Thin film organic electrochemical transistors based on hybrid PANI/PEDOT:PSS active layers for enhanced pH sensing

Silvia Demuru **, Brince Paul Kunnel, Danick Briand *

Soft Transducers Laboratory (LMTS), Ecole Polytechnique Fédérale de Lausanne (EPFL), 2000, Neuchâtel, Switzerland

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ABSTRACT

We report on organic electrochemical transistors (OECTs) with active channels made of hybrid inkjet-printed poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and electropolymerized polyaniline (PANI) layers, exhibiting simultaneously improved electrical and pH sensing characteristics. The aniline electropolymerization with an optimum 6-cycles of cyclic voltammetry forms a porous PANI microstructured layer on the PEDOT:PSS film, resulting in high signal linearity and sensitivity of about 100 mV/pH and 20 μA/pH. The electrochemical impedance spectroscopy analysis demonstrates a 9X higher-change of interfacial capacitance when decreasing the pH with the hybrid PANI-PEDOT:PSS layer, in comparison to a bare PEDOT:PSS layer. The simple fabrication process and the high signal amplification pave the way for flexible and higher-performance pH-sensitive OECTs. These scalable devices, combined with ion-selective OECTs, would lead to a novel tool for multi-parametric analysis in different biofluids.

1. Introduction

There is a growing interest to measure multiple analytes in biofluids such as blood, saliva, sweat, and tears, developing portable tools for multi-parametric analysis (Gao et al., 2016; Kim et al., 2019). These analytes include notably ions such as sodium, potassium, chloride, metabolites as lactate and glucose, and low-concentrated biomarkers such as proteins and cytokines (Bariya et al., 2018). A parameter of high importance is the monitoring of pH, as a valuable health-information itself or for the calibration of electrochemical sensors measuring other analytes. Notably, pH variations in the blood correlate to the cortisol levels (Sakharov et al., 2010), making it overall a promising indicator of the health status of individual. The pH in blood stays in the 7.35–7.45 range, with mild changes being dangerous for health, and generally cannot be outside the 6.8–7.8 values (Di Rollo et al., 2013). In the case of saliva, the pH can vary from 5 to 7.6 depending on the food and beverage consumption (Pachori et al., 2018). Considering sweat, the pH regulation is related to lactic acid production (Palacios et al., 2015). Its pH can significantly vary from 3 to 8 (Bariya et al., 2018), and values in the literature between 4 and 7, being mainly reported (Hussain et al., 2017). It was also shown that the measurement of pH can be applied to the calibration of enzymatic-based measurements, such as for accurate glucose monitoring in sweat (Lee et al., 2016).

Different types of bio-chemical sensors are being studied to develop such novel low-cost, wearable devices for personalized medicine and health analysis (Picca et al., 2019). Among these, organic electrochemical transistors (OECTs), thanks to their mixed ionic-electronic charge transport and their intrinsic flexibility, allow a high signal amplification and improved interfaces with soft biological systems (Hempel et al., 2017; Higgins et al., 2020; Kaphle et al., 2020; Lee et al., 2017; Malliras et al., 2018; Someya et al., 2016). The OECT, a three-terminal device, with the source and drain electrodes connected by an organic conductor (channel) and the gate electrode coupled to the conducting channel by an electrolyte, is of particular interest because of the very high sensitivities that can be achieved for multiple biochemical sensing applications (Picca et al., 2019; Romeo et al., 2015; Zeglio and Inganias, 2018; Zhang et al., 2018).

Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is a conjugated polymer-polyelectrolyte and the mainly used active material in OECTs (Kaphle et al., 2020). The PEDOT:PSS channel is doped and dedoped by cations in ionic solutions once a positive gate voltage is applied, exhibiting a mixed ionic-electronic transport and a very high signal amplification (Ghitorelli et al., 2018; Tu and Fabiano, 2020). Thanks to PEDOT:PSS, being a low-cost material that can be...
simply printed onto flexible substrates, the cost-effective manufacturing of OECTs sensors can be envisioned (Demuru et al., 2020; Mattana and Briand, 2016; Ruecha et al., 2014). PANI was also implemented as the active channel in OECTs, in the form of single-PANI nanowires (Lee et al., 2009) or recently PANI-microchannels on interdigitated electrodes demonstrating complementary circuits (Travaglini et al., 2020). However, in general, only few works report on PANI-channel OECTs compared to PEDOT:PSS, possibly due to their lower signal transduction.

PEDOT:PSS-based OECTs are reported for different sensing applications, such as ion-sensing of sodium and potassium, enzymatic-based sensing of glucose and lactate (Ghitorelli et al., 2018; Ji et al., 2016; Lin et al., 2010), or aptamer and antibody-based detection of different low-concentrated biomarkers (Macchia et al., 2018; Saraf et al., 2018). An OECT with an H⁺-selective membrane covering the PEDOT:PSS channel was recently reported (Demuru et al., 2020), but the devices had low signal linearity and limited dynamic range (4–7 pH). OECTs (PEDOT:PSS-based) for pH sensing are reported only with the integration of different pH-sensitive materials on the gate electrodes, such as a pH-sensitive dye (Mariani et al., 2015) or by using polyaniline (PANI) as gate electrode material (Scheiblin et al., 2017), the latter exhibiting however a sub-Nernstian response to pH variations.

Among the most commonly studied conductive polymers (Pappa et al., 2018), PANI is being considered for pH sensing since it has the unique property of the pH-dependent tuning of its doping and de-doping state (Li et al., 2019). Indeed, in an acid solution, PANI is doped by the H⁺ ions, passing from the emeraldine base to the emeraldine salt form, which exhibits high electrical conductivity. Instead, when the organic material is exposed to basic solutions, the captured H⁺ ions are neutralized by OH⁻, resulting in the opposite effect. Thanks to this mechanism, PANI is mostly used for pH-sensitive indicator electrodes in standard two-electrode potentiometric sensors (Oh et al., 2018) and, in the same configuration only, has been combined with PEDOT:PSS for improved electrochemical pH-sensing characteristics in terms of sensitivity and stability (Vacca et al., 2015).

Herein, PANI-PEDOT:PSS-based OECTs are proposed to simultaneously reach a high electrochemical transduction performance and a high and linear pH-sensing response. Therefore, we report for the first time on OECTs with a hybrid active channel made of inkjet-printed PEDOT:PSS thin film covered by an electro-polymerized PANI layer applied to pH sensing. The electrical characteristics of the transistors are analyzed in electrolyte solutions at different pH levels relevant for biofluids analysis. The PANI-PEDOT:PSS devices with 6-cycles aniline polymerization exhibit much higher pH sensitivity and linearity compared to the use of a bare PEDOT:PSS channel and to the devices with thinner and thinner PANI layers. The micro/nanostructure of the electropolymerized PANI-layers is studied using different techniques, such as SEM, AFM, and confocal microscopy. The working mechanism of the novel hybrid organic electrochemical transistors is analyzed through electrochemical impedance spectroscopy.

2. Materials and methods

2.1. Inks, chemicals and solutions preparation

The PEDOT:PSS solution (1 S/cm, 1.3 wt % dispersion in H₂O) was purchased from Sigma Aldrich. The silver nanoparticle ink was purchased from PV Nano Cell (Siccray, ISCT-13). The Phosphate Buffer Saline (PBS) 1X solution was made using 1 mM monopotassium phosphate (KH₂PO₄ from Merck), 155 mM NaCl (from Sigma Aldrich), and 2.966 mM disodium phosphate (Na₂HPO₄ from Merck). For the pH sensing tests, buffer concentrate solutions (Tritrisol) were employed. The aqueous solution for the electropolymerization process was made of aniline (0.1 M, from Sigma Aldrich) and HNO₃ (1 M, from Merck). Dimethyl sulfoxide (DMSO) was purchased from Sigma Aldrich.

2.2. Inkjet printing of the organic electrochemical transistors

Thin-film organic electrochemical transistors were inkjet printed with a Dimatix DMP printer (Fujifilm, 10-Pt. cartridges) on flexible polyimide substrates (125 µm-thick). The silver nanoparticle-ink was used for the source, drain, and gate electrodes, and the PEDOT:PSS ink for the active layer (Fig. 1a and b). The channel area is about 0.5 mm × 0.8 mm, and the gate-channel gap is about 0.5 mm. The electrical contact of 2 mm × 2 mm (Fig. 1b) is designed for a simple connection during the successive electropolymerization step.

For the fabrication of these devices, the PEDOT:PSS solution and the silver nanoparticle inks were sonicated for 5 min and subsequently filtered with a 0.2 µm pore-size filter when filling the respective cartridges. The polyimide substrate is treated with oxygen plasma before printing. The Dimatix plate is kept at 40 °C during the printing. First, two layers of the silver ink were printed for the gate, source, and drain electrodes, and subsequently sintered at 180 °C for 1 h. Then, the four layers of PEDOT:PSS were printed and subsequently post-treated with DMSO fully-covering the PEDOT:PSS film, and finally cured at 120 °C for 20 min. Such a DMSO post-treatment method is one of the most effective in the literature for achieving PEDOT:PSS films of high electrical conductivity and crystallinity (Lingstedt et al., 2019). The fabrication process is summarized in the schematic of Fig. 1c.

2.3. Electropolymerization of the PANI layer on the PEDOT:PSS channel

The electropolymerization of aniline on the PEDOT:PSS channel is carried out with a 3-electrode setup, as represented in Fig. 1d. The working electrode is the inkjet-printed PEDOT:PSS layer and an insulator is used to cover the silver and the silver-PEDOT:PSS contacts, leaving an open window of around 0.3–0.4 mm². An Ag/AgCl wire is employed as the reference electrode and a platinum wire as the counter electrode. Cyclic voltammetry is performed for the electropolymerization, with the potential applied from 0 to 0.95 V, then down to −0.01 V and back to 0, with a scan rate of 100 mV/s, similar to previously reported work (Vacca et al., 2015). The electrochemical transistors with different electropolymerization cycles equal to 3, 6, and 10, hence with varying thicknesses of deposited PANI, are tested for pH sensing, as shown in Fig. 1e. The electropolymerization was performed with a potentiostat (Multi Autolab M204, Metrohm).

2.4. Imaging

Thickness measurements and optical images were obtained with a laser scanning microscope (Keyence VK-X1000 Series). For the thickness measurements, the maximum magnification (50 ×) was obtained. Top-view images by SEM (instrument JEOL JSM-7500TFFE) and AFM (instrument Dimension Edge ScanAsyst) measurements were performed on PEDOT films without and with the PANI layer. A cross-section in the PANI-PEDOT:PSS was defined and the subsequent SEM images were acquired with a dual-beam FIB/SEM instrument (FEI Scios) with the addition of gold and platinum layers.

2.5. Testing

The OECTs electrical characteristics were acquired using a semiconductor parameter analyzer (Agilent 4155A). The I₃ₓVₐ characterization were repeated three to five times for stabilization of the signal, and each I₃ₓVₐ measurement took around 2 min. For confining the testing solutions, PMMA reservoirs were laser cut using a CO₂ laser and attached to the sensors thanks to a silicone adhesive. The sensors were washed three times with DI water when changing the test solution. Electrochemical Impedance Spectroscopy (EIS) measurements were acquired using the potentiostat and employing a 3-electrode setup, using the PEDOT:PSS or the PEDOT:PSS-PANI layers as the working electrode, an Ag/AgCl wire as the reference electrode, and a platinum wire as the
counter electrode. The frequency was changed from $10^5$ to 0.1 Hz, applying an AC voltage equal to 10 mV and a DC voltage equal to 0.1 V.

3. Results and discussion

3.1. Electropolymerization and morphology of the hybrid PEDOT:PSS-PANI layer

A study analyzing the PANI deposition process with different polymerization cycles equal to 3, 6, and 10 is performed. The OECTs, with only the PEDOT:PSS channel exposed as the working electrode, are electropolymerized in an aniline solution by cyclic voltammetry, as shown in Fig. 2a. The cycles of electropolymerization from 2 to 10 are reported. It can be seen the oxidation peak around $+250$ mV, which can be attributed to the conversion from the leucoemeraldine form into the emeraldine form (Kellenberger et al., 2013). Also, the current progressively increases with the number of cycles, indicating the growth of the PANI conductive layer on the channel surface. This optimal polymerization is achieved with the PEDOT:PSS layers post-treated with DMSO as working electrodes, while the untreated layers show a less visible growth of material (Fig. S1). As shown in Fig. S1b, the untreated layers do not exhibit well-defined peaks in the voltammogram. This behavior is possibly due to the higher resistance of the PEDOT:PSS electrodes without DMSO treatment (Vacca et al., 2015).

Optical images of the electrochemically synthesized layers on the PEDOT:PSS channels are reported in Fig. 2b, with an increase of the deposited material with the number of cycles. The average heights of the PEDOT:PSS layers were measured with the confocal microscope, and they are equal to $241 \pm 10$ nm ($n = 2$), while after PANI electropolymerization this value increases to $324 \pm 126$ nm ($n = 4$) for 3-cycles electropolymerization, $423 \pm 61$ nm ($n = 4$) for 6-cycles, and $926 \pm 327$ nm ($n = 3$) for 10-cycles (Fig. S2c). Also, the measured maximum height ($S_z$) is $473 \pm 72$ nm ($n = 2$) for the bare PEDOT:PSS layers, $1469 \pm 315$ nm ($n = 4$) for 3-cycles polymerization, $2082 \pm 467$ nm ($n = 4$) for 6-cycles, and $4053 \pm 241$ nm ($n = 3$) for 10-cycles (Fig. 2f).

The surfaces of the electrodes are analyzed with different microscopy techniques. SEM images without polyaniline (Fig. 2c) and with polyaniline (Fig. 2d) demonstrate the formation of a micro-nano structured PANI-layer following electropolymerization. The bare PEDOT:PSS layer shows the presence of nanostructured grains, likely PEDOT crystallites formed during the DMSO post-treatment (Chou et al., 2015; Jiang et al., 2013). Instead, the SEM images of the electropolymerized PANI-layer reveal a porous morphology, with a pores size of about 1 μm. Such a structured film is formed due to the agglomeration of PANI nanowires (Jiang et al., 2013). Further information on the morphology of the bilayer is obtained through a FIB cross-section (Figs. S2a and b), where micrometric pores can be seen in the section of the PANI film (Figs. S2c and d). The formation of the PANI porous microstructures compared to
Fig. 2. Electropolymerization on the PEDOT:PSS layers. (a) Voltammogram of the electrochemical oxidative polymerization of aniline from 2 to 10 cycles, (b) optical images of the PEDOT:PSS-DMSO layers with different polymerized cycles (3, 6, 10), SEM images at different scales without electrodeposited polyaniline in (c) and with polyaniline in (d). The samples in (d) were obtained by 6-cycles electropolymerization.

Fig. 3. Electrical characteristics in PBS 1X with the different electropolymerization cycles. (a) Transfer characteristics and (b) extracted transconductances without PANI and with different PANI-content. $V_{\text{drain-source}} = -0.4 \text{ V}$ in all the transfer curves.
the bare PEDOT:PSS granular structures can be seen also in the SEM and AFM images presented in Fig. S3.

3.2. Electrical characterization of the PEDOT:PSS-PANI transistors

The electrical resistance of the conducting polymer channel, equal to 252 ± 36 Ohms (n = 5) for single PEDOT:PSS layer, increased for the hybrid PANI-PEDOT:PSS layers to 595 ± 60 Ohms (n = 2) with 3 cycles PANI, 845 ± 243 Ohm (n = 4) with 6 cycles PANI, and 1590 ± 552 Ohms (n = 3) with 10 cycles PANI. By using the average dimensions of the layers, the approximate electrical resistivity of the different layers can be extracted. The resistivity of the layers changes from about 3.04 ± 0.4 mOhm.cm without PANI to 9.64 ± 0.9 mOhm.cm with 3 cycles PANI, 17.9 ± 5.1 mOhm.cm with 6 cycles PANI, and 73.6 ± 26 mOhm.cm with 10 cycles PANI. Hence, the hybrid layers show an up to 6X resistivity increase with the higher-PANI content, likely because the PANI layers, when not in acidic solutions, have a very low conductivity of less or equal to 1.10–10 S/cm (Wang et al., 2017).

The PEDOT:PSS-PANI transistors with the different number of polymerization cycles are tested electrically in PBS 1X (0.155 M NaCl), with their characteristics shown in Fig. 3. The transfer curves are acquired with a drain-source voltage at 0.4 V close to the linear regime.

As reported in Fig. 3a, the drain-source current decreases with the number of PANI cycles, particularly for 10-cycles PANI. This effect is possibly due to the increased resistance of the layers. Also, a contribution of this decrease in current may come from the more limited penetration of ions into the PEDOT:PSS layers with the porous PANI interface. This last phenomenon can explain the observed decrease of transconductance, as shown in Fig. 3b, defined as \(\Delta I_d/\Delta V_g\), and the fact that even with higher-PANI content (Fig. 3b and zoom in Fig. S4a) it is maintained a perfectly bell-shaped transconductance and optimal current modulation (Fig. S4b) typical of PEDOT:PSS-based OECTs.

3.3. Detection of pH variations

We report in Fig. 4 the effects of pH changes from 10 to 4 on the electrical characteristics of the organic transistors. Such a pH interval includes the pH variations observed in biofluids such as sweat and saliva. The transfer curves (V_{\text{drain-source}} = −0.4 V) show that the hybrid PANI-PEDOT:PSS transistors with the higher-PANI content, notably with 6 and 10 cycles polymerization (Fig. 4c and d), have very high voltage-shifts, particularly in the positive V_{\text{gate-source}} range. Within this potential range, the cations (H^+) are injected into the organic channel. On the other hand, for the bare-PEDOT:PSS devices (Fig. 4a) and the devices with a lower number of PANI-electropolymerization cycles (Fig. 4b), the curves in the positive V_{\text{gate-source}} region are very close to each other. This result shows that, at low PANI content, the lower sensitivity observed makes it very difficult to discriminate such pH changes.

For the transistors with the higher number of PANI deposition cycles (6 and 10), the calibration curves are extracted in terms of both the current shift by fixing the voltage in the positive region (at 0.4 V, Fig. 5a and b), and the voltage shift by fixing the current (correspondent to 0 V at pH 10, Fig. 5c and d). We found that the sensitivity in terms of voltage shifts is more reproducible than the current shifts. A standard deviation of about 20% was measured from the average sensitivity in terms of...
voltage shift, which is reasonable considering the variability of the printing fabrication process and the subsequent electropolymerization step. From the calibration curves, sensitivities of $102 \pm 22 \text{ mV/pH}$ ($n = 3$, Figs. 5a) and $16 \pm 13 \text{ μA/pH}$ ($n = 3$, Fig. 5c) for 6-cycles PANI-devices are calculated, exhibiting very good linearity ($R^2 \geq 0.98$ in all cases). Hence, 6 cycles of PANI electropolymerization provides a high and linear response within the pH range considered. On the other hand, a different trend was found for the 10-cycles PANI devices, with a higher response of $226 \pm 50 \text{ mV/pH}$ ($n = 3$, Figs. 5b) and $21 \pm 9 \text{ μA/pH}$ ($n = 3$, Fig. 5d) from neutral to low pH values, and the very low response of $23 \pm 5 \text{ mV/pH}$ and $5 \pm 1 \text{ μA/pH}$ from neutral to high pH values. Such a different behavior for acidic and basic variations with high-PANI content was previously reported in potentiometric analysis using PEDOT:PSS-PANI indicator electrodes (Vacca et al., 2015). Herein, the same behavior was observed for a transistor configuration, both in terms of voltage and current variations. The too-high PANI content causes a loss of linearity due to the strong reaction in acidic solutions. Finally, Fig. S5 shows the transfer curves with 6 and 10 polymerization cycles going from high to low pH (Figs. S5a and c) and back from low to high pH (Figs. S5b and d). Going back to pH 10 in Fig. S5b for 10-cycles PANI and Fig. S5d for 6-cycles PANI, the current decreases close to the initial values (in the positive gate region), proving that the reaction is reversible. For positive gate voltages, the curves are very stable with a low hysteretic effect. Considering the signal at a fixed voltage ($0.4 \text{ V}$), we can extract an average current variation between the back and forth pH measurements of less than 8% in the case of PANI-6 cycles and 20% in the case of PANI-10 cycles. The PANI-PEDOT:PSS devices with 6-cycle polymerization show better stability than the ones with higher PANI-content.

The flexible PANI-PEDOT:PSS devices with high-PANI content show a super-Nernstian sensitivity, so the signal is higher than the theoretical limit obtained from the Nernst equation and equal to 59.2 mV/pH. While it was previously shown in standard 2-electrode potentiometric configurations that PEDOT:PSS devices have sub-Nernstian responses equal to around 10 mV/pH, and PEDOT:PSS-PANI devices have a near-Nernstian behavior equal to around 58 mV/dec (Vacca et al., 2015), our work shows that with the OECTs we have a much higher chemical signal amplification. Compared to the standard potentiometric systems, OECTs can be significantly scaled-down in size and easily integrated into compact arrays onto flexible substrates for multi-parametric analysis. Considering the literature for pH-sensitive and flexible electrochemical transistors, Table S1 (Supplementary) compares their performances and main characteristics. It has been reported on OECTs with electro-polymerized PANI on a gold-gate electrode (20 cycles), having a sub-Nernstian sensitivity of 44 mV/pH (Scheiblin et al., 2017). Another sub-Nernstian response using OECTs with a PEDOT-pH dye gate electrode on a flexible PET substrate was presented, showing a sensitivity of 32 mV/pH (Mariani et al., 2018). An OECT with a super-Nernstian response of 73 mV/pH was shown employing an IrOx gate (Scheiblin et al., 2017). Also, an OECT with an $H^+$ ion-selective membrane on the PEDOT channel (Demuru et al., 2020) was tested in potentiostatic mode with a sensitivity of about 10 mA/pH. Hence, this work reports on OECTs exhibiting high transduction performances in terms of pH sensitivity for a pH range relevant for biofluids analysis. Finally, considering other devices in the literature, standard potentiometric sensors with a sensitivity up to around 188 mV/dec (Lee et al., 2018)
and with a pH-sensitive charge-coupled device exhibiting a sensitivity of 240 mV/pH (Nakata et al., 2018) were reported. Also, ion-sensitive OECTs with a sensitivity as high as 516 mV/dec (Ghittorelli et al., 2018) were shown. This can be attributed to changes in the Ag/AgCl or Ag pseudo-reference electrodes due to anions (Lee et al., 2018) or the amplification effects of the transistors or other transducers themselves (Ghittorelli et al., 2018) compared to standard potentiometric detection methods.

3.4. Analysis of the sensing mechanism

To bring further insights on the interfacial change with the bare PEDOT:PSS and the hybrid PANI-PEDOT:PSS layers, an electrochemical impedance spectroscopy (EIS) analysis was performed at different pH concentrations. The interface between the charged electrode and the liquid is represented by an electrical double layer (EDL). Since ions and dipole molecules at these interfaces can change the electric field, this separation of electric charges can be modeled with capacitors (Khademi and Barz, 2020). Schematics modeling the EDL as a single parallel plate capacitor following the simplified Helmholtz model are very used to qualitatively explain the sensing behavior of OECTs (Zhang et al., 2018).

From the EIS tests, the interfacial capacitances at low frequency were extracted. This was done using the inverse of the slope of the reactance versus the angular frequency, as presented in Fig. 6a and b where the typical behavior of the devices is reported. The capacitance values for the bare PEDOT:PSS layers were found to be 9.8 ± 0.3 μF at pH 10, 11 ± 0.6 μF at pH 7, and 13 ± 1 μF at pH 4 (n = 2 with all the solutions). On the other hand, the extracted capacitances for the PANI-PEDOT:PSS layers with 6-cycles polymerization were higher at 22 ± 9 μF at pH 10, 32 ± 8 μF at pH 7, and 50 ± 5 μF at pH 4 (n = 2 with all the solutions), hence finding a 28 μF increase from high to low pH compared to only a 3.2 μF change without the PANI layer (9X lower). This phenomenon is due to the fact that going to higher levels of H⁺ concentration, in particular with PANI on the channel, there is a rise of interfacial charge from the H⁺ doping that increases the capacitance (Oliveira et al., 2020). Also, the porosity of the PANI layer can contribute to the accumulation of ions at the interface, enhancing the capacitive coupling effect. This behavior of a higher increase of capacitance for the PANI-PEDOT:PSS, when increasing the acidiy, was observed systematically in our experiments. Considering these capacitance changes, a simplified analysis of the potential distribution between the gate-electrolyte and electrolyte-channel interfaces is proposed in Fig. 6c. When the capacitance at the electrolyte-channel interface increases, the voltage drop at the electrolyte-channel interface decreases (Macchia et al., 2018). Hence, there is a shift of the transfer curves towards higher gate voltages because the gate electrode is less effective in controlling the channel. As a result, the organic channel requires a higher gate voltage to obtain the same dedoping (Chem et al., 2012).

4. Conclusions

We have demonstrated for the first time hybrid PANI-PEDOT:PSS organic electrochemical transistors on a polymeric substrate that exhibit improved electrical performances and response to pH variations.
The hybrid devices were inkjet printed with a PEDOT:PSS channel integrating an electropolymerized PANI layer on top. 6-cycles of PANI electrodeposition was found to be optimal to achieve a linear sensing response from 10 to 4 pH with a sensitivity equal to 22 mV/pH (up to 2X the Nernst limit), extracted from the transfer characteristics of the transistors.

We have also shown that the change of interfacial capacitance when decreasing the pH is 9X higher with the hybrid PANI-PEDOT:PSS layer in comparison to using a single PEDOT-PSS layer, causing a change of potential distribution across the gate-electrolyte and electrolyte-channel interfaces. A complete understanding of the behavior of the hybrid PANI-PEDOT:PSS channel at different pH would require more accurate modeling, notably through the use of 2D drift-diffusion equations and ionic and electronic charge-distribution equations.

Thanks to the simple fabrication process and the high pH-sensing performances, the developed flexible OECS with hybrid organic channels are promising for being integrated into scalable, low-cost, multi-sensing platforms for wearable applications. To overcome the possible cations interference for real-sensing applications, the next step is to combine the pH sensor with ion-selective OECS into an array, considering differential measurements and investigating chemometric approaches for the discrimination of the different analytes.

**CRediT authorship contribution statement**

Silvia Demuru: Formal analysis, Writing – original draft, analyzed the data, designed, fabricated and tested the devices, wrote the manuscript. All the authors conceived of the idea and planned the experiments. Brinca Paul Kunnel: prepared the aniline solution and helped with the electro-polymerization experiments. All the authors conceived of the idea and planned the experiments. Danick Briand: edited it. All the authors conceived of the idea and planned the experiments. All authors discussed the results and contributed to the final manuscript.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bios.2021.100665.
Biosensors and Bioelectronics: X 7 (2021) 100065

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