.[19,24] The effects of mixing DBU with DMSO on the dedoping process of PEDOT:PSS films and their use of these treated films as battery anode were studied. Using this simple dedoping process is possible to fabricate anodes in all polymer air-PEDOT batteries, which present low oxidation level and preserve good electrical conductivity. Because of the neutral PEDOT chains are sensitive to being reoxidized in air, PEI was put on the DMSO-DBU/PEDOT:PSS anode to ensure its air stability and to maintain its low level of oxidation during the battery operation. The optimized batteries presented $V_{OC} \approx 0.80$ V for several hours in air, an electrical discharge current of ≈ 2 μA using a 0.1 MΩ load during approximately 10 h of operation. Additionally, the batteries showed an output power ≈ 1.2 μW with a discharge current of ≈ 1.5 μA using a 265 kΩ electrical load, implying that they could be used in applications such as powering wireless transceiver and sensor [13].

2. Experimental method

The solution was prepared using an aqueous dispersion of PEDOT:PSS (Clevios P, purchased from Heraeus). This PEDOT:PSS aqueous dispersion was previously filtered through a 1 μm syringe filter. Dow Corning glass substrates were successively ultrasonically cleaned in acetone, methanol and isopropyl alcohol for 20 min each time. Immediately, after evaporation of the solvents, the substrates were maintained in a UV-ozone ambient for 25 min. Both electrodes, cathode and anode, were made of PEDOT:PSS. Thin films were fabricated on these glass substrates by spin-coating of PEDOT:PSS solution (1870 rpm for 5 s, followed by 40 s at 2500

rpm) and then dried at 100 °C for 15 min, then a second film was deposited over using exactly the same conditions. On the other hand, thick films were deposited on the glass substrates by drop casting of PEDOT:PSS solution and dried at 100 °C for 30 min. Oxidized (*p*-doped) $PEDOT^+$ was used as cathode whereas partial neutral $PEDOT^0$ was used as the anode. For the reduction of $PEDOT^+$, the following post processing was performed: after deposition, thin and thick films, the dried PEDOT:PSS films were immersed into a solution made of DMSO (1 ml = 14.08 mmol) and DBU (1 ml = 6.68 mmol) at room temperature and at two different v/v ratios (2:1, 6 ml of total mixture and 10:1, 5.5 ml of total mixture). These films were immersed at different times (3, 9 min and 20 min), then the samples were dried at 100 °C for 30 min to evaporate the residual solvent. Film thicknesses of pristine (ca. 165 nm, 6 μm and 8 μm) and immersed PEDOT:PSS samples were obtained averaging six measurements made on each sample using an Alpha Step 500 surface profiler along two parallel scratches going from center to and edge of the films. In addition, to avoid the reoxidation of the neutral PEDOT chains in air, branched PEI (Sigma Aldrich with Mw= 800 g/mol) was put on the DMSO-DBU/PEDOT anode. The battery with an area of 2 cm^2 was finally fabricated in sandwich configuration (Figure 1) using as solid electrolyte poly(styrenesulfonate) (PSSNa, Sigma Aldrich Mw=70000 g/mol) between both electrodes. Absorption measurements were performed with an UV-Vis-NIR Varian Cary 5E spectrophotometer.

3. Results

Clevios P PEDOT:PSS aqueous dispersion is generally used for antistatic applications as a raw material or in formulations with conductivity enhancer and binders optimizing its coating in different kind of substrates. Even though Clevios P as a raw material shows a good conductivity

(σ ~1 S/cm pristine film and σ ~80 S/cm with DMSO conductivity enhancer), this aqueous dispersion is not used for the fabrication of organic electrodes, since other PEDOT:PSS formulations such as PH100 present a better conductivity (σ ~800 S/cm with 5 wt% DMSO). However, Clevios P is much cheaper than PH1000. In this work, we have used Clevios P to show that a key parameter in the fabrication of batteries based on PEDOT:PSS is the optimization of the oxidation level of PEDOT:PSS layer used as anode.

The effects of mixing DBU with DMSO on the dedoping process were studied. Figure 2 shows the measured Vis-NIR absorption spectra of dedoped PEDOT:PSS films using DMSO-DBU at different v/v ratio mixtures and immersion times. Dedoped PEDOT:PSS film presents same features previously reported, that is one absorption band at ~600 nm and the other one at ~900 nm [25-28]. The first band at 620-639 nm is related to the neutral PEDOT [27,28] and attributed to π-π* transition. The second one is assigned to the polaronic band, [25,26,29-32] characteristic of the oxidized state. The disappearance or decrease of the polaronic band is an indication of the conductivity loss of the PEDOT: PSS film. From figure, we observe that a large number of PEDOT:PSS chains in the treated films were dedoped, the intensity of the π-π* band is relatively greater than the polaronic band (Fig. 2).[33-35]. At low DBU concentration in the mixture (DMSO-DBU, 10:1) and larger immersion times (9 and 20 min), PEDOT absorbance spectra show the same features whereas when the immersion time is around 3 min, the band at 900 nm is smaller compared with the previous ones. This indicates that the effect of the DMSO-DBU treatment mixture on the PEDOT:PSS film is first to reduce the $PEDOT^+$ chains closer to the surface by means of electron transfer from DBU to $PEDOT^+$, then the DMSO, which is in greater ratio in the treatment mixture, oxidizes some $PEDOT^0$ chains or remove them from the

film. On the other hand, when the ratio of DBU to DMSO in the mixture is increased, the intensity of the polaronic band is also reduced and the π-π* band becomes relatively more intense. For this high DBU concentration, the immersion time is not relevant for the dedoping efficiency; the reoxidized chains can be reduced again or those $PEDOT^0$ chains washed away by DMSO are replaced by new DBU reduced PEDOT chains. Using this simple dedoping process, it is possible to fabricate organic electrodes with a required level of oxidation for their use as anode in all polymer air-battery.

The thin film battery was fabricated using thin cathode and anode (170 nm); the anode consisted of a PEDOT:PSS film that was dedoped using a DMSO-DBU (10:1) mixture immersed during 3 or 9 min. This kind of battery device gives a V_{OC} of about 0.55 V, which quickly drops to 0.30 V in the first minutes of self-discharge in air. Moreover, the effect of thick electrodes and the role played by PEI on the stability and performance of these devices were studied. The thick anode was fabricated with PEDOT:PSS films treated using concentration of DMSO-DBU mixture and immersion times previously discussed for the thin electrodes. For batteries with thick $PEDOT^+$ cathode and $PEDOT^0$ anode electrodes (both around 8 μm), the devices show a $V_{OC} \approx$ 0.7 V, then the V_{OC} drops to 0.50 V during the first 30-40 min of self-discharging measurement in air. This shows that although it is possible to obtain V_{OC} much larger than 0.5 V optimizing the oxidation levels of the anode, the instability in air of the $PEDOT^0$ chains is a problem that must be solved. To avoid the rapid reoxidation of the anode, a second type of thick polymer battery was fabricated where PEI was deposited on the anode electrode. Figure 3a shows the V_{OC} change of the device exposed in air and the discharging curve of a battery using PEI on the anode, operated in air at room temperature without encapsulation. For measuring the V_{OC} in air, the

battery was connected all time with a multimeter, V_{OC} value was measured each minute until reach 20 min, from here, each 5 min until reach 40 hours, continuing each 30 min until reach 61 h. After that, V_{OC} measurement continued each 24 hours (61-229 h). Finally, V_{OC} value was measured each 48 hours, because we did not observe significant changes in self-discharge curve, indicating a high stability of the battery under ambient conditions. From figure, we observe that at the beginning, the battery shows a V_{OC} of 0.63 V and the voltage slowly increases until reaching 0.80 V after around 12 hours of being fabricated; this value was maintained for more than 400 hours. All batteries, after PEI deposition on DMSO-DBU/PEDOT anode, were immediately stacked in sandwich configuration and they showed a similar trend, around 384-432 hours a V_{OC} of 0.80 V is maintained.

V_{OC} behavior in the first 12 hours of the batteries exposed to air shows that, after had been assembled, the reduction reactions of $PEDOT^+$ chains continue due to the PEI on the anode, until the redox processes occurring on the anode reach a dynamical equilibrium, then V_{OC} is stabilized. The study of the discharge current curves of the battery was carried out when the devices reached a V_{OC} of 0.80 V, using three different loads as shown in Figure 3b. From figure, we observe that the discharge current drops faster for an electrical load of 0.1 MΩ, but not faster as is reported in other work. [7] After 10 h of battery operation, the discharge current is ≈2 μA, which decreases to ≈ 1 μA after 100 h of battery operation. For a 10 MΩ electrical load, the discharge current is almost constant during all the battery operation. This kind of device, however, still presents a small current and, as was discussed before, this all polymer air battery could be used in limited applications. [7,12,13] The slow self-discharge process, the high V_{OC}, and high discharge current, compared with other works [7,12] can be attributed to: (a) PEDOT films conforming the electrodes, anode and cathode, are thicker, as well as the PEI layer, consequently, the amount of

active material of the battery is much larger; (b) the process of optimizing the oxidation level of the anode using DMSO-DBU mixtures; (c) the dynamical reactions between PEI with the dedoped PEDOT:PSS films, additionally, the PEI layer protects the anode of the fast reoxidation.

The study of the oxidation level optimization of the anode using the DMSO-DBU treatment mixtures as well as the role played by PEI layer on the change of the optical properties for thin dedoped films were carried out. This study was performed using different v/v DMSO-DBU mixture ratios combined with different treatment times. Also, the effect of the interaction time of DMSO-DBU treated PEDOT films with PEI layer was considered (Fig. 4). As is observed from the absorption spectra of PEI/dedoped and PEI/pristine films, a decreasing of polaronic absorption bands in the near infrared (~ 900 nm) always occurred under different treatment conditions. From figure 4a, we observe that after of 20 min PEI interaction, PEDOT:PSS film treated with DMSO-DBU mixture during 3 min shows the most intense polaronic band whereas the decreasing of this band is larger for the PEI/pristine film. However, after some hours of interacting with PEI (Fig. 4b and 4c), all films have reached almost the PEDOT neutral state, which is indicated by the disappearing of the polaronic band. It has been established that PEI acts as a reductant by donating electrons to the $PEDOT^{+}$ [7]. Thus, something similar must be occurring with DBU, which has been previously shown that acts as reducer [14]

$$PEDOT^{+}: PSS^{-} + DBU \rightarrow PEDOT^{0} + DBU^{+} : PSS^{-} \quad (1)$$

However, as is observed in the dedoped film using a high quantity of DMSO for short immersion time with PEI put on it, this PEDOT film does not reach the same reduction level of the other films (Fig. 4a). Hence the use of DMSO in the mixture has an influence on the performance and/or stability of the device. The role played by DMSO in PEDOT:PSS films is mainly related

with a partial phase separation of the excess of the PSS and the increase of the PEDOT rich average grain size, which leads to the effective reduction of the PSS insulation barrier between the PEDOT grains. [36] Additionally, we can infer that dedoping, using the DMSO-DBU mixture, is performed on the first surface layers of PEDOT:PSS films (Fig 4a), since the absorption spectrum still shows the presence of a polaronic band after 30 min of PEI treatment. However, PEI continues penetrating the DMSO-DBU treated PEDOT:PSS film, dedoping PEDOT:PSS chains, until the film is almost completely reduced (Fig 4b and 4c). Note that in these cases we are only considering the effect of PEI in the DMSO-DBU treated and pristine PEDOT films, not the battery as a whole, so it is possible to reduce almost all PEDOT chains.

On the other hand, in the case of the battery, after the reduction process of the DMSO-DBU treated PEDOT: PSS films (Eqs.1), the operation of the battery is given by the following half reactions during electrical discharge [7]

Anode:

$$PEDOT^{+}:PSS^{-} + PEI \rightarrow PEDOT^{0} + PEI^{+}:PSS^{-} \quad (2)$$

$$PEDOT^{0} + PSS^{-}:Na^{+} \rightarrow PEDOT^{+}:PSS^{-} + Na^{+} + e^{-} \quad (3)$$

Cathode:

$$PEDOT^{+}:PSS^{-} + Na + e^{-} \rightarrow PEDOT^{0} + PSS:Na \quad (4)$$

$$PEDOT^{0} + 1/4\ O_2 + 1/2\ H_2O + PSS:Na \rightarrow PEDOT^{+}:PSS^{-} + NaOH \quad (5)$$

Thus, $PEDOT^{0}$ chains of the anode are reoxidized (Eq. 3) during the battery operation and the effect of PEI is to reduce these $PEDOT^{+}$ chains again to the neutral state or to reduce new

$PEDOT^+$ chains (Eq. 2), keeping an optimal oxidation level in the anode obtained in the initial DMSO-DBU treatment (Eq. 1) and, consequently, a high V_{OC}. Another effect of the PEI viscous layer is to hinder the interaction of the surface of the reduced anode with the dioxygen (O_2) in the ambient and to avoid an immediate re oxidation of the $PEDOT^0$ chains, thus allowing a potential difference between both electrodes and stable battery operation for several hours. Finally, the effect of optimizing the oxidation levels of the anode through DMSO-DBU treatment allows the reduction of PEDOT chains, preserving a good conductivity in this electrode and, in this way, a good discharge current during the battery operation, where a key parameter in the current electric generation in a battery is the electronic transfer rate at the electrode surface [37].

To ensure that the optimization of the oxidation level is a very important parameter in the efficiency of the batteries and the role played by DBU-DMSO mixture in this optimization, we have fabricated batteries with two different kind of anode dedoping. One where the PEDOT film was dedoped only with the interaction of the PEI layer, without any previous dedoping process, and one where the PEDOT film was dedoped using only DBU, then the PEI layer was put on it. In the first case, PEI layer was deposited on pristine PEDOT:PSS film and allowed to interact during 120 hours before assembling the battery. The importance of the interaction time of PEI with the PEDOT:PSS film will be explained later. The maximum V_{OC} reached was around 0.50 V; the battery gave a discharge current of ≈ 1.3 μA using a 265 kΩ electrical load. In the second case, the PEDOT anode was dedoped with DBU using immersion times of 3 and 9 min. After that, a PEI layer was deposited on these dedoped films and allowed to interact with the DBU-PEDOT film for about 3 min and 120 hours, respectively, before the battery assembling. In the case of batteries with the anode dedoped using different immersion time and immediately

assembled (3 min), V_{OC} was around 0.42-0.46 V and, after 36-40 hours of air exposition, the maximum V_{OC} ~0.73 V was reached. When PEI was allowed to interact 120 hours with the dedoped films, the initial V_{OC} was around 0.72-0.78 V and was slowly decreasing; after of 72 hours of self-discharged in air V_{OC} was ~ 0.66 V. The discharge current for these batteries was ≈ 1.5 μA using an electrical resistor of 265 kΩ. Additionally, conductivity measurement in thin PEDOT:PSS films showed that DBU dedoped films presented high resistance, its conductivity value was below the measuring range of our multimeter, while the DMSO-DBU dedoped film showed conductivity of 0.08 and 0.54 S/cm for 2:1 and 10:1 DMSO-DBU concentrations, respectively. Thus, all these experimental evidences show the importance of optimizing the oxidation level of the anode, where the reduction in excess of the $PEDOT^+$ chains results in loss of electrode conductivity and, consequently, hinders the electronic transfer rate at the interface between PEDOT:PSS and PEI layer.

Where various battery parameters such as the capacity are related to the amount of electrochemically active material, we have varied the cathode thickness to study its effect on V_{OC} in function of the self-discharge time, preserving the same PEDOT thickness anode (8 μm) and the same amount of PEI deposited on the anode. Figure 5 shows the influence of the thickness of the cathode 8 μm (Fig. 5a), 6 μm (Fig. 5b) and 165 nm (Fig. 5c) on the V_{OC} value. The PEDOT:PSS films used as anode were dedoped using different v/v DMSO-DBU ratio mixtures (10:1 and 2:1) and different immersion times (3 and 9 min). In all the batteries of Figure 5, the anode PEDOT films were interacting with PEI during 120 hours before their assembling. It was found that the optimal time of PEI interaction is around 120-144 hours before battery assembling. Comparing the initial V_{OC} for the device in Figure 3 (0.63 V) with those showed in Figure 5a

(0.80 V), all made with the same electrode thickness, the same condition of v/v ratio DMSO-DBU mixture (10:1) and immersion time (9 min), we can observe the dependence on the initial V_{OC} with the PEI interaction time before they are assembled. Furthermore, we observe for the battery fabricated with thick cathodes and treated with 10:1 DMSO-DBU mixture the battery reached at the beginning of battery operation a V_{OC} value of around 0.80-0.82 V and, after some hours, the V_{OC} value increased reaching a maximum around 0.82-0.85 V (Fig. 5a). The V_{OC} behavior as a function of cathode thickness can be understood as follow: as is shown in the absorption spectrum of dedoped PEDOT:PSS film using 10:1 v/v DMSO-DBU ratio mixture and 9 min immersion time (Fig. 4b), the maximal reduction of the PEDOT chains is performed during the first hours (~20 h) of interacting with the PEI layer. After this time, the absorption spectrum of dedoped PEDOT:PSS film remains basically the same (Fig. 4c), which implies that the whole film has been dedoped or that a process of equilibrium of the redox reactions between reoxidation due to O_2 and the reduction of PEI has been reached in the PEDOT chains. Similar behavior was observed for all the dedoped films obtained with different DMSO-DBU mixtures and different immersion times. When the device was finally assembled, V_{OC} slowly increased, implying a continuous reduction of $PEDOT^+$ chains due to its interaction with PEI (Fig. 5a). Both devices, with the same 10:1 v/v ratio mixture and similar cathode thickness (8 μm) but with different immersion times, showed similar V_{OC} trends as a function of self-discharge time (Fig. 5a). Additionally, similar V_{OC} trend was observed for the batteries fabricated using a cathode thickness of around 6 μm and 10:1 v/v DMSO-DBU mixture and different immersion times (Fig. 5b). On the other hand, for batteries fabricated using PEDOT:PSS anodes treated with DMSO-DBU (2:1 v/v) mixture, i.e that containing a large ratio of DBU, the V_{OC} behavior is more irregular as a function of time and V_{OC} values are smaller than those anodes treated with reducing

mixtures containing a small DBU ratio. Note that in all the batteries showed in figures 5a and 5b, V_{OC} is in general greater than 0.6 V even after 1500 hours (around 60 days), of self-discharge in air, which indicates their great stability. In the case of thin film cathode (~ 165 nm), the V_{OC} values, after reaching their maximum, rapidly decreases in comparison with those fabricated with thick cathodes. This effect and the V_{OC} fluctuations as a function of the self-discharge time can be explained using Eqs. 4 and 5, which describe chemical reactions occurring on the cathode. Because the cathode thickness is small, the PEDOT film can be completely reduced (Eq. 4), implying a small V_{OC} value, and it is necessary to wait a certain time for its reoxidation (Eq. 5) with the consequent V_{OC} increasing.

Figure 6a shows the absorption spectra of dedoped anodes after self-discharge in air from batteries fabricated without and with a PEI layer on them. Those with a PEI layer correspond to the devices showed in Figure 5c. From figure, we observe that both spectra show a strong π-π* absorption band (around 580–690 nm), which is also observed in DMSO-DBU treated PEDOT films (Fig. 2). The intensity of this band is stronger in the dedoped-PEI anode in comparison with those where PEI was not deposited onto the dedoped anode. This shows again the protection of the PEI layer against the fast reoxidation of neutral $PEDOT^0$ chains as well as PEI reduction action on the oxidized $PEDOT^+$ chains during the battery operation. In addition, the enhancement of absorption band at ~900 nm for those anodes without PEI is attributed to the lack of this layer [7]. Pristine PEDOT:PSS film, which is used as the cathode layer, presents an absorption band at approximately 850 nm, attributed to polaronic states (Fig. 6b). After its self-discharge in air, the cathode of batteries fabricated with thin (165 nm) and thick (8 μm) anodes shows differences in its absorbance spectrum between them and with respect to the pristine PEDOT:PSS film. A

negligible change in the absorption spectrum of cathode (Fig. 6b) is observed in films from batteries with DMSO-DBU treated anode, no PEI deposited on it. On the other hand, a large change in the absorption spectrum is observed when PEI is deposited onto the thin/thick anode film (Fig. 6b). The growth of the absorption band at ~ 600 nm in the cathode indicates that some $PEDOT^+$ chains are reduced to $PEDOT^0$ due to the battery operation (Eq. 4), which implies a decrease of the V_{OC} value and explains its fluctuations, particularly for thin cathodes, as a function of time (Figure 5). From the cathode and anode absorption spectra of the discharged battery (Figure 6), we can deduce where the great stability and durability shown mainly in batteries with thick electrodes comes from. When the anode is very thin with respect to the PEI layer, the continuous interaction of the PEI with the PEDOT:PSS almost completely reduces the PEDOT:PSS film, decreasing the conductivity to very small values, and hindering the electron transfer processes. In addition, PEI layer hinders the reoxidation of the reduced chains. In the case where the cathode is very thin, the reduction of a large number of PEDOT:PSS chains, due to electrons coming from the anode (Eq. 4), is performed faster than its reoxidation due to O_2 (Eq. 5). Consequently, the oxidation level of the cathode is very similar to that of the anode and the battery loses its electrical characteristics.

4. Summary and Conclusions

A simple physical dedoping process of PEDOT:PSS films has been developed to fabricate the anode of air-PEDOT battery with its optimized oxidation level. The optimizing of the oxidation level of the anode was performed by dipping the PEDOT:PSS films into DMSO-DBU mixture. The treated PEDOT:PSS films showed a strong absorption band at 630 nm (π-π^* transition), indicating the dedoping of the PEDOT chains, whereas the intensity of the polaronic band (~ 900 nm) depended of the DBU concentration in the mixture as well as the immersion

time. The reduction in excess of the $PEDOT^+$ chains results in the loss of electrode conductivity hindering the electron transfer at the interface between PEDOT:PSS and PEI layer. In this way, varying these experimental parameters, the PEDOT oxidation level can be modified and, thus, its conductivity in order to preserve its electrode character. The use of DMSO in the treatment mixture has an influence on the performance and/or stability of the device, as well as the PEI viscous layer, which avoids an immediate reoxidation of the $PEDOT^0$ chains, allowing a potential difference between both electrodes and stable battery operation for several hours. The battery provides a V_{OC} of around 0.80 V, which is almost constant for several days (around 30 days). Additionally, the battery provides a discharge current of ≈2 μA (for a load of 0.1 MΩ) during 10 h of battery operation, which decreases to ≈ 1 μA after 100 h of operation. Finally, these batteries can provide an output power of ≈ 1.2 μW, using a 265 kΩ electrical load, which is in the required range for powering wireless transceiver and sensor applications.

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References

1. F. Jonas and W. Krafft, *E. Pat*., 440 957, 1990.

2. A. Elschner, S. Kirchmeyer, W. Lövenich, U. Merker and K. Reuter, *PEDOT Principles and Application of an Intrinsically Conductive Polymer,* CRC Press: Boca Raton, FL 2011.

3. M. M. de Kok, M. Buechel, S. I. E. Vulto, P. van de Weijer, E. A. Meulenkamp, S. H. P. M. de Winter, A. J. G. Mank, H. J. M. Vorstenbosch, C. H. L. Weijtens and V. van Elsbergen, *Phys. Status Solidi a*, 2004, **201**, 1342−1359.

4. H. Kim, S. Nam, H. Lee, S. Woo, C. S. Ha, M. Ree and Y. Kim, J. Phys. Chem. C, 2011, 115, 13502−13510.

5. L. Lindell, A. Burquel, F. L. E. Jakobsson, V. Lemaur, M. Berggren, R. Lazzaroni, J. Cornil, W. R. Salaneck, X. Crispin, Transparent, Plastic Low-Work Function Poly(3,4-ethylenedioxythiophene) Electrodes, Chem. Mater. 2006, 18, 4246.
6. F.L.E. Jakobsson, X. Crispin, L. Lindell, A. Kanciurzewska, M. Fahlman, W.R. Salaneck, M. Berggren, Toward all plastic flexible light emiting diodes, Chem. Phys. Lett. 433 (2006) 110.

7. Y. Xuan, M. Sandberg, M. Berggren and X. Crispin, *Org. Electron*., 2012, **13**, 632−637.

8. H. Park, S. H. Lee, F. S. Kim, H. H. Choi, I. W. Cheong and J. H. Kim, *J. Mater. Chem. A*, 2014, **2**, 6532.

9. S. H. Lee, H. Park, W. Son, H. H. Choi and J. H. Kim, *J. Mater. Chem. A*, 2014, **2**, 13380−13387.

10. B. Winther-Jensen, O. Winther-Jensen, M. Forsyth, D. R. MacFarlane, Science 321 (2008) 671.

11. M. Hilder, B. Winther-Jensen, N. B. Clark, J. Power Sources 194 (2009) 1135.

12. Z. Tehrani, T. Korochkina, S. Govindarajan, D.J. Thomas, J. O'Mahony, J. Kettle, T.C. Claypole, D.T. Gethin, ***Ultra-thin flexible screen printed rechargeable polymer bathery for wearable electronic applications***, Organic Electronics 26 (2015) 386-494.

13. J. Wusten, K. Potje-Kamloth, ***Organic thermogenerators for energy autarkic systems on flexible substrates***, J. Phys. D: Appl. Phys. 41 (2008), 135113.

14. I. Cruz-Cruz, M. Reyes-Reyes, I. A. Rosales-Gallegos, A. Yu. Gorbatchev, J. M. Flores-Camacho and R. Lopez-Sandoval, *Phys. Chem. C*, 2015, **119**, 19305−19311.

15. D. Fournier, M. L. Romagne, S. Pascual, V. Montembault and L. Fontaine, *Eur. Polym. J*., 2005, **41**, 1576–1581.

16. T. Ishikawa, *Superbases for Organic Synthesis: Guanidines,Amidines, Phosphazenes and Related Organocatalysts*, John Wiley & Sons: Chichester, U.K., 2009.

17. C. Shieh, S. Dell and O. Repic, J. *Org. Chem*., 2002, **67**, 2188−2191.

18. I. Cota, R. Chimentao, J. Sueiras and F. Medina, *Catal. Commun*., 2008, **9**, 2090−2094.

19. J. Y. Kim, J. H. Jung, D. E. Lee and J. Joo, *Synth. Met*., 2002, **126**, 311-316.

20. F.L. Xue, Y. Su and K. Varahramyan, *IEEE T. Electron Dev*., 2005, **52**, 1982–1987.

21. J.A. Lim, J.H. Cho, Y.D. Park, D.H. Kim, M. Hwang and K. Cho, *Appl. Phys. Lett*., 2006, **88**, 082102.

22. F. X. Jiang, J. K. Xu, B. Y. Lu, Y. Xie, R. J. Huang and L. F. Li, *Chinese Phys. Lett*., 2008, **25**, 2202–2205.

23. D. Bagchi and R. Menon, *Chem. Phys. Lett*., 2006, **425**, 114–117.

24. I. Cruz-Cruz, M. Reyes-Reyes and R. Lopez-Sandoval, *Synth. Met*., 2010, **160**, 1501-1506.

25. M. Reyes-Reyes, I. Cruz-Cruz and R. Lopez-Sandoval, J. Phys. Chem. C, 2010, 114, 20220−20224.

26. I. Cruz-Cruz, M. Reyes-Reyes and R. Lopez-Sandoval, Thin Solid Films, 2013, 531, 385−390.

27. M. Dietrich, J. Heinze, G. Heywang and F. J. Jonas, *Electroanal. Chem*., 1994, **369**, 87−92.

28. C. Kvarnström, H. Neugebauer, S. Blomquist, H. J. Ahonen, J. Kankare and A. Ivaska, *Electrochim. Acta*, 1999, **44**, 2739−2750.

29. I. C. M. Palumbiny, C. Heller, C. J. Schaffer, V. Korstgens, G. Santoro, S. V. Roth and P. Müller-Buschbaum, *J. Phys. Chem. C*, 2014, **118**, 13589−13606

30. M. Łapkowski and A. Pron, *Synth. Met*., 2000, **110**, 79−83.

31. J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Lib and J. Shinar, *Polymer*, 2004, **45**, 8443−8450.

32. S. Garreau, G. Louarn, J. P. Buisson, G. Froyer and S. Lefrant, *Macromolecules,* 1999, **32**, 6807−6812.

33. M. Dietrich, J. Heinze, G. Heywang and F. J. Jonas, *Electroanal. Chem*., 1994, **369**, 87−92.

34. C. Kvarnström, H. Neugebauer, S. Blomquist, H. J. Ahonen, J. Kankare and A. Ivaska, *Electrochim. Acta*, 1999, **44**, 2739−2750.

35. S. Garreau, G. Louarn, J. P. Buisson, G. Froyer and S. Lefrant, *Macromolecules,* 1999, **32**, 6807−6812.

36. A.M. Nardes, R.A.J. Janssen, M. Kemerink, Advanced Functional Materials 18 (2008) 865–871.

37. A. J. Bard, and L. R. Faulkner, *Electrochemical Methods Fundamental and Applications,* J. Wiley 2dn. Ed., NY 2001.

Figures

Figure 1. Schematic diagram of cross section of the polymer battery.

Figure 2. Absorbance spectra of treated PEDOT:PSS films with DMSO-DBU at v/v ratio of a) 10:1 and b) 2:1 at different times of immersion.

Figure 3. a) The self-discharge curve exposed the battery to air, b) the discharge curves of the battery for various loads, (i) 0.1 MΩ, (ii) 1 MΩ and 10 MΩ.

Figure 4. The vis-NIR absorption spectra of pristine and dedoped films, with DMSO-DBU at v/v ratio of 10:1 and 2:1 at different times of immersion, and their interaction with PEI at a) 20 min, b) 20 h and c) at different times on dedoped film with 10:1 (DMSO-DBU) at 9 min of immersion.

Figure 5. The self-discharge curve of the battery fabricated using various thickness of cathode a) 8 μm, b) 6 μm and c) 165 nm. The anode of all devices were made with PEDOT:PSS (8 μm) dedoped with DMSO-DBU at v/v ratio of 10:1 and 2:1 at different times of immersion. PEI material was deposited on the dedoped films of all devices.

Figure 6. The Vis-NIR absorption spectra of a) the thin anodes after discharge, with and without PEI layer deposited on them and b) cathodes after discharge. These cathodes correspond to batteries in which the anode was fabricated using different v/v DMSO-DBU ratios and immersion times, with and without the deposited PEI layer onto thin (165 nm) and thick (8 μm) dedoped films.

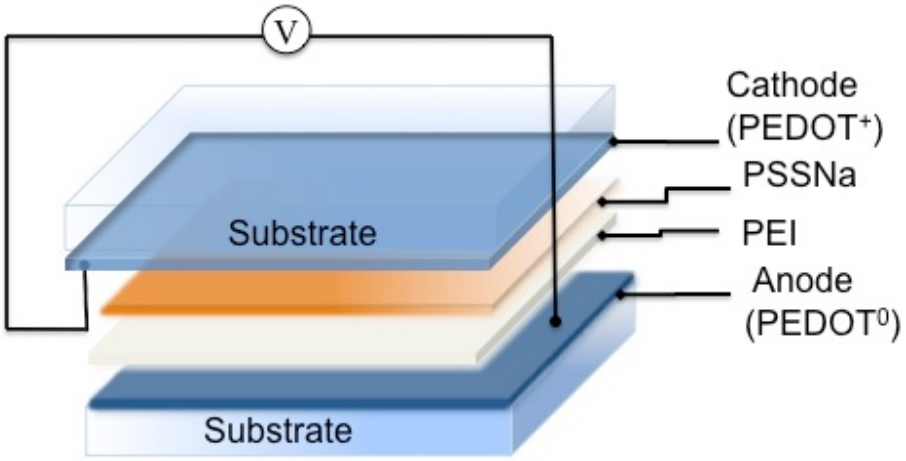
V
Cathode
(PEDOT+)
PSSNa
PEI
Anode
(PEDOT0)
Substrate
Substrate

Figure 1

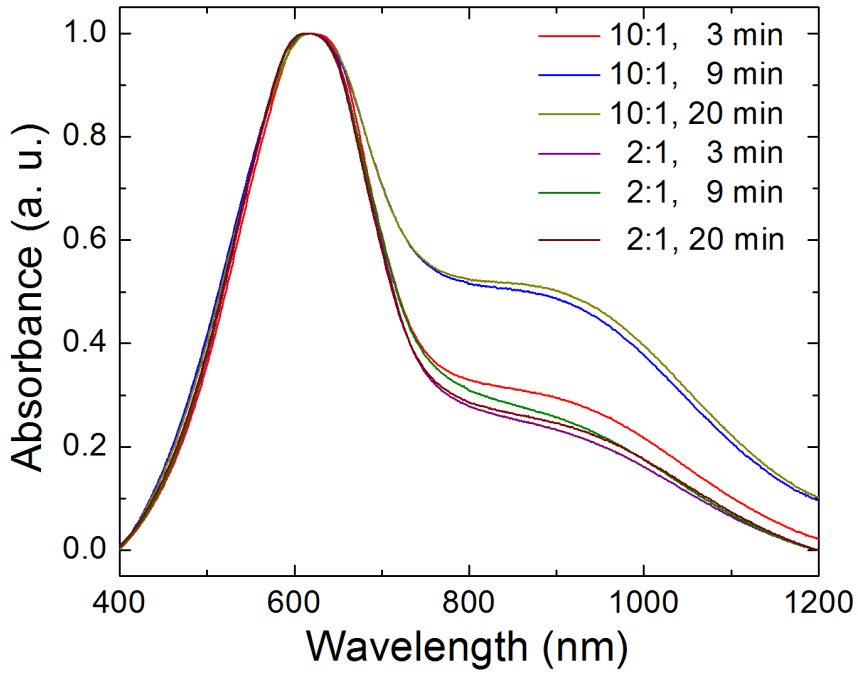
Absorbance (a. u.)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
10:1, 3 min
10:1, 9 min
10:1, 20 min
2:1, 3 min
2:1, 9 min
2:1, 20 min

Figure 2

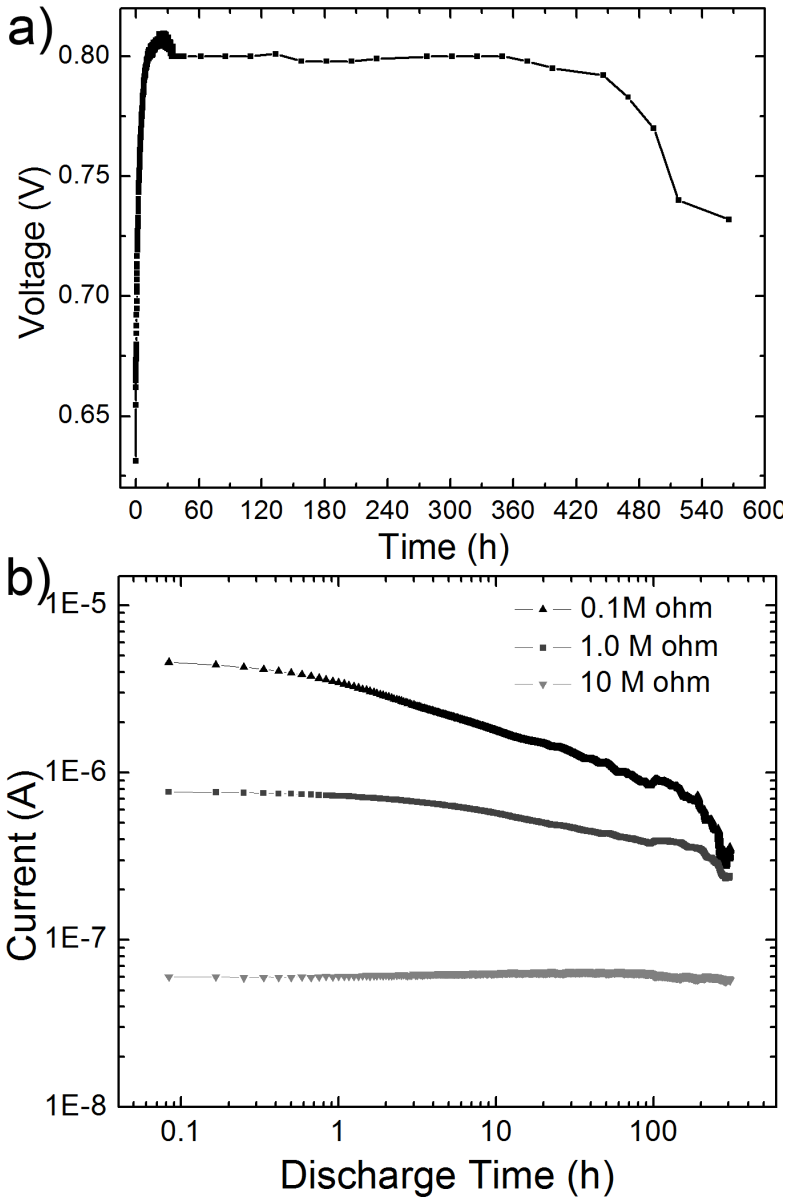
a)
0.80
0.75
0.70
0.65
Voltage (V)
0
60
120
180
240
300
360
420
480
540
600
Time (h)
b)
1E-5
1E-6
1E-7
1E-8
Current (A)
0.1M ohm
1.0 M ohm
10 M ohm
0.1
1
10
100
Discharge Time (h)

Figure 3

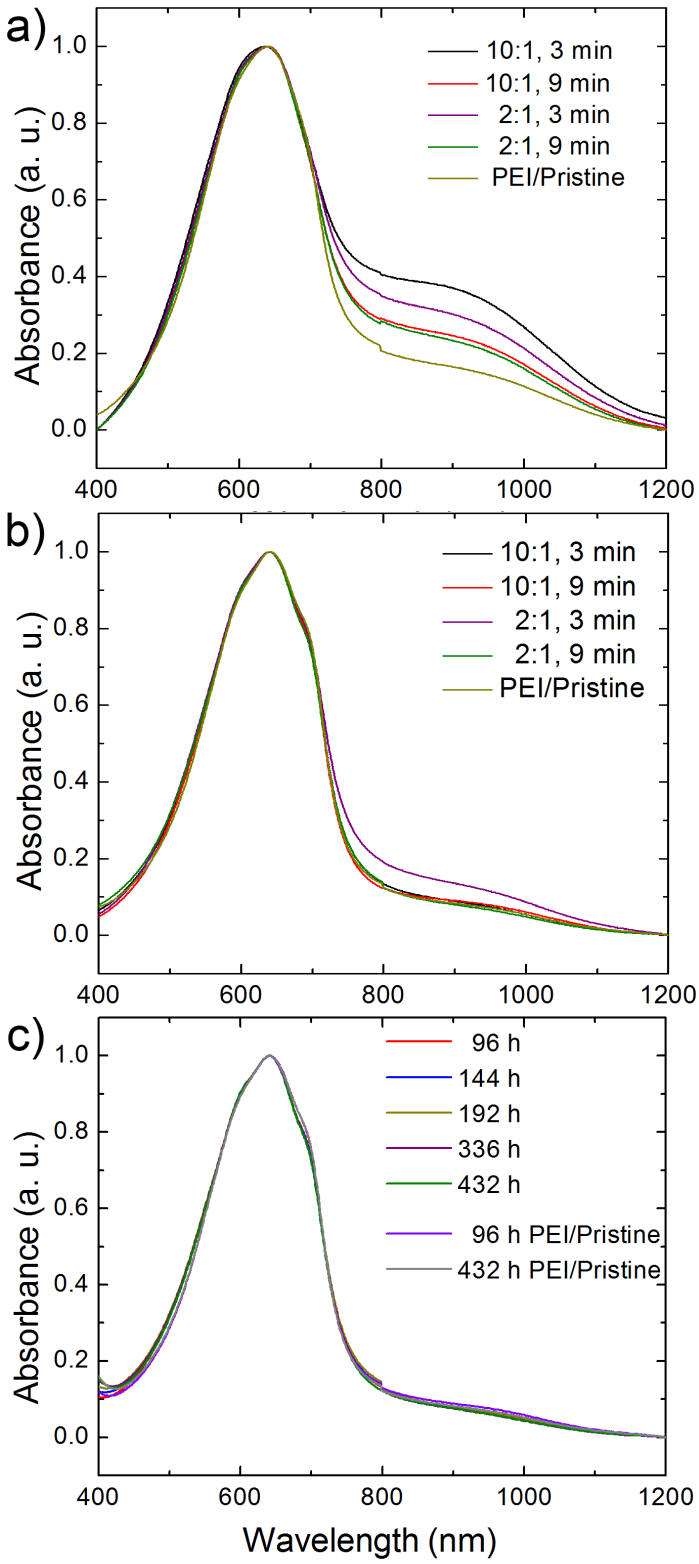
a)
Absorbance (a. u.)
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
10:1, 3 min
10:1, 9 min
2:1, 3 min
2:1, 9 min
PEI/Pristine
b)
Absorbance (a. u.)
10:1, 3 min
10:1, 9 min
2:1, 3 min
2:1, 9 min
PEI/Pristine
c)
Absorbance (a. u.)
96 h
144 h
192 h
336 h
432 h
96 h PEI/Pristine
432 h PEI/Pristine
Wavelength (nm)

Figure 4

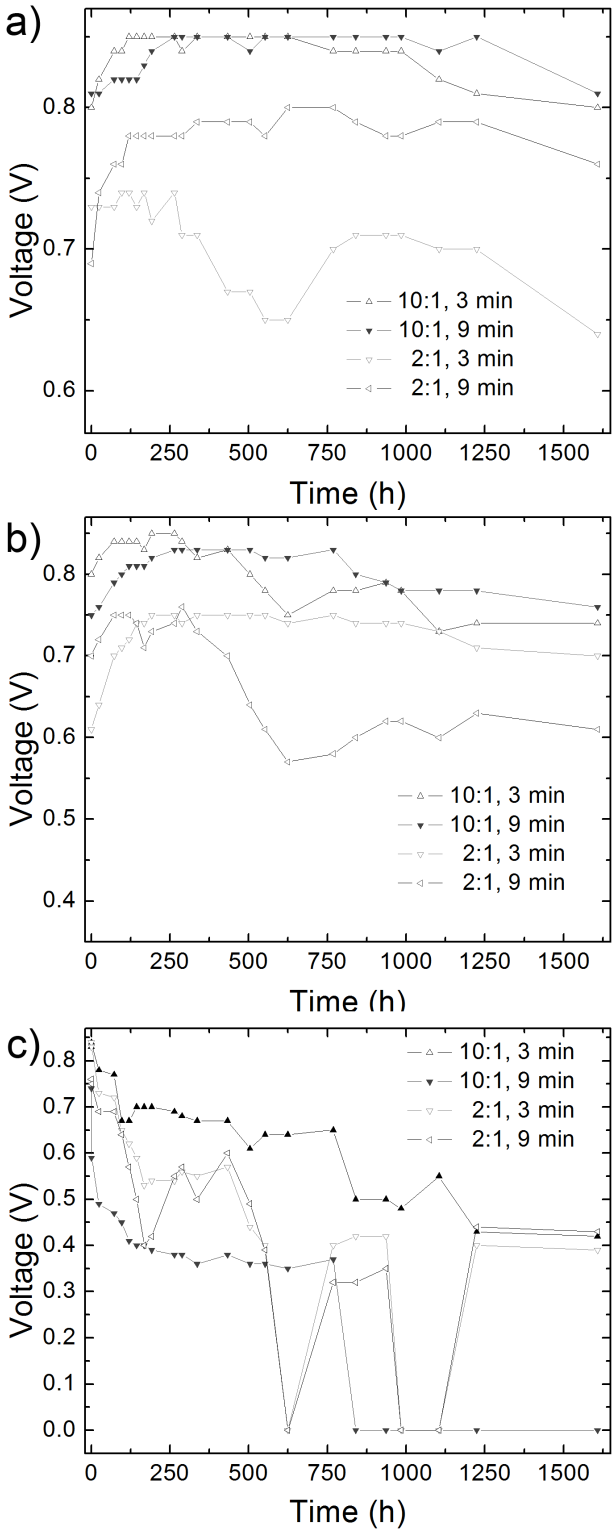
a)
Voltage (V)
0.6
0.7
0.8
0
250
500
750
1000
1250
1500
Time (h)
10:1, 3 min
10:1, 9 min
2:1, 3 min
2:1, 9 min
b)
Voltage (V)
0.4
0.5
0.6
0.7
0.8
0
250
500
750
1000
1250
1500
Time (h)
10:1, 3 min
10:1, 9 min
2:1, 3 min
2:1, 9 min
c)
Voltage (V)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
250
500
750
1000
1250
1500
Time (h)
10:1, 3 min
10:1, 9 min
2:1, 3 min
2:1, 9 min

Figure 5

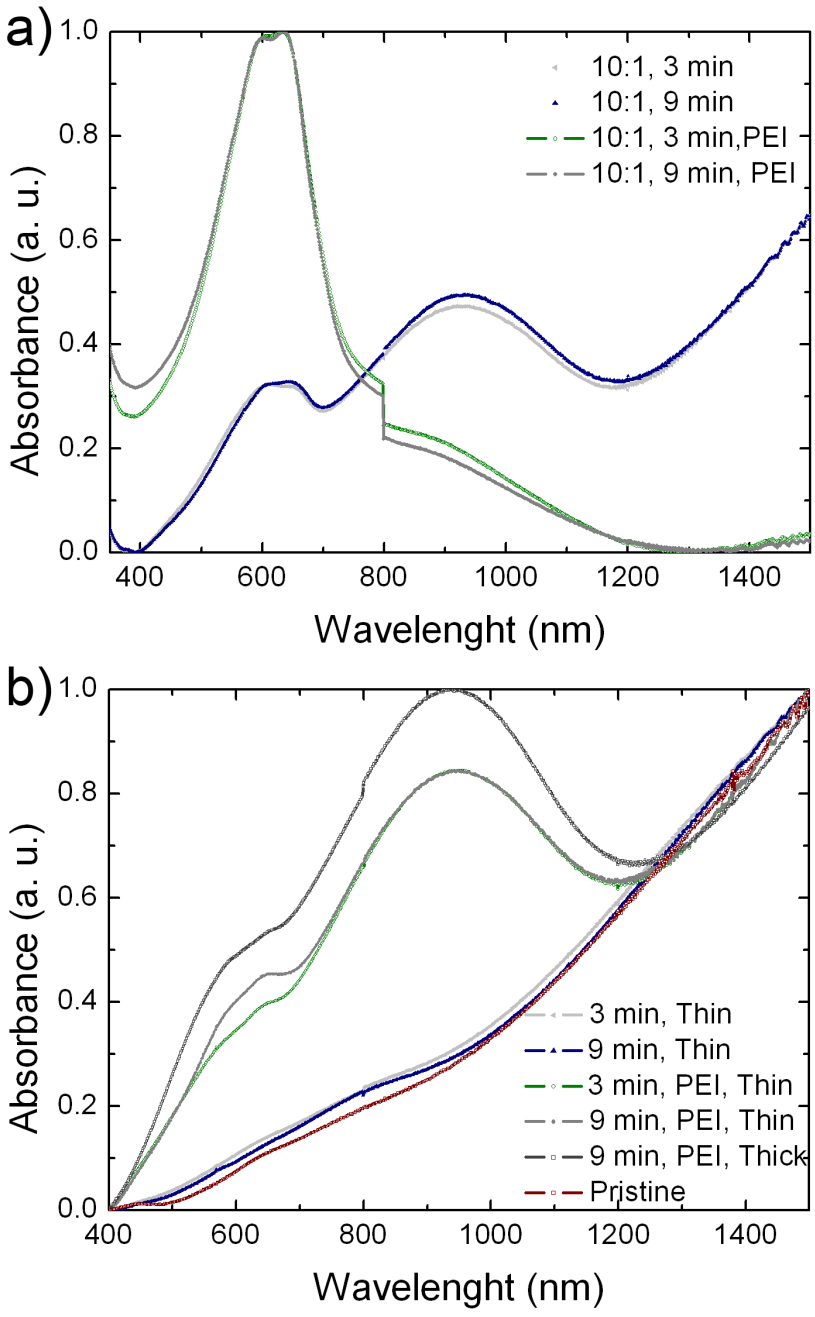
a)
Absorbance (a. u.)
Wavelenght (nm)
10:1, 3 min
10:1, 9 min
10:1, 3 min,PEI
10:1, 9 min, PEI
b)
Absorbance (a. u.)
Wavelenght (nm)
3 min, Thin
9 min, Thin
3 min, PEI, Thin
9 min, PEI, Thin
9 min, PEI, Thick
Pristine

Figure 6

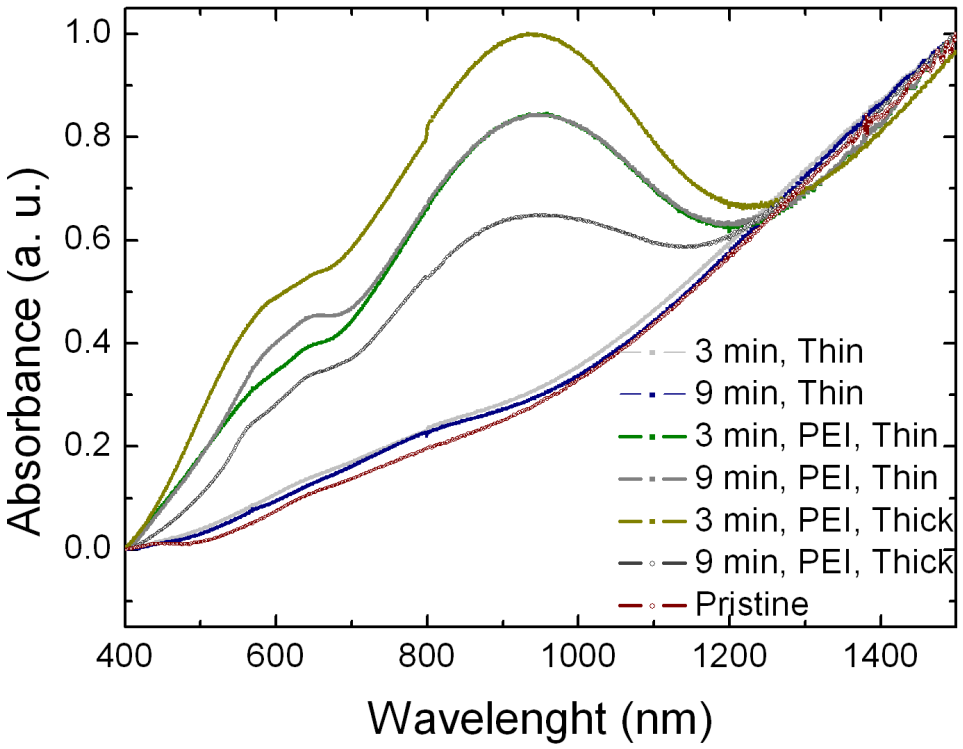
Absorbance (a. u.)
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
1400
Wavelenght (nm)
3 min, Thin
9 min, Thin
3 min, PEI, Thin
9 min, PEI, Thin
3 min, PEI, Thick
9 min, PEI, Thick
Pristine

Figure 6b