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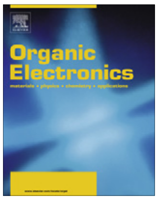

An all-polymer-air PEDOT battery

Yu Xuan [a], Mats Sandberg [b], Magnus Berggren [a], Xavier Crispin [a,]*

[a] Department of Science and Technology, Campus Norrköping, Linköping University, S-60174 Norrköping, Sweden
[b] ACREO AB, Bredgatan 34, SE-602 21 Norrköping, Sweden

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ABSTRACT

Mass-produced organic electronics for internet-of-things, point of care diagnostics, smart labels and more suggest development of a "green" and recyclable electronics. One of the greatest challenges in achieving such a technology platform is to establish low-cost batteries that are metal-free. Here, we demonstrate a thin all polymer-air battery where the anode and cathode are based on the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT). Polyethyleneimine (PEI) is combined with the PEDOT electrode to ensure air stability of its neutral or rather "low oxidized" form at the anode, while PEDOT is in its oxidized state at the cathode. The difference in the oxidation level between the two PEDOT electrodes produces an open circuit voltage of about 0.5 V. Upon discharge, PEI is consumed at the PEDOT anode, while O_2 reacts with the PEDOT cathode; thus demonstrating the first all-polymer-air battery.

One of the target areas for printed electronics is low-cost electronics manufactured onto flexible substrates, such as paper or plastic foil, where integrated electronic circuits are combined with a sensor and perhaps a display all being powered via a printed energy storage system [1]. Conducting polymers are attractive materials for this technology and application because they may combine several desired properties: electronic conduction, ionic conduction, sensor functionality and electrochromism. Various electrochemical devices have been explored as platform for low-cost printed electronics. Besides that only few different materials are needed to form electrochemical devices (a conducting polymer and an electrolyte), one major advantage of these devices is that they require typically very low operating voltages (<1.2 V). This makes them possible to power using common battery cells. Poly(3,4-ethylenedioxythiophene) combined with the counterion poly(styrenesulphonate), PEDOT:PSS (Fig. 1a), is one of the most explored polymers in electrochemical devices because it combines printability from water-based inks with fast reversible electrochemical switching while included in devices. The reduction and oxidation potentials of PEDOT is about −450 mV, and 40 mV, respectively [2,3]. The change in the redox state of PEDOT is accompanied with ions and electrons migration that can provide a specific functionality to the electrochemical devices [4,5]. PEDOT:PSS is active electroactive material in a vast array of electrochromic displays [6], sensors [7], transistors based electronic circuits [8] and supercapacitors [9].

Among all printed electronic or electrochemical devices that have been developed, the fabrication of a printable battery able to power printed electronic circuit systems is still a major challenge. When printing a battery, one of the major difficulties is air stability and printability of the anode and cathode materials, which prevents the use of Li-ion batteries using metal oxide cathodes [10,11]. The effective cost for the society does also include recycling issues including costly material separation (e.g. metals and polymers). All-polymer based batteries promise for using common easy de-inking of the active materials from the flexible carrier and common recycling procedures. Conducting polymers are printable, however in order to provide a large open circuit voltage, the oxidation level of the two electrodes must differ as much as possible (the potential difference of the neutral (undoped) state and

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* Corresponding author.
E-mail address: xavcr@itn.liu.se (X. Crispin).

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oxidized (doped) state). However, a very low electrical conductivity of the neutral state of the conjugated polymers often prevents its use as the electrode material. Additionally, typically one of the oxidation states of the polymer is air sensitive. Hence, very few strategies and material combination have been proposed for all-polymer batteries and only poor performance have been reported [12,13].

Here, a thin, flexible and all-polymer battery based on PEDOT:PSS is reported. P-doped PEDOT:PSS constitutes the cathode, while the anode is made of PEDOT in its neutral state. Polyethyleneimine (PEI, see Fig. 1b) reduces the oxidized PEDOT and has the unique property to keep the neutral state of PEDOT stable in air through a dynamic redox process. The anode is fabricated by either depositing directly the viscous PEI onto PEDOT:PSS film (AGFA Geveart, Orgacon™ EL-350Ω/□) or casting a solution of the polymer blend made of PEI mixed in the PEDOT:PSS water emulsion (AGFA Geveart, ICP-1010) onto a PEDOT:PSS substrate. After water evaporation, the PEI–PEDOT:PSS forms a solid polymer blend. The battery cell provides an electric potential difference of 0.4 V (Power ≈ 0.67 µW, Energy density ≈ 2 kJ/kg, when a resistor of 265 k ohms applied), and a few battery cells coupled in series are able to switch a PEDOT:PSS electrochromic display.

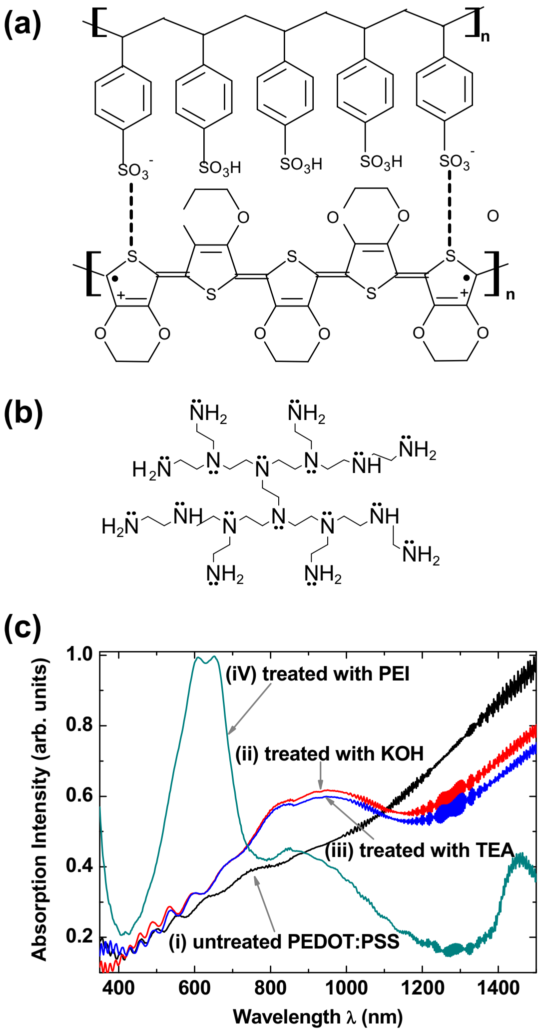

Fig. 1. Chemical structures of (a) PEDOT:PSS and (b) PEI. Graph (c) displays the absorption spectra of PEDOT:PSS (i) after treatments with (ii) KOH, (iii) triethylamine (TEA), and (iv) PEI.

PEI (Aldrich, Cat. No. 40, 871-9, M_w = 800 (LS), M_n = 600 (GPC)) is a highly branched polymer composed of primary amine groups, secondary amine groups, and tertiary amine groups. When PEI contacts PEDOT:PSS, the conducting polymer turns dark blue with a pronounced optical absorption feature at 600 nm and a reduction of (bi)polaronic absorption bands in the near infrared (full line in Fig. 1c). The absorption at 900 nm is attributed to polarons, which indicates that there is still a low oxidation level in PEDOT, which allows electrical conductivity at the anode [14]. This modification in optical properties is associated to an electron transfer from amine groups of PEI to the oxidized PEDOT chains. This hypothesis is also supported by the significant changes in electrical conductivity of thin films from about 20 S/cm to about 10^{-4} S/cm upon reaction with PEI [15,16]. Additionally, PEI has a basic character, such that a reaction with the sulfonic acid groups of PSSH is concomitantly taking place, which might affect the stability of PEDOT:PSS. In order to investigate whether it is the basic character of the polymer amine alone or if the electron donor character contributes to the change of the band gap, the PEDOT:PSS layer is dipped in a Bronsted base (KOH solution) and also in a Lewis base (triethylamine). The absorption spectrum changes with both types of base treatments. PEDOT:PSS appears slightly less oxidized and turns light blue (dashed line in Fig. 1c). However, those changes are much less pronounced as compared to the reaction with PEI (dotted line in Fig. 1c). After evaporation of the volatile triethylamine, the original absorption spectrum of the oxidized PEDOT is recovered. Note that strong amines, such as tetra-kis(dimethylamino)-ethylene TDAE, are known to decrease the oxidation level of PEDOT–PSS to its neutral form [17]. Hence, the proposed reaction between PEDOT:PSS and PEI is a redox reaction where PEI functions as a reductant by donating electrons to the PEDOT$^+$, thus producing PEDOT^0 and PEI:PSS (Eq. (1)). Note that the rate of this reaction increases significantly with temperature.

The polymer battery cell is constructed with one oxidized (p-doped) PEDOT(:PSS) anode, and a cathode made of PEI and PEDOT:PSS). Those two plastic electrodes are separated by the solid electrolyte poly(styrenesulfonate sodium) (PSSNa). An illustration of the thin film battery is given in Fig. 2a.

The self-discharging curve of the polymer battery exposed to air is displayed in Fig 2b. At the beginning of this process, the open circuit voltage of PEDOT:PSS–PEI battery drops from 0.53 V to 0.48 V during the first 50 h, and then subsequently decreases slowly down to 0.43 V for the following 300 h after which the measurement is terminated. For the sake of comparison, a PEDOT:PSS-based electrochromic cell, of identical architecture as the battery, is made but that excludes the PEI material (same dimensions and identical electrolyte). For comparison, this symmetric electrochromic cell is externally charged to 0.53 V and then

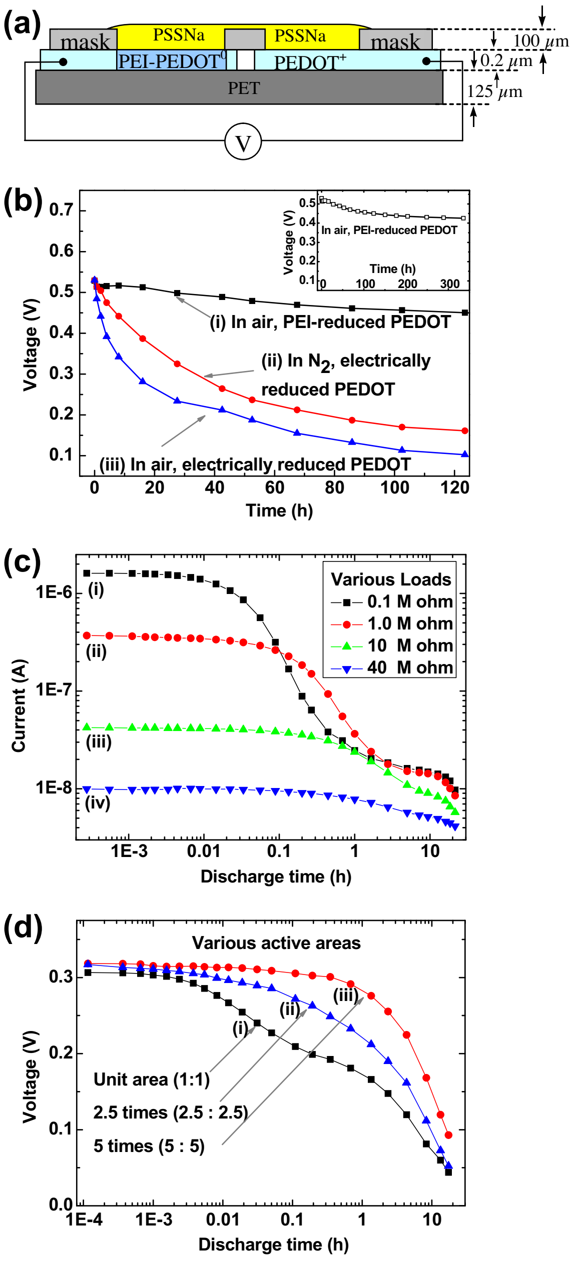

Fig. 2. (a) The schematic diagram of cross section of the all polymer battery device on an Orgacon™ EL350 substrate. The anode (left hand side) is composed of a blend of PEI and PEDOT:PSS deposited on a 200 nm-thick conducting PEDOT:PSS film coated on a polyester substrate. The cathode (right hand side) is a pristine 200 nm-thick semi-oxidized layer of PEDOT:PSS film on a polyester substrate (Orgacon foil by AGFA Geveart). The electrolyte is a few hundred microns-thick polyelectrolyte PSSNa. (b) The self-discharge curves of (i) the polymer battery exposed to air (squares), (ii) A PEDOT:PSS electrochromic cell externally electrically reduced before exposed to nitrogen (circles), (iii) A PEDOT–PSS electrochromic cell externally electrically reduced before exposed to air (triangles). The inset is a long-time self-discharge process of the polymer battery exposed to air. (c) The discharge curves of the polymer battery for various loads, (i) 0.1 MΩ (squares), (ii) 1 MΩ (circles), (iii) 10 MΩ (upwards triangles), (iv) 40 MΩ (downwards triangles). (d) The discharge time of various sizes of the battery scales (various areas of an anode and cathode), (i) one unit area (squares), (ii) 2.5 times (triangles), (iii) 5 times (circles).

left to self-discharge, unloaded, in air and in nitrogen, respectively. In air, this cell undergoes a drastic voltage drop from 0.55 V to 0.18 V within 50 h. In nitrogen, the self-discharge of the cell slightly slows down and reaches 0.25 V after 50 h. The behavior of the display cell demonstrates the poor air stability of neutral PEDOT^0 segments and its detrimental effect on self-discharging. O_2 oxidizes the neutral PEDOT^0 chains spontaneously to a specific oxidation level before it stops. Surprisingly, PEI seems to prevent the self-discharge of PEDOT:PSS to a great extent. Our hypothesis is that reduction of PEDOT:PSS with PEI incorporated in the bulk is a dynamic process competing with the oxidation with O_2. Interestingly, PEI is viscous and characterized with a $T_g \approx -52\,^{\circ}\mathrm{C}$ [18]. Hence, the solid blend PEDOT:PSS–PEI is composed of PEI domains where the PEI chains are mobile at room temperature. Those observations lead us to propose the following mechanism at the anode: the slow dynamics of the PEI chains regenerate interfaces between the PEDOT:PSS and PEI domains; such that if some PEDOT chains are oxidized in air, they are reduced back to PEDOT^0 by the electron transfers at the interface between PEDOT:PSS and PEI domains. Eventually, as PEI becomes fully consumed, the battery should be entirely self-discharged by reaction with oxygen at the anode.

Thin polymer batteries were fabricated and characterized. Here, the PEDOT:PSS film is only 200 nm thick and the electrode area is 2 cm^2. The discharge curves of the battery are presented in Fig. 2c for various loads (0.1 MΩ, 1 MΩ, 10 MΩ and 40 MΩ); the discharge current drops faster for higher loads as expected. The generated current is small and is either limited by the ionic conductivity of the electrolyte or the low electrical conductivity of the PEI/PEDOT:PSS anode. Hence, with those performances, the thin polymer batteries could only serve limited applications such as powering the source for wireless transceivers and sensors [19]. In order to investigate the potential for technology, the battery is fabricated on larger area of a plastic foil. The size of the battery scales with the discharge time; the larger area of the battery the longer it lasts as indicated in Fig. 2d (unit area (black squares), 2.5 times (blue triangles) or 5 times (red circles) the unit area). The capacity does not increase linearly versus the amount of the active materials included in the battery. The uneven internal resistance, which stems from the low oxidation level of PEDOT at the anode, is a possible explanation to the non-linear correlation. Finally, four 2×1 cm^2 battery cells are put in series to provide 2 V and are proven able to switch a small PEDOT:PSS electrochromic display cell (1×0.5 cm^2).

Now, that the basic electrical characteristics of this ultra-thin polymer battery have been investigated, some interrogation points remain as far as the mechanism is concerned. The electrochromic property of PEDOT:PSS provides an easy measure of the degree of oxidation of the involved electrodes. Hence, to further understand and monitor the electron transfer reactions at the cathode and the anode, the absorption spectrum of the PEDOT:PSS electrodes is recorded continuously upon discharging. The proposed corresponding half-reactions upon discharge are:

Anode:

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

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

Cathode:

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

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

The spontaneous oxidation of the neutral PEDOT^0 segments by dioxygen and the reaction of PEDOT$^+$ with PEI make PEI (Eq. (1)) and dioxygen (Eq. (4)), the two actual reactants of this polymer-air battery. PEDOT in the electrodes appear as intermediate reactant and product in the chains of reactions. Note that the conducting polymer PEDOT has already been demonstrated as possible cathode in metal – air batteries [20,21].

Before discharging, the PEDOT:PSS–PEI anode is dark blue to its color as indicated by the strong absorption in the visible region about 600 nm. Note that it possesses a small absorption feature attributed to polaronic transitions at 900 nm. After discharging, the anode becomes more transparent as indicated by the relatively lower absorption in the visible region and enhancement of absorption in the NIR absorption (Fig. 3a). This proofs that the anode oxidizes during the discharging process (Eq. (2)).

Conversely, the cathode is initially in the pristine (oxidized) state before discharging as indicated with the NIR absorption (Fig. 3b). PEDOT:PSS (provided by Agfa Gevaert), is on an average oxidized to a level of 80%; oxidized PEDOT$^+$ chains are balanced by the polyanion PSS$^-$ and only 20% of the polymer segment are then neutral (PEDOT^0) [22]. Upon discharging, PEDOT$^+$ is reduced and bipolarons are transformed into polarons featured by the two absorption contributions at 900 nm and above 1500 nm [23]. In addition to the reduction of cathode upon discharging, a simultaneous oxidation process takes place at the cathode: PEDOT chains are oxidized by O_2. The optical absorption spectra display a difference when the PEDOT cathode is discharged in an inert N_2 atmosphere and then exposed to air. The difference in absorption spectra before and after exposure to air reveals the presence of neutral segments (absorption at 600 nm) and polarons (absorption at 900 nm) in the PEDOT cathode after discharge (Fig. 3c). Those spectral features become less pronounced upon exposure to air, indicating that the oxidation level of PEDOT increases up to a certain higher level in air than in N_2.

The reaction of the PEI at the PEDOT cathode in the presence of air makes this two-electrode device being first all-polymer-air battery. Interestingly, if PEI and O_2 are the actual reactants of such a primary battery, the cathode could be much smaller than the anode, since O_2 easily penetrate from air into the porous PEDOT:PSS cathode. The discharging of the battery is measured for different mass ratios of the anode material (PEDOT^0) versus the mass of the cathode material (PEDOT$^+$) (see Fig. 4a). The charge is integrated over 22 h. Unlike the conventional batteries, the amount of charge is not limited by the fixed amount of material on the cathode. By increasing the mass ratio of PEDOT between anode and cathode from 1:1 to 15:1 does not result in a saturation of the charge that becomes released; on the contrary, the charge rises almost linearly with the amount of PEDOT of the anode. The slow reaction involving PEI, likely due to its viscosity, prevent from calculating accurately the total charge released during the discharge. However, in order to provide the order of magnitude, Fig. 4b displays the charge per mass over discharge time. The mass ratio between PEI–PEDOT versus PEDOT in this battery is 4:3 and the load resistance is 265 kΩ. The mass used is the total mass of the battery (0.03 g), including the anode (0.008 g), the cathode (0.006 g) and the electrolyte (0.015 g). The discharge characteristic displays a fast discharge mechanism within the first hour, which is associated to the direct oxidation and reduction of

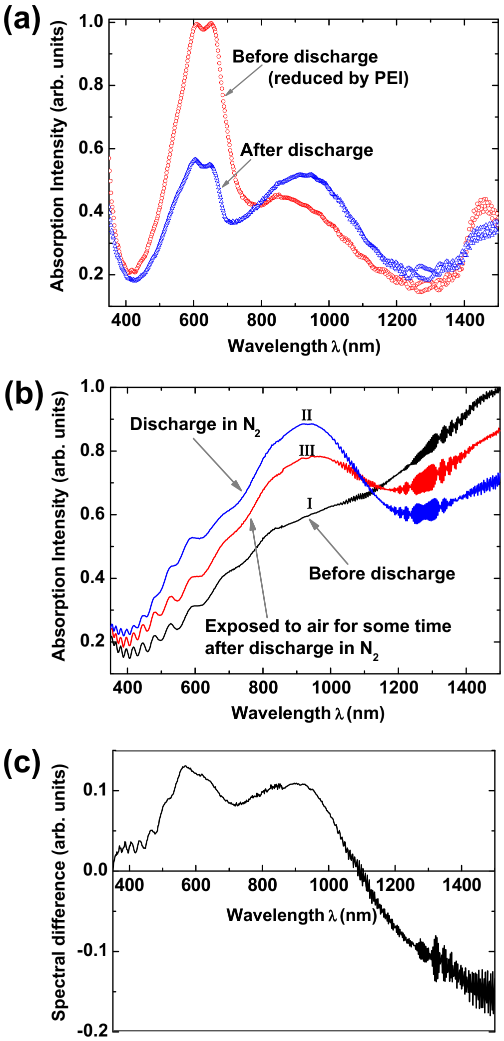

Fig. 3. (a) The Vis–NIR absorption spectra of the anode before and after discharge. (b) The Vis–NIR absorption spectra of the cathode before (curve I) and after discharge in N2 (curve II), and finally exposed to air (curve III). (c) The difference of Vis–NIR absorption spectra of the cathode between curves II and III reveals the reaction with dioxygen as expected in Eq. (4).

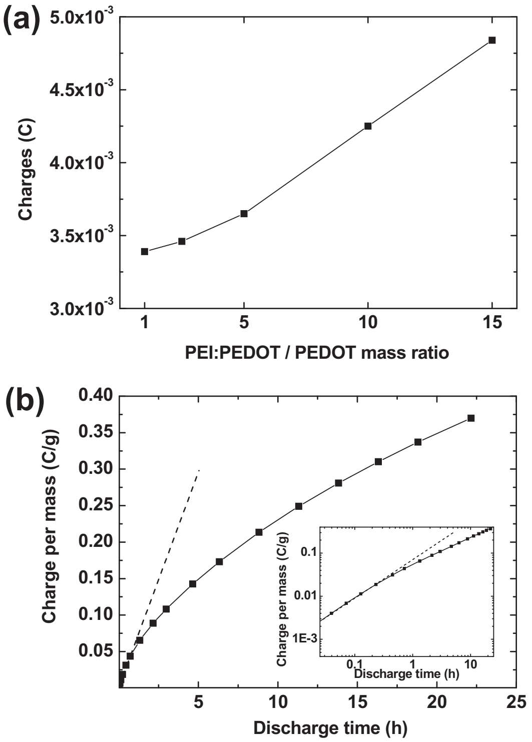

Fig. 4. (a) The amount of charge in the first discharge versus the mass ratio of the anode material (PEDOT0) to the cathode material ($PEDOT^+$) from (1:1) through (15:1). The charge is integrated over 22 h. (b) The plot of charge per mass over a discharge time. The mass ratio between PEI–PEDOT versus PEDOT in this battery is 4:3 and the load resistance is 265 kΩ.

PEDOT–PSS at the two electrodes. Afterward, the discharge slows down and becomes constant over many hours. This slow discharge is associated to the chemical reaction involving the PEI and PEDOT:PSS.

Since this is still at the proof of concept level, the stability of the battery has not been at the moment investigated in details. However, after 1 month shelf storage and without any encapsulation, the open circuit voltage and charge almost reduced by 30%. We attribute this to the continuous slow reactions involving PEI, PEDOT and dioxygen (reactions 1 and 4 taking place at the PEDOT–PEI electrode) and eventual mass transport of PEI through the electrolyte towards the other PEDOT electrode.

In summary, we have demonstrated a first prototype of an all-polymer-air battery. The thin battery cell is made of conducting polymers, a polymer base and a polymer electrolyte, which together provides an open circuit voltage of 0.5 V. The important feature of this all-polymer battery is its air stable anode, which shows a long almost constant open-circuit voltage. The polymer base PEI plays a dominant role to balance the reaction to oxygen in air and to keep the oxidation level of PEDOT low at the anode, and O_2 in air maintains the PEDOT at cathode in its oxidized state as well. This all-polymer-air battery has successfully been used to drive a PEDOT:PSS electrochemical pixel. We foresee utilizing this polymer air-battery as the power source for various printed and low-power consumption devices.

Experimental

First, a planar electrochemical cell was prepared by cutting a partition line across prefabricated films PEDOT:PSS on a polyethylene terephthalate substrate (OrgaconEL350). A masking layer was laminated on the sheet evenly crossing the partition line with two identical rectangular openings (2 cm × 1 cm) locating at each side with the separation of 1 mm to define spatially the dimensions of the battery's anode and cathode area. On one side of the partition, a thin layer of PEI patch was coated on one exposed rectangle domain of PEDOT:PSS. The semi-finished device was heated on a hot-plate kept at 50 °C for 15 min, while the PEI coated PEDOT:PSS area turning deep blue. After it going back to the room temperature, the anode (PEI/PEDOT:PSS) and the cathode (PEDOT:PSS) of the battery device were ready. Next, a layer of polyelectrolyte of poly(sodium styrenesulfonate) (PSSNa) was cast covering the entire electrodes area. The polymer battery device with 2 cm^2 anode and cathode was manufactured.

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