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An electrochromic bipolar membrane diode

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Organic materials are successfully exploited in a wide range of electronic components and devices. Some of the main advantages of organic electronics technologies include ease-of-processing, flexibility and a lower industrial barrier of entry (which translates to lower consumable prices).¹⁻⁴ One of the most successful application paths of organic electronics is the technology of organic light emitting diodes. Yet-another field of potentially great impact is the organic electrochemical displays (OECD), a technology which may be flexible, fully-printed, low-cost and easily integrated within a wide range of systems and substrates.

The large-area flat panel display technology is currently dominated by transmissive screens in the form of back-lit liquid crystals (LCD).⁵ In applications where low-power is desired (such as portable devices), transfective screens offer a very acceptable compromise.⁶ Emissive screens wherein each and every pixel consists of a light emitting diode are slowly displacing LCD screens.⁷ Non-emissive display technology is a superset of what is commonly termed "electronic paper" (e-Paper). E-Paper may be based on a number of techniques, including electrochromic displays which utilize chromogenic materials that (reversibly) change color when they undergo a redox reaction.⁸ Electrochromic displays are attractive because they consume little power. In addition to that, their production technology and overall processing is fully compatible with well established roll-to-roll printing tools.⁹ A display's (or pixel's) fill-factor is defined as the ratio between the active area to the total area of the display (or pixel). The fill-factor is typically sacrificed in electrochromic matrix displays to accommodate the active addressing circuitry.¹⁰ A passive matrix (PM) addressing circuit is constructed by placing the display medium between a crisscross of front and rear electrodes. The resulting grid forms the rows and columns of the display matrix and their intersection constitutes the pixel.¹¹ The addition of thin-film diodes or transistors to address the pixels in active matrix (AM) displays sacrifices the fill-factor in favor of higher refresh rates and lower energy consumption. Alas, active matrix addressing schemes are also significantly more expensive and complex to produce (as compared with passively addressed display circuits). Figure 1 shows the layout for a PM and a transistor-enabled AM addressing scheme. In both cases, a pixel is selected by applying a voltage on the corresponding row and column. The addition of an active component in the AM constrains the voltage to the selected cell. In the PM, however, the whole row and column are affected by the voltage, which leads to cross-talk on the adjacent cells. Cross-talk voltage results in severe picture distortion. The active component may be a transistor or a diode depending on the desired performance.

Electrochromic materials exhibit the property of change, evocation, or bleaching of color as a result of undergoing a redox process (or by a sufficient electrochemical potential).¹² Since their advent some four decades ago, electrochromic materials have attracted considerable attention for their potential use in display applications.¹³ Electrochromic materials may be inorganic (e.g: oxides of transition metals) or organic (e.g: resonance stabilized aromatic molecules).¹² Because the latter are compatible with printing technology, they are generally considered good candidates for low-cost displays in packaging, point-of-care testing, authentication applications, and the so-called Internet of Things.¹⁴ Due to a high level of self-discharge, OECDs suffer from poor retention time. This drawback increases the power consumption enormously, because the display has to be refreshed at regular intervals. Addressing of OECD is currently done through complex backplane electronic circuitry, which hardly qualifies as printable (as it requires drilling of vias) or low-cost (due to the price of the active electronic components).

The basic structure of an OECD includes two polymer electrodes and a common electrolyte. The current versus voltage (I-V) characteristics of the OECDs is governed by the charging and discharging of the electrodes in an electrochemical supercapacitor. Therefore, the I-V characteristics lack a threshold or rectification behavior that would make passive matrix addressing possible.

One of the most common printable conducting polymer explored in electrochromic display settings is poly(3,4-ethylene-dioxythiophene) doped with poly(styrene-sulfonate) (PEDOT:PSS) .

Upon biasing, the PEDOT phase changes from a transparent light blue (oxidized and electrically conducting) state to an opaque dark blue (neutral and semiconducting) state when it is reduced according to Equation 1.¹⁵

Figure 2a shows the absorption spectra of PEDOT:PSS at different potentials (for an ECD structure similar to Figure 3a. It is worth noting that the largest absorption peak shift occurs around 660nm (red in the visible spectrum), and that there is a polarity-dependent absorption asymmetry (Figure 2b).

A PEDOT:PSS electrochemical display is composed of two PEDOT:PSS electrodes separated by an ionic conductor (typically, a solid electrolyte).⁹ Figure 3a-c illustrates the electrochromic switching characteristics in a PEDOT:PSS OECD subjected to a potential bias. Figure 3a depicts the pristine state with no potential applied across the device. In Figure 3b, the negatively biased electrode undergoes reduction and the PEDOT:PSS changes from (transparent) light blue to (opaque) dark blue. Figure 3c illustrates the reversibility of the reaction when oppositely biased. Figure 3d shows a typical I-V curve for a PEDOT:PSS electrochromic display. The box-like shape is reminiscent of a pseudocapacitor's cyclic voltammogram.¹⁶

Alongside electrochromic displays, an emerging area of research is that of organic iontronics, i.e. devices that possess classical or novel electronic device functions but where the signal carriers are ions instead of electrons. Iontronics may combine ion-selective membranes to achieve specific functions. A cation [anion] selective membrane is composed of immobile anionic [cationic] groups that favor the transport of mobile cations [anions] while preventing the penetration/transport of anions [cations] through electrostatic repulsion (Donnan exclusion). In electronics, there are hole- and electron-transporting materials, known as p-type and n-type semiconductors; in iontronics, there are cation- and anion-transporting materials, so called P-type and N-type materials. Iontronic circuits consist of a combination of various types of ionic devices, such as PN-diodes also called bipolar membrane diodes, PNP or NPN ion bipolar junction transistors and "ion pumps".¹⁷⁻¹⁹ Iontronics may interface with biological

systems since many biologically active molecules (such as neurotransmitters) are essentially ions and can easily be transported through (or along) membrane device configurations.²⁰ One of the basic devices is the bipolar membrane which consists of an anion-selective membrane and a cation-selective membrane in contact with one another. Figure 3e-g illustrates the BM diode concept and its operating mechanism. Bipolar membrane diodes with a rectification ratio beyond 1000 have been reported in the past. The rectification of an ion current may potentially be used in electronic, electrochemical and iontronic devices and circuits to achieve electronic current rectification and desired non-linearity in bias response.^{21,22} Figure 3e shows the mobile ions distribution when the device is unbiased. Figure 3f shows the forward bias mode where the anions/cations, propelled by the electric field, migrate towards the BM junction. This accumulation of mobile ions along the junction gradually increases the conductivity.¹⁷ In reverse bias mode, illustrated in Figure 3g, the mobile ions migrate away from the BM junction and towards the electrodes. This depleted junction causes a significant drop in ion concentration which, in turn, leads to a decrease in ionic conductivity.¹⁷ The current-voltage characteristics is therefore similar to that of a diode (Figure 3h).

In this work, we propose to integrate addressability and electrochromism within the same device by using an ionic diode based on a bipolar membrane (BM) stack sandwiched between two PEDOT:PSS layers (see Figure 3i-k). In this combined architecture, current rectification and addressability is provided by the bipolar membrane electrolyte, while the color switching derives from the PEDOT:PSS electrode layer. We demonstrate that the integration of a BM into an EC display introduces a non-linear I-V characteristics, a prerequisite for addressability in a 2D matrix of EC pixels (Figure 3m)

To demonstrate this concept, we use monopolar and bipolar membranes to build vertical ECDs similar to the devices depicted in Figure 3a and 3i (respectively). Figure 4a shows the I-V characteristics of a monopolar membrane ($\approx 450\ \mu\text{m}$ thick Ralex CMH PAD) sandwiched

between two conducting polymer electrodes (200 nm thick AGFA-Gevaert Orgacon F-350 PEDOT:PSS film coated on a polyethylene terephthalate substrate). The I-V curve of this OECD with a monopolar membrane electrolyte is typical for an electrochemical capacitor wherein the current scales linearly with the scanrate ($I = C \partial V / \partial t$). Figure 4b shows the I-V characteristics for a bipolar membrane ($\sim 180 \mu\text{m}$ Fumatech Fumasep FBM) sandwiched between two PEDOT:PSS electrodes. It is clear that asymmetry is introduced in the I-V curve – with little current passing in the reverse bias regime. The capacitive component of the current is evident in forward bias since the current (at 0.8 V) scales linearly with the scanrate. This clearly demonstrates that the integration of a BM in an EC device introduces a current non-linearity dictated by the combination of the electrochemical capacitor and the bipolar diode. Biasing the PEDOT:PSS/BM/PEDOT:PSS cell in forward mode, as is the case in Figure 3j, pushes the mobile ions towards the junction. This, in turn, increases the conductivity through the BM and leads to a current flow through the cell. The redox reaction takes place according to Equation 1. That is, the negatively biased electrode turns deep blue while the positively biased one turns slightly more transparent (i.e. is further oxidized). In Figure 2k, the BM junction is depleted and the PEDOT:PSS electrodes slowly recover their original states and colors. Note that a simplified model of this EC diode can be seen as a diode in series with a capacitor. Indeed, a conventional electronic diode (NXP - BAP1321-04,215) connected in series with the EC display leads to a similar asymmetry in the I-V characteristics with a pinched current in the reverse bias (see supplementary information). However, since the BM is mostly transparent, it is difficult to follow the color switching characteristics during operation of the device. Moreover, there is a residual current, likely due to water splitting, in the reverse bias beyond -0.8 V that severely restricts the device's window of operation.^{21,22} This residual current also limits the rectification of the EC diode.

The I-V characteristics of both membranes are shown for a series of different scan rates (5, 25, 50, 100 mV/s). The innermost curve corresponds to the slowest scan rate (5 mV/s), while the outermost curve corresponds to the fastest one (100 mV/s). The slower the scan rates, the less current passes through the devices. Figure 4a is similar in shape to that of Figure 3d. Figure 4b shows the asymmetry in the I-V characteristics of an OECD with a bipolar membrane.

With the aim of studying the electrochromism on both electrodes simultaneously, as well as to improve the rectification properties of the EC diode, we built a planar version of the device as depicted in Figure 5. Using a combination of photolithography with liquid-phase and plasma etching, we microfabricated a bipolar membrane (50x50 μm channel) with two PEDOT:PSS electrodes (2500x2500 μm) on a flexible substrate. The bipolar membrane was made from a stack comprising a 800 μm thick polyphosphonium as well as a 200 μm thick polystyrene sulfonate (PSS) film. The chemical structure of these materials is displayed in figure 5. Polyphosphonium was used as a polyanion since it was reported to prevent electric field-enhanced water dissociation in BM diodes.^{21,22} Figure 5 illustrates the microfabricated planar bipolar membrane diode embedded in an electrochromic display as it would appear under forward bias.

We applied a +/-8 V square pulse to the OECD-BM-diode and recorded the current response (Figure 7a). The left probe is connected to the positive terminal while the right probe is connected to the negative terminal of the power supply. Despite voltages outside the electrochemical window of aqueous electrolytes, the electric field-enhanced water dissociation is hindered owing to the inclusion of a non amine-based polycation.²³ And because the PEDOT:PSS electrodes are polarizable, the electrochemical water splitting into hydrogen and oxygen gas is also prevented here.²⁴ The on/off ratio of the device is found to be close to 100. The device is operated longer in reverse bias than in the forward mode. The

reverse current is low ($I_{\text{off}} \approx 1^{0-9}$ A), so in 120 s only 3 μC passes through the device which is not enough to cause any substantial electrochromism in the PEDOT:PSS electrodes. The color of the two electrodes thus remains unchanged (Figure 6a). In forward bias, however, after 60 s operation the total charge displaced between the two electrodes exceeds 120 μC and the right hand side electrode becomes dark blue (Figure 6a). This is explained by the high ionic current that passes through the bipolar membrane ($I_{\text{on}} \approx 10^{-6}$ A) which leads to a significant reduction of PEDOT on the right electrode and oxidation of the left electrode (see Equation 1). The fact that the right electrode undergoes a strong color change compared to the left electrode is due to the non-linear absorption versus voltage profile for PEDOT (as expounded in Figure 6a). Reversing the current leads to a sharp current peak attributed to the transitory double-layer formation followed by a steep decline in current level. This kind of I-V characteristics is observed in similar bipolar membrane devices.¹⁷ Only 2 μC are transferred between the PEDOT electrodes during a time period of 120 s. And because of the aforementioned small charge transfer, the electrodes don't recover their initial (pristine) color. The right electrode, however, becomes slightly less blue (Figure 6b).

The color change of the two electrodes is tracked simultaneously with a digital microscope camera. Because PEDOT becomes blue when reduced (absorption around 600 nm as indicated by Figure 2a), the red channel of the camera should be the one most sensitive to the change in color. With this in mind, we follow the current vs. time (Figure 7a) and the red RGB color space value versus time (Figure 7b). The solid line represents the right electrode (cathode in forward bias mode) of the display (analogous to the top terminal in Figure 3e-g). Similarly, the dashed line represents the left electrode (anode in forward bias mode) of the display/diode (bottom terminal in Figure 3j-l). Since the RGB color space follows an additive color mixing scheme, dark blue color is reflected as low values in the red channel of the camera. When the voltage is reversed, the right electrode becomes slightly more transparent,

while the signal from the left electrode is almost constant. In contrast, when forward biased, we observe sharp dips in the RGB red value of the right terminal, while there is virtually no change in the left electrode. The periodicity of these dips matches the forward mode biasing of the device. The variation in RGB red values of the right electrode (around 30 %) is substantially larger than the variation in RGB red values of the left electrode (<2 %). The electrochromism of the latter is barely visible to the naked eye as evidenced by Figure 6a and 6c.

To explain these results, we propose the following mechanism: Substituting the BM for the ionic conductor (i.e. the electrolyte) in the electrochemical display described in Figure 3a-c is equivalent to embedding a diode within the display cell. Therefore, biasing the PEDOT:PSS/BM/PEDOT:PSS cell in forward mode, as is the case for Figure 3j, pushes the mobile ions towards the junction. This, in turn, increases the conductivity through the BM and leads to a current flow through the cell. The redox reaction takes place according to Equation 1, and the negatively biased electrode turns deep blue while the positively biased one turns slightly more transparent. In reverse bias, however, the BM junction is depleted and the PEDOT:PSS electrodes return to their original colors (see Figure 3k).

In summary, we demonstrate the feasibility of incorporating an ionic diode inside an electrochromic display using a bipolar membrane. The asymmetric conductance of this embedded diode may be exploited to address a matrix of electrochemical display cells. Current rectification is known to provide addressability in passive matrix circuits. Both PEDOT:PSS electrochromic displays and bipolar membrane diodes are compatible with printing techniques. Despite relying on photolithography in this work, the solution-processability of all materials involved indicates that the manufacturing process may be adapted for printing. This may potentially enable the manufacturing of cheap large-area

electrochromic displays. In such a configuration, the bipolar membrane electrolyte plays the dual role of providing reactants for the electrochromism as well as rectifying the current for addressing purposes.^{2,9} In effect, this provides a cost-effective way of building an electrochromic display matrix by utilizing the bipolar membrane's rectification to address the display and selectively switch one side of the pixel only. These results also provide an easy way to improve the retention time (bistability) of polymer electrochromic displays. Moreover, the ionic bipolar membrane diode does not add any device features alongside that of the display cell; it is incorporated between the electrodes and plays the role of both the electrolyte and the rectifier. The integration of the BM diode into OECD cells would allow organic displays to retain very high fill factors. However, due to the slow turn-on and turn-off times, this technology is constrained to niche display applications where refresh rates in minutes are acceptable (billboards, linear/matrix barcodes, electrochromic wallpaper, etc.).

Experimental Section

ECDs with commercially available membranes: The monopolar membrane (Ralex CMH PAD) and the bipolar membrane (Fumatech Fumasep FBM) were soaked for 72 h in a 1 M NaCl solution. The membranes were then sandwiched between two ($<1\text{ cm}^2$) PEDOT:PSS electrodes (5 μm thick Clevios PH1000 cast on PET) and held together by a clamp. We added ($<0.5\text{ vol. \%}$) octadecyltrimethoxysilane (obtained from Sigma-Aldrich) and heated the film to 70°C for 120 s to crosslink the PEDOT:PSS. The devices were placed in a humid container ($>50\text{ \% RH}$) to maximize the ionic diffusion inside the membrane (by maintaining an optimal swelling).

Preparation of poly(vinylbenzyl chloride) solution: Poly(vinylbenzyl chloride) (PVBC, Sigma-Aldrich) was dissolved with tetrahydrofuran (THF) at 200 mg/ml and the solution filtered through a $0.2\text{ }\mu\text{m}$ PTFE-membrane.

Preparation of polyphosphonium: 5 ml of a (0.2 μm PTFE-membrane filtered) 200 mg/ml solution of Poly(vinylbenzyl chloride) (PVBC, Sigma-Aldrich) dissolved in tetrahydrofuran (THF) was mixed with 1720 mg of triphenylphosphine (Sigma-Aldrich) and heated at 60° C for 24 h. The formed precipitate was dried in vacuum, dissolved in 4.5 ml of H₂O and 2.46 ml of 1-propanol and filtered through a 0.2 μm nylon filter. Finally, we add 6 ml of H₂O and 8 ml of 1-propanol.

Microfabricated planar ECDs: The electrodes and the cation-selective membrane were patterned from PEDOT:PSS on polyethylene substrate (AGFA-Gevaert Orgacon F-350). The substrate was cleaned using water and acetone, baked (110° C, 5 min) and poly(methyl methacrylate) (PMMA, Sigma-Aldrich, average m.w. 120000, 4 mg/ml in Diethyl carbonate) and Shipley S1805G2 photoresist was deposited by spin coating (4000 rpm, 30 s spin, 110° C 5 min bake each). The photoresist was patterned using a Karl Suss MA/MB6 mask aligner and Microposit MF319 developer, followed by rinsing in H₂O and baking (110° C, 5 min). A CF₄/O₂ plasma was used to dry-etch the exposed PEDOT:PSS. The remaining photoresist and PMMA was removed using Shipley Remover 1112A and acetone and rinsed in H₂O. The cation-selective channels were overoxidized (rendered electronically insulating) by exposure to aqueous sodium hypochlorite (1 % vol/vol) for 45 s through openings in a patterned 1.3 μm thick Microposit S1813G2 photoresist layer. The photoresist was removed and cleaned using Shipley Remover 1112A, acetone, and water. A 2.5 μm thick SU8 (SU8-2002, Microchem) layer was then deposited (1000 rpm, 30 s) and patterned, according to the manufactures instructions, on top of the cation-selective channels to produce the 5x100 μm interface of the BM. The PEDOT:PSS electrodes were shielded during the following processing steps by a hard baked (110°, 1 h) 1.3 μm thick patterned Shipley S1813G2 layer. The anion-selective membrane was deposited by spin coating (1500 rpm, 45 s) and baked at 110° C for 1 h, followed by a layer of PMMA (40 mg/ml in DEC, 2000 rpm for 30 s) and a 1.3 μm thick

Shipley S1813G2 layer (each baked 110° C, 10 min). The anion-selective membrane was patterned in a similar way as the PEDOT:PSS, but with acetone and isopropanol for removing and rinsing. A 10 µm thick SU8-layer (SU8-2010, MicroChem) was deposited (3000 rpm, 30 s) and patterned to encapsulate the device, again according to the manufactures instructions. Carbon contacts were painted onto the electrodes (baked 110° C, 5 min). The devices were then soaked in H₂O for 24 h prior to measurements. A 0.1 M aqueous sodium chloride solution was used as electrolyte.

Characterization: We recorded the current response using a LabVIEW-controlled Keithley 2602A source meter, we ran a +/-8 V square pulse (respectively for 60/120 s) on the bipolar membrane diode-display and recorded the current response. Pictures of the device were recorded using a Nikon SMZ1500 microscope illuminated with white LEDs. The JPEG files extracted from the Nikon NIS-Element Viewer did not undergo any form of post-processing. RGB values were extracted with ImageMagick's "convert" tool (in Bash 4.3.11). All measurements were performed in ambient atmosphere at 23° C and 40 % relative humidity.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. a) Passive matrix and b) active matrix addressing circuit layouts.

Figure 2. Optical properties of PEDOT:PSS. a) Optical absorption spectrum. b) Optical absorption at 660 nm. c) Chemical structure of PEDOT:PSS.

Figure 3. Illustration (and typical I-V characteristics) of an electrochromic display, a bipolar membrane, and the electrochromic bipolar membrane diode device. a-d) Organic electrochromic display schematic and I-V characteristics. e-f) Electrode-agnostic bipolar membrane schematic and I-V characteristics. i-m) Electrochromic bipolar membrane display schematic and I-V characteristics. n) Schematics' color code.

Figure 4. ECDs with commercially available monopolar and bipolar membranes. a) IV curve for a monopolar membrane ECD at different scanrates (5, 25, 50, 100 mV/s). b) IV curve for a bipolar membrane ECD at different scanrates (5, 25, 50, 100 mV/s).

Figure 5. Illustration of a microfabricated planar bipolar membrane diode embedded within an electrochromic display.

Figure 6. Bipolar membrane diode in electrochemical display in a) reverse bias, b) forward bias, and c) return to reverse bias.

Figure 7. Electrical and optical characterization of the bipolar membrane diode embedded in an electrochemical display. a) Current rectification of the bipolar membrane diode. b) R(GB) values of the bipolar membrane diode-display. Solid lines represent the cathode of the diode and the dashed lines represent the anode.

Conducting polymers are solution processible and offer bipolar membrane is a complementary stack of selective membranes that may be used to rectify current.

Integrating a bipolar membrane into a polymer electrochromic display obviates the need for an addressing backplane while increasing the device's bistability. Such devices can be made from solution processible materials.

PEDOT:PSS, printed displays, bipolar membranes, ionic diodes, electronic paper

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An electrochromic bipolar membrane diode

Supporting Information**An electrochromic bipolar membrane diode**

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In order to show how a BM is essentially a monopolar membrane with a diode in series, we fabricated a device similar to the one presented in Figure 3a (and Figure 4a). The I-V characteristics is shown in Figure S1a. The box-like shape and the I-V curve's symmetry were expected. Figure S1b shows the I-V characteristics of an NXP BAP1321-04,215 solid state diode. We then put the diode in series with the monopolar membrane device (Figure 4a), and the result is presented in Figure S1c. The hysteresis is due to the large capacitive component of the current, while the excellent rectification of the solid-state diode prevents any current from flowing in the reverse direction.

Figure S1. Monopolar membrane supercapacitor with a solid-state diode. a) Monopolar membrane. b) Solid state diode. c) Diode in series with a monopolar membrane.

For the sake of comparison, we include the I-V plot of one of the better ionic bipolar membrane diode. The BM diode is similar to the one in Figure 4b (i.e: Fumatech Fumasep FBM membrane) but with 10 μm thick electrodes. The diode's I-V characteristics include "initialization time" (held in reverse bias for 80 s).¹⁷ Two sweeps at 500 mV/s are shown in Figure S2. The device exhibits hysteresis comparable to the circuit in Figure S1c, albeit with considerably more current flowing in reverse bias mode.

Figure S2. I-V curve of a bipolar membrane diode.