Low-voltage, Dual-gate Organic Transistors with High-sensitivity and Stability towards Electrostatic Biosensing

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ABSTRACT: High levels of performance and stability have been demonstrated for conjugated polymer thin-film transistors in recent years making them promising materials for flexible electronic circuits and displays. For sensing applications, however, most research efforts have been focusing on electrochemical sensing devices. Here we demonstrate a highly stable bio-sensing platform using polymer transistors based on the dual-gate mechanism. In this architecture a sensing signal is transduced and amplified by the capacitive coupling between a low-k bottom-dielectric and a high-k ionic elastomer top-dielectric that is in contact with an analyte solution. The new design exhibits a high signal amplification, high stability under bias-stress in various aqueous environments and low signal drift. Our platform furthermore, while responding expectedly to charged analytes such as the protein BSA, is insensitive to changes of salt concentration of the analyte solution. These features make this platform a potentially suitable tool for a variety of biosensing applications.

Introduction

Semiconducting conjugated polymers offer a range of attractive features such as easy-processing, tunability, mechanical stretchability and biocompatibility making them attractive for applications such as on-skin wearable biosensors^{1,2}. Using these soft and conformable materials for real-time detection and monitoring of biomarkers or disease agents in biological liquids such as saliva, blood and even sweat has the potential to offer hitherto unmatched opportunities in personalized healthcare and monitoring³. For this reason, various sensing architectures have recently been suggested that play to the strength of polymer semiconductors (**Figure 1**). Among the most established architectures is the organic electrochemical transistor (OECT) where the unique nature of mixed electrical and ionic conduction of conjugated polymers is used to allow ions from an analyte solution to selectively dope and de-dope the bulk active material^{4,5}. Due to a large volumetric capacitance, these devices feature high transconductances and low-voltage operation, making them an ideal tool for detection of ions^{6,7}. However, for selective sensing of small molecules and biochemicals, despite promising results obtained on combining nonporous or

molecular imprinted membranes with OECTs⁸, it remains challenging to extend such approaches to complex biologically relevant fluids⁹.

An alternative architecture to OECTs are electrolyte-gated transistors (EGOFET), where ions do not penetrate the semiconductor, but instead devices are gated through an electrical double layer formed at the gate /electrolyte and electrolyte/semiconductor interfaces which then form the effective gate-insulator layer. Due to the high capacitance of these double layers as well as their sensitivity towards any disruption, EGOFETs are among the most sensitive architectures for the detection of analytes^{10,11}. For instance, Torsi and co-workers have used water-gated devices to show the label-free single-molecule detection on the zepto molar scale³. This dramatic result was obtained by functionalizing the reference or gate electrode, rather than the semiconductor interface, with a bioreceptor. However, a down side of EGOFETs and especially water-gated EGOFETs, is their sensitivity to other external factors, such as PH or salt concentration of the analyte solution, causing signal drift when operated in analyte solutions^{12,13}. To overcome this issue, several

groups have used EGOFTs with an extended, floating gate electrode^{14,15} which has shown good sensitivity towards detection of thiol or protein binding on the gate¹⁶.

Figure 1: Schematic illustration of the most common architectures used for biosensing a) Organic electrochemical transistor (OECT) operating by ions (blue/orange) penetrating and oxidizing the active semiconductor. Limited selectivity can be achieved through gate functionalisation and/or nanoimprint membranes that interact with analyte molecules (red) as shown in the illustration; b) electrolyte gated organic transistor (EGOFET) operating by forming an electrical double layer (EDL) at the analyte solution/ semiconductor and gate interfaces. Through functionalization, specific biomarkers can selectively attach and disrupt the EDL; c) organic field-effect transistor (OFET) with a functionalized gate-electrode. An analyte can selectively bind to the gate electrode which modulates the accumulated charge. An additional gate electrode can be included in the substrate to allow control of the operating point of the transistor; d) an OFET with an extended gate used for analyte binding. The extended gate can be positioned on the same substrate as its transistor or be separated and positioned as a “remote gate” on an external substrate (as shown). Separating the analyte solution from the active semiconductor can yield higher stability and hence, lower signal drift.

Sensors using conventional dielectrics instead of electrolytes have also been conceived¹⁷. In such conventional organic-field effect-transistors (OFETs), ions generally do not penetrate the active material and the transistors channel is separated from the active sensing area through a dielectric layer. This can have the advantage of avoiding microstructural changes in the active semiconductor from repetitive ionic doping and de-doping and hence, improve cyclability and lifetime. Recently, there has been a lot of progress in improving the performance, operating voltage, environmental and operational stability of polymer OFETs, which significantly enhance their effectiveness for sensing applications^{18,19,20,21,22}. Due to the electrolyte being separated from the active channel, OFET

sensors are only sensitive to the amount of charges accumulated at the semiconductor-dielectric interface. The influence of the accumulated charges on the OFET device characteristics depends entirely on the dielectric capacitance and the amount of charges induced at the gate electrode through e.g. the binding of an analyte. Generally, this makes OFET-based sensors less sensitive as compared to their electrolyte gated counterparts. For the selective detection of analytes, choosing an OFET architecture is nevertheless advantageous, since the mechanism for sensing related to the interface between a metal gate and an analyte solution is far less complex than in electrochemical devices. Furthermore, to enable selective sensing towards a specific analyte, well-known surface chemistry can be applied to functionalize an OFET gate electrode with appropriate receptors^{23,24,25}. In comparison, spatially separating the analyte binding sites and the OFET-based amplification through an extended gate architecture has been the method of choice to improve the overall sensor's lifetime²⁶. However, this architecture is less compact and for this configuration to work effectively, the capacitance of the extended gate needs to be carefully selected and parasitic capacitances can limit the detection limit.

A specific OFET architecture which has been proposed for biosensing applications is the dual-gate field-effect transistor. Dual-Gate sensors make use of an additional back gate yielding an increased slope in the sensor response. The device still operates according to conventional field-effect transistor mechanism (i.e. generally no ions are present in the semiconductor channel), and instead a surface charge on one gate electrode is amplified through capacitive coupling to a secondary gate that is used to set the operational point of the sensor^{27,28,29}. With this, two independent amplification mechanisms are acting in a dual-gate transistor. The first mechanism is an intrinsic current amplification achieved, when a large channel current increase results from a small gate potential through the field-effect. The second mechanism is a threshold voltage shift amplification, that is achieved because a change in charge density triggered e.g. by top surface chemistry (such as analyte binding) is measured as a change in the threshold voltage scaled to the lower capacitance bottom gate. Oxide and silicon MOSFET dual-gate sensors have previously been realized for Protein or pH sensing applications where high resolutions beyond the Nernstian sensitivity limit could be demonstrated^{30,31,32}. Also, for vapor sensing, dual gate architectures have been proposed²⁸. However, the thin top-gate dielectric thicknesses that are required for achieving high amplifications pose a challenge to the fabrication of these devices. The maximum obtainable amplification in such a device is known to be dominated by the capacitances of the two dielectrics according to:

$$\Delta V_{th} = -\frac{C_{Top}}{C_{Bottom}} \Delta \Phi_{Top} \quad (1)$$

It is therefore desirable to have a high top-gate

capacitance in order to achieve a maximum threshold voltage shift ΔV_{th} for a small change in surface potential $\Delta \Phi_{Top}$ triggered by e.g. a charged analyte clamping to a top electrode. Given that the capacitance per unit area (C_i) scales linearly with the dielectric constant ϵ_r , and inversely linearly with the dielectric thickness (d) according to $C_i = \epsilon_r \epsilon_0 / d$, the conundrum here represents achieving a high ratio between the top and bottom capacitances. While this is relatively easy to achieve by fabricating devices with a thick (and hence, low capacitance) bottom dielectric^{27,30}, in reality, for capacitances below a few nF/cm² this leads to impractical high voltages required for device operation. For any wearable device operation this is unfeasible. Alternatively, it is possible to increase the capacitance of the top dielectric which can be achieved through high-k dielectric materials with a few 10s of nm of thickness. Unfortunately, under these circumstances, leakage becomes an issue, especially if these devices are operated in analyte solutions for extended time. Here, we present a method to prepare such an architecture that overcomes this issue by using an ionic dielectric³³, yielding dual-gate biosensor OFETs with high stability in aqueous and buffer solutions, low-voltage operation as well as high signal amplification.

2. Blocked ionic top-dielectric for low-voltage transistors (BID-OFET)

We first want to focus on the ionic top dielectric stack used in our dual-gate transistor. This interface will later be exposed to an analyte solution and detect the charge from an analyte binding to the top-gate electrode. The resulting charge accumulation or depletion will hence, modulate the sensing-channel of our device. Since the typical clamp charge (Zeta Potential) induced by charged analytes are on the order of 10s of mV³⁴, the device requires both a high transconductance around 0V as well as low-voltage operation. We have discovered earlier, that thick dielectric layers of the polymeric elastomer dielectric ePVDF-HFP with a small amount of ionic impurity are ideal for this type of application because they exhibit high capacitances at low frequencies and yield devices with a subtle shift towards positive threshold voltages³⁵ (Supplementary Figure S1). Here, we first fabricated OFETs with a conventional bottom-contact top-gate architecture using the high-mobility polymer indacenodithiophene-co-benzothiadiazole (IDT-BT) and a thick ionic dielectric (1.2 μ m) in combination with a thin interlayer of Cytop (15 nm) (Figure 2a). We selected IDT-BT due to its excellent electrical properties, uniformity and intrinsic stretchability making it attractive for future on-skin applications³⁶. The Cytop interlayer was found necessary to shield dipoles and the ionic effect from the high-k ePVDF-HFP and has demonstrated an excellent surface passivation capability in the past^{20,37}. Therefore, in contrast to an organic electrochemical device such as an OEET, in our devices the ions are restricted to move within the dielectric so that the transistor is operated based on electrostatic without complications arising from ions penetrating into and

altering the active channel (Figure 2b). Our device is different from a typical electrolyte-gated transistor (EGOFET) where gating occurs through an electrolytic (analyte) solution, where ion can potentially enter the semiconducting layer. For this reason, we will use the term blocked ionic-dielectric OFETs (BID-OFETs) to describe our device architecture. It should also be noted, that even though bilayer devices with high-k dielectrics are well known^{38,20}, in this case, we intentionally use a dielectric layer with a small amount of ionic impurity so that we can obtain low-voltage operation with low leakage current by using dielectric thicknesses that are 10-20 times greater than those normally used (Supplementary Figure S1). This feature is essential as the thick dielectric layer encapsulates the device against the harsh operating environments needed for many sensing applications, such as in aqueous or buffer solutions. For the resulting dielectric stack with a thickness of 1.2 μ m (1.2 μ m ePVDF-HFP + 0.015 μ m Cytop) we measured a capacitance of 90 nF/cm² at low frequencies < 10 Hz (Figure 2c). This is lower than the 500 nF/cm² obtained for devices with only ePVDF-HFP (thickness 1.2 μ m). It should be noted that, for typical polymer dielectrics, such as polystyrene or polymethylmethacrylate, a thickness of 5 nm is needed to achieve such a high capacitance. Such a thin layer will easily have pin-holes and large leakage current. We also attempted to spin-cast ePVDF-HFP directly on top of the polymer semiconductor without the Cytop interlayer, however, observed significantly lower performances which we attribute to interfacial degradation. Due to the ion movement in the ePVDF-HFP dielectric, operational speeds of our devices are furthermore, relatively low (10 Hz). Fortunately, for sensing applications, we are only interested in the longer time scale binding events instead of short-time scale dynamics. The resulting speeds are therefore, sufficient for this purpose.

Figure 2: Performance of the proposed BID-OFET design a) Visualization of the top gate IDOFET with the ionic elastomer ePVDF-HFP containing a small amount of ionic impurity. A thin ion blocking layer prevents the diffusion of ions into the semiconductor; b) Comparison of the operation of the ionic-dielectric gated IDOFET in comparison to an OEET; c)

Measured capacitance of the dielectrics with and without the Cytop interlayer in comparison to SiO₂; d) Low-Voltage transfer characteristics ($V_{DS} = -1V$), e) output characteristics and f) extracted charge carrier mobility of an IDOFET with a channel length of 80μm and a channel width of 194400nm; g) Transfer characteristics before, during and after a 24h-voltage stress ($V_G = -2V$; $V_{DS} = -1V$).

To test the general device performance of the top channel of our BID-OFETs, we fabricated low-voltage transistors using the new dielectric stack. We found that the devices showed good transport characteristics, switching-on at slightly positive voltages of 0.4 V with threshold voltages at approximately 0 V (**Figure 2d**). Consequently, our device operates in the sub-threshold regime at approximately 0 V giving it a high amplification capability for small changes in the gate voltage which is desirable for future biosensing applications. The transistors furthermore, exhibit an on-off ratio of 10000 and can be fully switched-on at gate and source-drain voltages of -1 V. The highly linear and ideal output characteristics also suggest that the contact resistance is sufficiently low at the channel length used here (**Figure 2e**). With these features, we were able to obtain low-voltage OFETs with a mobility of 1 cm²/Vs, which is slightly lower than values reported for high-voltage devices previously reported for IDT-BT³⁹, which is nevertheless, a trend commonly seen for bilayer-dielectrics,⁴⁰ (**Figure 2f**).

What's surprising about our devices, however, is their exceptional stability under extended bias-stress conditions. We stressed these devices for 24 h in full saturation conditions ($V_{DS} = -1V$, $V_G = -2V$) and did not observe any degradation in their transport properties and shifts in the threshold voltages are indistinguishable (**Figure 2g**). Again, this feature is highly desirable for sensing applications, as any stress on the device due to charging of the interface will diminish the sensor's sensitivity and cause an undesirable drift of the signal. To the best of our knowledge, the achieved stress stability of our devices are among the best reported for organic FETs^{22,19}. We attribute this exceptional stability to the trap-free interface from Cytop as reported before²⁰ and the excellent encapsulating from the thick dielectric layer^{22,41}.

3. Dual-Gate operation

To fully test the suitability of our BID-OFET for sensing applications, we integrated the developed top-gated channel into a dual-gate sensing architecture (**Figure 3a**). In this configuration, a change in charge applied by the top-gate induces a threshold voltage shift in the bottom-channel according to equation (1). The bottom-gate can therefore be used to select an ideal operational point to maximize the linearity or sensitivity for different operational conditions. In our architecture, the bottom-channel is formed with a conventional Si/SiO₂ dielectric stack which is treated with a monolayer of hexamethyldisilazane (HMDS) to improve the charge transport interface and allow low-voltage

operation. To test operational conditions in harsh aqueous environments, we mounted a small well made with polydimethylsiloxane (PDMS) on top of our device and filled it with phosphonic buffer solution (PBS). We then used an Ag/AgCl reference electrode to charge the solution with an external potential Φ_{Top} . Since the device's active area is furthermore covered with a gold top-electrode, the resulting interfacial effects of the top potential are acting on that gold surface and in fact, not on the surface of the ePVDF fluoropolymer. For different potentials applied to the top solution, we subsequently measured the transfer characteristics of the Si/SiO₂ bottom-channel at low source-drain-biases ($V_{DS} = -1V$). Without any potential applied to the top-gate (Φ_{Top} grounded at 0V), our devices exhibited a positive turn-on and threshold voltages (**Figure 3b**). We attribute this positive threshold voltage to two factors: firstly, the polymer-HMDS interface, which has been shown before to result in positive threshold voltage shifts as compared to devices on SiO₂ without a self-assembled monolayer treatment⁴²; secondly, our ePVDF-HFP top-channel is not completely depleted at gate voltages of 0V (see Figure 2) which is also the reason for the rather gradual and sluggish device turn-on. Therefore, in this configuration some residual charge flows through the top interface very much akin to the formation of a back-channel in a conventional field-effect transistor (FET) on an insulating substrate (**Figure 3c**). Once a potential of +0.5 V is applied to the top-gate through the reference solution we observed a significant shift in the transfer characteristics (Figure 3b). The turn-on is now well defined and shifts towards negative voltages. In this configuration, the top-channel is completely depleted and therefore, the transfer characteristics are entirely defined by charges flowing through the bottom channel (i.e. the polymer-HMDS/SiO₂ interface) which significantly reduces the overall current the transistor can deliver. When the top potential is switched to $\Phi_{Top} = -0.5 V$, the transfer curve moves significantly towards positive threshold voltages and is now entirely defined by the accumulated charge at the top-gate interface (Figure 3c). Due to the strong mismatch of the capacitances of the two dielectrics, we also cannot discern a device turn-on in the chosen measurement range anymore; the fully accumulated top-channel now dominates the shape of the transfer characteristics. Since in this configuration the sensing channel is operating in the sub-threshold regime, we are able to modulate the current over 5 orders of magnitude for small voltage shifts of only approximately 800mV applied to the top-interface (Supplementary Figure S2a). As predicted by the capacitive coupling C_{top}/C_{bottom} , for every volt applied to the top reference solution, we observe an average threshold voltage shift of approximately 9 Volt in the bottom-channel with better amplifications obtained at negative top-gate voltages (Supplementary Figure S2). To the best of our knowledge, this is the highest amplification ever reported for a dual-gate OFET operated in an aqueous solution or at low-voltages. We should also note, that due to the high thickness of the ionic-dielectric, paired with its low ionic

conductivity, the overall leakage current is extremely low at both the bottom-gate and the top-gate even when operated in a PBS buffer solution. Therefore, this architecture is extremely robust for applications in aqueous environments (Supplementary Figure S3).

Figure 3: Architecture and operation of a dual-gate transistor with ionic top-dielectric. a) Visualization of the dual-gate architecture with the top-potential applied through a PBS buffer solution confined in a PDMS well; b) transfer characteristics of the bottom-channel (i.e. Si/SiO₂ bottom gate) for Voltages of $\Phi_{top} = 0.5, 0$ and -0.5 V; c) Visualization of the state and position of the accumulation layer (at $V_G = -2$ V) for each Φ_{top} . While the charge accumulated at the bottom-interface remains the same in each case, the accumulation layer at the top-interface is modulated significantly; d) extended stability test of the dual-gate transistor's response to a potential applied at the top-interface. Plotted is the bottom-channel read-out at $V_{BG} = -2$ V. After 380 minutes the current returns to its initial value; e) resolution limit of the dual-gate architecture (derived from the signal standard deviation over 20 minutes) approaching the sub-mV range.

Motivated by these results, we evaluated the long-term stability of our architecture to estimate the overall drift and signal resolution that can be expected when for instance, monitoring a charged analyte over an extended time frame. We scanned the top-gate from $\Phi_{Top} = 0.5$ V to $\Phi_{Top} = -0.5$ V in steps of 0.1 V (as well as smaller step sizes between -0.1 and 0.1 V) with each voltage being applied for 20 minutes (**Figure 3d**). It is worth noting that the signal drift is very small over this extended time period. For each 20-minute period, the signal is essentially constant and only when Φ_{Top} is changed, the signal responds in a unit-step-like manner. This enables us to reliably resolve voltages as small as 10 mV representing the limit of our semiconductor parameter analyser (SPA). Due to the high stability and low signal drift, the real resolution limit of our dual-gate architecture therefore can even approach the sub-mV range, especially when the bottom channel is operated at positive biases (**Figure 3e** and Supplementary Figure S2). To receive an upper bound on the overall signal drift, we computed the mean and standard deviation of the signal for each 20-minute time interval. For all voltages we found standard deviations that are in the range between 1 and 0.1 % of the signal value, and especially for negative potentials

applied at the top-gate indiscernible in comparison to the overall signal (Supplementary Figure S4). The excellent operational stability enabled by the Cytosol/ePVDf-HFP top-channel as well as the high signal amplification made possible by the ability of the sensing channel to operate reliably in the sub-threshold regime, render the given dual-gate architecture an excellent tool for biosensing applications.

4. Invariance to conductivity and choice of analyte solution

A key motivation of using dual-gate architectures for biosensing, is their ability to separate an analyte solution from the active semiconductor. This represents a possible route to realize biosensors that are less susceptible against unwanted fluctuation in pH-caused doping or de-doping or ion conductivity and hence, more selective towards the charges or capacitance changes induced by a given small molecular analyte or protein. To detect these biomarkers, such as for on-skin sweat sensing, it is essential to design planar device architectures that can be seamlessly integrated into sensor patches. For this reason, we slightly altered our design and integrated a thin platinum reference electrode which we placed next to the dual-gate's top-gate electrode (**Figure 4a**). In this configuration the platinum reference electrode is used to either ground the solution or alternatively apply a small voltage to characterize the sensor response. Next, we evaluated the robustness of our architecture against changes in composition of the analyte solution. We placed droplets of DI water, PBS solutions as well as various levels of diluted PBS solution onto both the top-gate electrode as well as the reference electrode (**Figure 4a**). For each analyte solution we measured the bottom-gate's transfer characteristics for the case of the grounded analyte solution as well as applied potentials of -0.5 and 0.5 V. We found that in each case, the transfer characteristics are identical and not affected by the conductivity of the analyte solution (**Figure 4b**). These tests confirm that our sensing architecture only responds to charges that are directly induced at the top-gate electrode such as e.g. a clamped charge of a charged analyte. For biosensing applications, the specific sensing mechanism will however, play a vital role in determine the sensitivity towards additional external factors such as a change in the ionic strength of the analyte solution which will change the Debye length and consequently, the induced charge. Although such a change in Debye length is not expected to impact the high device stability, it has been shown to represent a major challenge to the sensitive detection of biomarkers by other field-effect biosensor designs⁴³. This issue can be overcome by interface optimization and functionalization. One example is tuning the sensor's response to be fully capacitive by achieving the formation of Donnan's equilibria which would make the response insensitive to the Debye's length value⁴³. Nevertheless, all this can be achieved by optimized interfacial engineering and hence, underlines the usefulness of the developed

architecture to test various surface chemistry treatments for the targeted sensing of specific biomarkers.

Figure 4: Invariance of the sensor's response to conductivity of analyte solution a) Sketch and image of the proposed dual-gate biosensing architecture. A droplet is placed directly onto the device and a platinum electrode is used to ground the solution; b) Bottom-gate transfer characteristics for potentials of -0.5, 0 (ground) and 0.5 V applied through the platinum electrode. The characteristics do not change when altering the choice of analyte solution.

5. Sensing of non-specifically absorbed bovine serum albumin (BSA)

Figure 5: Sensing of Bovine serum albumin (BSA) a) Sketch of the electrode configuration used to study the binding kinetics of BSA in PBS buffer solution using impedance spectroscopy (top) and the proposed dual-gate biosensing architecture (bottom); b) as well as the signal phase as a function of frequency for BSA concentrations between 15nM and 15μM using impedance spectroscopy; Bottom-Gate transfer characteristics of a dual-gate sensor exposed to BSA in DI water at concentrations between 15nM and 15μM; c) response plotted on a logarithmic scale; d) response plotted on a linear scale. A simplified crystal structure of the protein BSA made up from the Genistein amino acid derivatives 4a–4d is shown in the inset.

To demonstrate the utility of our dual-gate architecture for potential biosensing, we tested the sensing of non-specific absorption of bovine serum albumin (BSA) protein onto the top-gate surface in the nM to μM range. BSA was chosen as it readily non-specifically binds to gold surfaces and hence, offers a simple way of assessing the architecture's response in a biosensing configuration without the need to

modify the top-gate surface with a receptor. BSA is often detected through capacitance changes but is also negatively charged and hence, represents a good proof-of-concept model protein to test our architecture. Before determining the response of our dual-gate sensor however, we used LCR spectroscopy to evaluate the overall binding kinetics of BSA. For these tests, we used a simple 2-electrode design which was immersed in a PDMS flow cell and connected to an LCR- impedance analyser (**Figure 5a**). We subsequently tested several concentrations of BSA in PBS buffer solution and evaluated the signal phase. We found that the overall response is non-faradaic as evident by the incomplete semi-circles and absence of charge transfer resistance in the Nyquist plot (Supplementary Figure S5). As expected, the signal shows a resistive response for high-frequencies, however, at lower frequencies the signal phase ranges between 65° and 80° and is therefore, mostly capacitive (**Figure 5b**). At low frequencies we can therefore, attribute the change in impedance to capacitive binding at the electrodes. Evaluating the response at a frequency of 100 Hz we can furthermore, estimate an upper bound (given by saturation of the planar electrodes) and lower bound (due to signal/noise) on the sensitivity; as an approximation, we found that a response can be expected for concentrations ranging between 15 nM and 15 μM. We then exposed our dual-gate biosensor to the identical concentrations of BSA. We used the same sensing configuration as shown in Figure 4a however, operated the reference in a floating configuration. Instead of a simple droplet of the analyte solution, we also used a PDMS-well to confine the droplet size and volume making the sensor more reliable. To further demonstrate the sensor's invariance to the analyte liquid, we replaced PBS with DI-water as an analyte solution. For the BSA concentrations determined earlier, we find that the sensor showed a good response with the on-current increasing for increasing BSA concentrations (**Figure 5c, d**). The FET response also sheds some additional light on the underlying sensing mechanism that is acting when BSA is adsorbing onto the top gate of our devices. Although the complex impedance experiment shows that BSA adsorption yields a capacitance change, the Nyquist plot indicates an increasing capacitive impedance with increased BSA concentration. Since the FET current is however, increasing with increased BSA concentration (and at pH=7 the protein is negatively charged), we conclude that here, the domination sensing mechanism is an interfacial potential (field effect). This could mean that the two mechanisms (i.e. field-effect and capacitance change) cancel each other to some degree. Therefore, we expect that there is potential to make this dual-gate platform more sensitive towards biomarker detection by further interface optimization. Despite the different sensing mechanisms that are most likely at play, we were, however, surprised by the similar resolution which can be obtained between the LCR-meter and our biosensing architecture (also given the different analyte solutions). For both, the highest sensitivity (i.e. current increases or shift in phase) is observed for concentration

between 15 nM and 1.5 μM whereas the signal saturates for concentrations higher than 1.5 μM and becomes small for concentrations below 15 nM. Given the complex electronics of the LCR including an auto-balancing bridge used for signal amplification, our biosensing architecture offers a greater signal amplification than what can be achieved using a sophisticated and expensive precision LCR meter (Supplementary Figure S6). Since our architecture is agnostic to the real-part of the impedance signal, we can reliably detect and quantify analyte binding without the need for an expensive wave-function generator or frequency dependent measurement setup. We should also note, that for more sophisticated sensing applications, we can tune the operational voltage and choose a voltage range in which the signal offers a maximum in linearity (Supplementary Figure S7).

Figure 6: Reversible sensing of Bovine serum albumin (BSA). Response of a dual-gate biosensor to repetitive exposure to 15 μM of BSA after being washed with a detergent.

In addition, we tested the sensor's ability to repeatedly detect a given BSA concentration. For these tests, we exposed a device to 15 μM of BSA and subsequently washed the surface using a detergent (**Figure 6**). After re-exposing the same device to 15 μM of BSA, the response returns precisely to its original value. Although this simple wash was not able to remove all BSA from the surface and thus, fully reset it to its pristine value (this would have corresponded to an I_D/I_{D0} of 0.55), the detection of high BSA concentrations is nevertheless, fully reversible. This demonstrates that our sensor is capable of reliably detecting a given protein concentration repetitively and gives a reproducible current output. The above dual-gate structure is therefore an excellent architecture to detect charged analytes with minimal drift. We want to point out that BSA detection only serves as a proof of principle to demonstrate the dual-gate's capability to reliably measure analyte binding. With proper attachment of receptors on the surface of the top gate, one can expect sensing of specific targets as well as tuning of the sensor's response to be fully capacitive. Such sensors can be potentially explored for on-skin capacitive sensing of analytes. With the excellent

stability of the dual-gate device structure, a variety of surface chemistry may be integrated on the top-gate electrode. Furthermore, our current architecture may be improved by optimizing the ionic concentration of the ePVDf-HFP layer. By increasing the speed of the sensor, it may open up possibilities for applications beyond biosensing such as electrocardiogram (ECG) measurements, where the signals are typically in the mV range.

6. Conclusion

We present an electrically stable dual-gate transistor structure and show its ability for sensing changed proteins binding to the top gate surface. By using a thick high capacitance ionic-dielectric combined with a low-k ion blocking layer, the resulting dual-gate transistor device can operate with the high stability in the sub-threshold regime. This allowed the dual-gate transistor to achieve sub-mV resolution as a result of the exceptionally low bias stress and drift. As a demonstration of concept, we show reliable and reversible detection of the non-specific absorption of the protein bovine serum albumin (BSA) with the same level of accuracy as a precision LCR-meter. The dual-gate transistor top gate can be potentially modified using various surface chemistries to impart selective sensing. This platform therefore serves as an excellent tool to combine advancements in receptor discoveries with the electronic long-term monitoring of an analyte concentration. It therefore has the potential for developing low-cost on-skin sensors for detection of charged biomarkers for wearable health monitoring.

ASSOCIATED CONTENT

Supporting Information. General experimental methods and additional device and sensing characteristics.

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Author Contributions

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OECT

EGOFET

OFET

Extended gate OFET

a)

b)

c)

d)

a)

OEFT

b)

EGOFET

λ = Gate functionalization

● = Cation

● = Anion

● = Analyte

c)

OFET

d)

Extended gate OFET