Roll to roll printable technology platform consisting of electrolyte-based components

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Abstract

A lot of effort has been spent on developing components in the field of organic electronics. Some of the components have shown excellent performance and also printability. However, printed electronics has not yet reached the market. One reason for this is that the integration of components into useful products has proven more challenging than expected. One of the major challenges is the large variety of materials and processes that are used during manufacturing, which often results in complex processing lines. Another challenge is how to design electronic systems that can accommodate the differences in drive voltage between different components. Here, a roll to roll printable technology platform is presented, which primarily consists of electrolyte-based components; electrochromic displays, thin film transistors, and systems thereof. These components have the benefit of being based on a small set of materials, and at the same time the components show millisecond switching time at drive voltages around 1 volt. The latter is critical upon integration of thin film transistors with batteries, displays and sensors.

1. Introduction

Electronic components and systems manufactured by printing and coating techniques are predicted to dramatically change the utilization of electronics in many business areas. The ability to add various kinds of electronic functionalities on flexible paper or plastic substrates is attracting a lot of focus, and electroluminescent lighting, sensors and indicators incorporated in packages, and matrix-addressed displays utilized for advertising purposes are a few examples of targeted applications. However, despite all research and development activities that have been performed during the last decade, printed electronics has not yet become as prospering as expected. There are probably many reasons for this, but the integration of the required components in order to obtain useful products has clearly proven to be more challenging than expected. Too complex processing lines due to the large variety of materials required to obtain the desired product, the narrow dimensions required to obtain functional field-effect driven components, and how to handle the difference in operating voltage that often occurs when various components are incorporated into an electronic system are all examples that have proven to be very challenging in the field of printed electronics.

2. Experimental section

All devices described herein are measured in ambient atmosphere. The absorption spectra were recorded by a Perkin Elmer Lambda 900 UV/VIS/NIR absorption spectrometer. The L*a*b* color coordinates of the electrochromic displays were recorded with a Datacolor Mercury spectrophotometer. The drain-source current vs. drain-source voltage at varying gate voltages were recorded with a HP/Agilent 4155 B parameter analyzer, while the switching time of electrochemical transistors were determined by using two Keithley 2400 sourcemeters. The devices were manufactured by using various kinds of printing and coating techniques. Narrow lines deposited at high resolution were typically printed by using a Dimatix DMP-2800 inkjet printer, while more relaxed dimensions were deposited by using a TIC SCF 550 screen printing machine or subtractively patterned by using a Summa S75 T Series cutter. Roll to roll manufacturing of electrochromic displays was performed by using a Nilpeter Rotolabel FA3300/5 printing press. Poly(3,4-ethylenedioxythiophene) (PEDOT) has been used as the coloring and counter electrode material in electrochromic displays, the transistor channel material and the conductive material in conducting lines. The electrically conducting form of PEDOT is obtained by chemical doping of the pristine conjugated polymer, and charge neutrality is then maintained by an excess amount of poly(styrene sulfonic acid) (PSS), which is a polyanion. Hence, the air-stable and electrically conducting polymer complex PEDOT:PSS is formed [1]. The commonly used PEDOT:PSS is commercially available in many different forms, and several of them have been used here; Orgacon EL-350 and ICP-1010 purchased from Agfa as well as P Jet HC and SV3 purchased from H. C. Starck/Heraeus. 7102 screen printing carbon paste purchased from DuPont and U5603 nanoparticle silver ink for inkjet printing purchased from Suntronic were occasionally used to increase the electronic conductivity in conducting lines etc. An electrolyte consisting of ~35 wt.-% poly(sodium 4-styrenesulfonate), ~10 wt.-% D-sorbitol, ~10 wt.-% glycerol and ~10 wt.-% titanium dioxide, all dissolved or dispersed in deionized water, was typically used to enable the electrochemical switching in displays and transistors.

3. Printed electrolyte-based components

The oxidized form of PEDOT:PSS is close to transparent in the visible wavelength region and the absorption occurs in the near-infrared region because of the increased amount of bipolaronic states in the doped state. However, PEDOT:PSS is responsive to electrochemical reduction, i.e. dedoping, which results in that the absorption is shifted to visible wavelengths peaking at around 640 nm, hence the material appears dark blue. This change in absorption is caused by that the number of bipolaronic states is dramatically decreased upon electrochemical reduction of the material. Thus, it is not only the color of the material that can be switched, but also the electronic conductivity. The color change of the material is therefore utilized in electrochromic displays, while the change in electronic conductivity is taken advantage of in electrochemical transistors. Figure 1 shows the chemical structure of PEDOT:PSS along with the absorption characteristics of the oxidized and reduced states that the material can be reversibly switched in between. Manufacturing the electrolyte-based devices presented herein is fairly straight-forward, and the main reasons for this is that the chosen materials have already been up-scaled and are commercially available in printable solutions and the number of required materials as well as the number of printing steps have been kept at a minimum. More information on the respective device will follow in the subsequent chapters.

3.1. Printed electrochromic displays (ECDs)

The electrochromic property of PEDOT:PSS that is utilized in printed ECDs results in a color change. The displays presented here are operating in reflective mode and, hence, possess an extremely wide viewing angle. PEDOT:PSS is switching between transparent and dark blue in its oxidized and reduced state, respectively. However, the deposited electrolyte is made white and opaque, which results in an observable color change between white and dark blue. Color contrast is a research topic in itself that starts already during the chemical synthesis of the electrochromic materials [2], and continues via device design and the characterization of the resulting display. There are several alternatives on how to report on color contrast, and the method chosen herein relies on the CIE L*a*b* color system, where the color coordinates L*, a* and b* corresponds to lightness, green-red and blue-yellow, respectively. The CIE L*a*b* color coordinates span the color space of the human eye very well, which is a strong motivation for the utilization of this color system. The color contrast is calculated from the measured color coordinates according to:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

3.1.1. Lateral architectures

This is a very simple and robust ECD architecture that has been manufactured roll-to-roll on various kinds of flexible substrates, such as plastic and paper. Its simplicity originates from the fact that only two printed layers are required in order to obtain the display functionality, even though an encapsulation layer typically is printed as well. The counter and pixel electrodes are located adjacent to each other and the electrolyte layer that is bridging the electrodes enables the ionic connection and hence the electrochromic switching. Figure 2 shows a drawing of this display architecture, and a photograph of the resulting display is shown in the left panel of Figure 3.

3.1.2. Vertical architectures

The vertical display architecture contains a pixel electrode that is stacked on top of the counter electrode, with an electrolyte layer sandwiched in between the electrode layers. Hence, the counter electrode is hidden beneath the pixel electrode and no display area is wasted as compared to the lateral display architecture. The fill factor of the display, which typically is defined as the ratio between the active pixel area and the total display area, can be dramatically increased in vertical architectures as compared to lateral dittos, and this is an important advantage when comparing the two architectures. The vertical display requires three printed layers; the counter electrode, the electrolyte and the pixel electrode, even though an encapsulation layer is printed many applications. A printed vertical ECD in which the color contrast ΔE* is exceeding 35 is presented in the right panel of Figure 3.

3.2. Printed electrochemical transistors (ECTs)

Transistors that are gated by an electrolyte is attracting a lot of attention at present time, and there are two different mechanisms that govern the operation of electrolyte-gated transistors; electrochemical or field-effect. Electrolyte-gated field-effect transistors, EGOFETs, are operating in enhancement mode, and this architecture is therefore suitable for logic circuits due to low power consumption [3]. In a p-channel EGOFET it is important to use a polyanion as the dielectric material between the organic semiconductor and the gate electrode. Mobile cations in the electrolyte are attracted towards the gate electrode, while the immobile polyanions are inducing a conducting channel at the interface between the electrolyte and the semiconductor. Electrochemical doping is prevented by the immobile polyanion. The ECT, on the other hand, is instead requiring mobile ions capable of penetrating into the bulk of the transistor channel, which implies that the on-current is higher in ECTs as compared to EGOFETs. The electrolytic interface enables an extremely high capacitance, typically on the order of $\mu F/cm^2$ instead of nF/cm^2 that typically is reached in transistors relying on for example silicon dioxide as the dielectric material. The major advantage of the dramatically increased capacitance it that low-voltage operation is enabled, that is, electrolyte-gated transistors respond to gate voltages far below 1 V.

3.2.1. Architectures including reduction front

The ECT functionality is easily obtained by using PEDOT:PSS as both the transistor channel and the gate electrode, where the latter can be placed laterally aside, or vertically on top, of the transistor channel. The transistor channel and the gate electrode are electronically separated but ionically connected by bridging them by an electrolyte, as shown by the drawing in Figure 4 [4]. This is a very simple and robust transistor architecture that can be manufactured at high yield, and its corresponding current vs. voltage characteristics at various gate voltages are shown in Figure 5. However, the major disadvantage is that its switching time becomes non-symmetric, i.e. the on-to-off switching time is typically shorter than the opposite switching event. This is due to that the voltage applied between the drain and source electrodes causes a reduction front that propagates outside the electrolyte edge [5]. This, in turn, creates a highly resistive spot inside the conjugated polymer but outside the edge of the electrolyte, which requires long time to relax to its conducting state. This is clearly not a desired device feature, and in combination with the fact that this type of ECT is operating in depletion mode indicate that such transistor device is rather complex to use in logic circuits and active matrix addressed displays because of the strain generated on the drain side of the ECT channel in such applications.

3.2.2. Improved switching characteristics by modified architecture

In an ongoing research activity the switching characteristics of the ECT has been improved by minimizing the reduction

front, which results in the short switching time and symmetric switching characteristics shown in Figure 6.
Due to the ability of the ECT to modulate the current through the channel at very low input signals, the device has been integrated into fully printed sensor systems containing ECTs, ECDs and pyro- or piezoelectric sensors, wherein each ECT amplifies the output signal of its corresponding sensor [6].
In addition to this, an electrochemical transistor operating in enhancement mode is currently being developed in an ongoing research activity. The motivation for employing enhancement mode operation, in favor of depletion mode, is prolonged lifetime because of less strain on the ECT and decreased power consumption.

3.3. Printed matrix-addressed displays

A matrix-addressed display is obtained by arranging electrochromic pixels in a cross-point matrix, and the major advantage of matrix-addressed displays is the ability to show any arbitrary message by applying a specific voltage pattern across the rows and columns. Examples of envisioned applications for printed matrix-addressed ECDs are eye-catching point-of-purchase displays, billboards, shelf labels, sensor indicators and displays integrated in packages. Two different updating techniques are available; passive and active matrix addressing. In general, the latter architecture shows less cross-talk effects but becomes more complex to manufacture since transistors are required to control the current to the pixels.

3.3.1. Printed active-matrix displays

An electrochemical smart pixel is created by combining the electrochromic display and the ECT, wherein the transistor controls the current, and hence also the color state, of the display. The active-matrix display is then obtained by arranging several smart pixels in a cross-point matrix. The same chemical compound, in this case PEDOT:PSS, is used as the active material in the subdevices of the electrochemical smart pixel. Hence, the electronic property of the conjugated polymer is utilized in the transistor, while the electrochromic property is taken advantage of in the display. Additionally, both subdevices are using the same kind of electrolyte. This is of course advantageous from a manufacturing perspective by that the number of materials as well as the number of processing steps are kept at a minimum. Figure 7 shows an active-matrix display containing only two different materials; PEDOT:PSS and a PSS-based electrolyte [7].

Active-matrix displays that rely on another device architecture, in which the switching characteristics of the ECTs have been improved, have recently been obtained.

3.3.2. Printed passive-matrix displays

Displays that are updated according to a passive-matrix addressing scheme is of course highly desired. The main reason is that it is sufficient to arrange the electrochromic pixels in a cross-point matrix, that is, the ECTs can be omitted, which in turn simplifies the manufacturing dramatically. Displays that are updated by passive-matrix addressing typically suffer from cross-talk effects, unless a diode is combined with every pixel. However, passive-matrix displays in which PEDOT:PSS is utilized as the active material have recently been achieved in an ongoing research project.

4. Figures

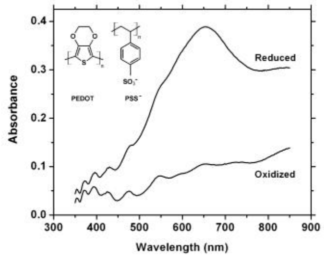

Figure 1. The chemical structures of PEDOT and PSS are illustrated. PSS^- maintains charge neutrality when PEDOT is oxidized, and Na^+ is typically used as the cation. An electrolyte based on PSSNa has also been used in many of the presented components herein. The upper and lower graph represents the reduced blue-colored and the oxidized white-colored state, respectively.

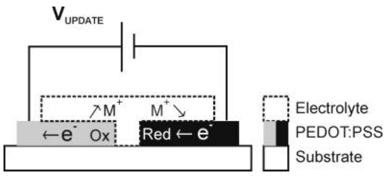

Figure 2. The architecture of a lateral ECD is shown. A vertical display device is obtained by simply stacking the electrodes on top of each other with the electrolyte layer sandwiched in between.

Figure 3. Left: a lateral 7-segment ECD manufactured by roll to roll printing on top of a paper substrate is shown. Right: the photograph shows the colored state of a vertical ECD upon applying 3V. The display pattern resembles the logotype of Acreo.

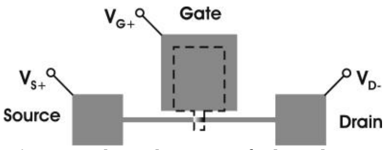

Figure 4. The architecture of a lateral ECT is shown. A vertical ECT device is obtained by simply stacking the gate electrode on top of the transistor channel with the electrolyte layer sandwiched in between.

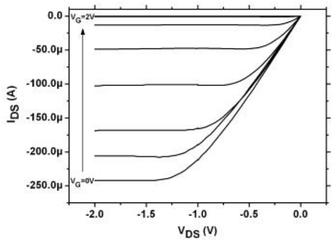

Figure 5. The current through the transistor channel is recorded while sweeping the voltage between the drain and source electrodes. Each voltage sweep corresponds to a certain gate voltage.

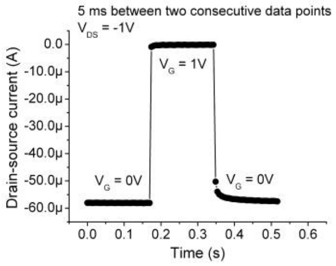

Figure 6. The switching characteristic of a printed ECT is shown, wherein each switching event occurs in less than 5 ms.

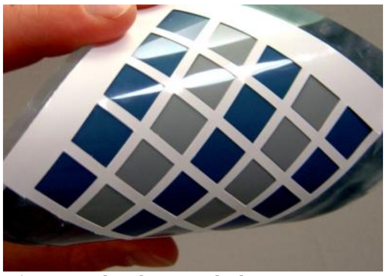

Figure 7. The photograph shows an active-matrix display containing 5×5 smart pixels.

5. Summary

A fully printable technology platform has been presented, in which the components are relying on an electrolyte interface between the counter electrode and the active material. This results in that both electrochromic displays and electrochemical transistors are being formed, as well as systems containing both subdevices. The small set of materials required to obtain the device functionalities enables a relatively simple manufacturing process. Another advantage of using electrolyte-based components is that low-voltage operation is achieved, which is an important feature when integrating transistors, displays, sensors and batteries into printed electronic systems.

6. Acknowledgements

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7. References

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