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# pH and ion sensitivity of a field-effect EIS (electrolyte-insulator-semiconductor) sensor covered with polyelectrolyte multilayers

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**Abstract** Field-effect capacitive EIS (electrolyte-insulator-semiconductor) sensors have been utilised for a label-free electrical monitoring of the layer-by-layer adsorption of polyelectrolyte multilayers (PEM). Anionic poly(sodium 4-styrene sulfonate) and cationic poly(allylamine hydrochloride) have been used as model system. The effect of the number of PEMs and polarity of the terminating layer on the sensor signal have been investigated. In addition, pH and ion sensitivity of EIS sensors covered with PEM have been studied by constant-capacitance method. Alternating potential shifts, having a tendency to decrease with increasing the number of PE layers, have been observed after the adsorption of each polycation and polyanion layer. The possible mechanisms for the sensor response are discussed.

**Keywords** Capacitive EIS sensor · Field effect · Polyelectrolyte · Charged macromolecules · pH

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## Introduction

Layer-by-layer (LbL) sequential deposition of oppositely charged polyelectrolytes (PE) from solutions provides an efficient method of preparing ultrathin films of a desired architecture, functionality and with a nanoscale control of the thickness [1–7]. Polyelectrolytes are linear macromolecule chains bearing a large number of charged or chargeable groups when dissolved in a suitable polar solvent, generally water. Providing that each adsorption step of charged macromolecules leads to a charge inversion of the surface (charge overcompensation effect), the subsequent deposition finally results in a polyelectrolyte multilayer (PEM), stabilised by strong electrostatic forces. The LbL technique is very attractive due to its simplicity, with practically no limitations on the size and shape of the substrate, its versatility as well as low-cost and environment-friendly technology. The potential applications of the LbL technique and PEMs range from surface modification, preparation of functional and stimuli-responsive materials, coated colloids, hollow capsules and containers, drug release systems up to biosensors, actuators and organic electronic devices [1–9].

For the practical realisation of these devices, it is important to understand the internal structure and formation process of PEMs as well as the influence of fabrication parameters on the film characteristics. Adsorption and formation of PEMs on solid substrates is determined by a number of factors, like the nature and charge of the surface, the charge density and concentration of the polyelectrolyte, the salt concentration and non-electrostatic interactions of the macromolecules with the surface and with each other [1–7]. Despite extensive experimental and theoretical studies of polymer adsorption at the solid–liquid interface including the surface coverage, the water or ion content and

the swelling behaviour of different PEM systems, a detailed picture of the internal electrostatic properties, ion (including proton) distribution and interfacial behaviour of PEMs is far from being complete.

Among the variety of proposed concepts studying molecular interactions at the solid/liquid interface, a semiconductor field-effect device (FED) platform is one of the most attractive approaches providing a label-free detection of adsorption and binding of charged macromolecules with a direct electronic readout (see, e.g. [10–15] and references therein). Recently performed experiments on the detection of PEMs using a field-effect transistor [16, 17], a capacitive EIS (electrolyte-insulator-semiconductor) sensor [17–20] and a silicon thin-film resistor [21–23] as transducer, have demonstrated that FEDs (in combination with the LbL self-assembly technique) could be a powerful tool not only for a real-time direct electrical monitoring of molecular interactions at the solid/liquid interface but also for fundamental investigations of the electrical characteristics, internal electrostatic properties and interfacial behaviour of PEMs.

In the present work, the pH and ion (ionic strength) sensitivity of field-effect capacitive EIS structures covered with PEMs have been investigated. The influence of the pH value and ionic strength of the electrolyte solution on the internal electrostatic charge redistribution and interfacial behaviour of the post-deposited PEMs as well as possible mechanisms of signal generation in FEDs during the adsorption of PEMs have been discussed. Anionic poly(sodium 4-styrene sulfonate) (PSS) and cationic poly(allyl-amine hydrochloride) (PAH) have been chosen as a model system because most of the fundamental work in the field of study of adsorption and formation of PEMs at the solid/liquid interface has been carried out with these polyelectrolytes (see, e.g. [3–7]).

## Experimental

### Preparation and modification of the EIS sensors with PEMs

For the experiments, Si–SiO$_2$ (p-Si, $\rho$=5–10 $\Omega$cm; 30 nm SiO$_2$) structures with chip sizes of $10 \times 10$ mm$^2$ have been fabricated. As contact layer, a 300-nm Al film was deposited on the rear side of the p-type wafer.

The EIS sensors were covered with PEMs composed of a PAH/PSS system using the LbL assembly technique by a consecutive adsorption of PAH and PSS from the diluted PE solution (see Fig. 1a). It is assumed that the charge of the outer layer overcompensates the charge of the underlying layer and thus enables the adsorption of the next layer, finally resulting in a PEM stabilised by strong electrostatic forces. The PSS and PAH polyelectrolytes in powder form with an average molecular weight ($M_w$) of about 70,000
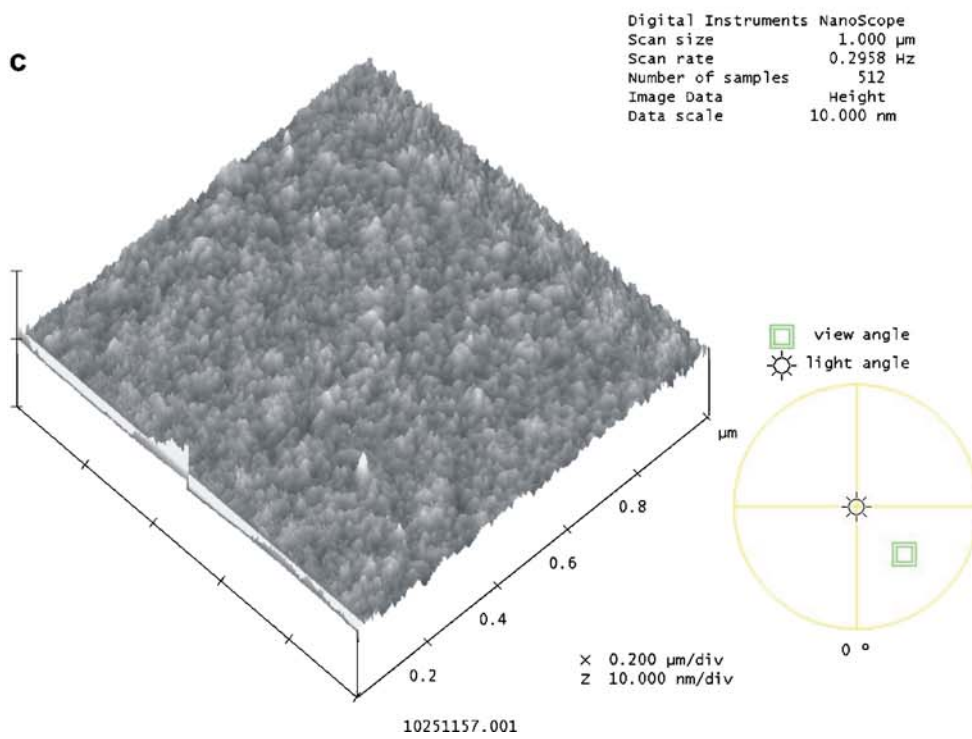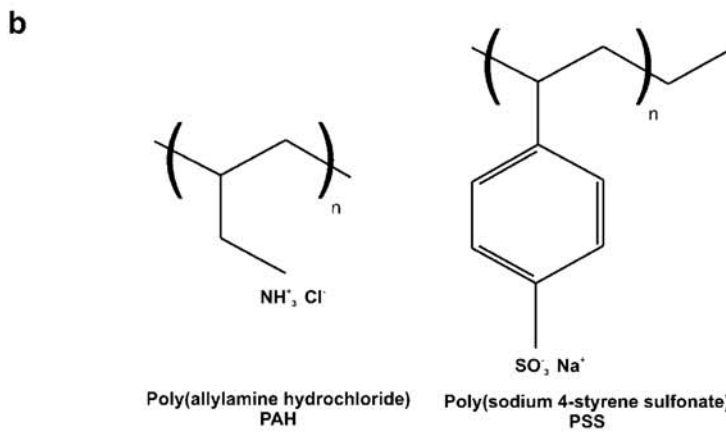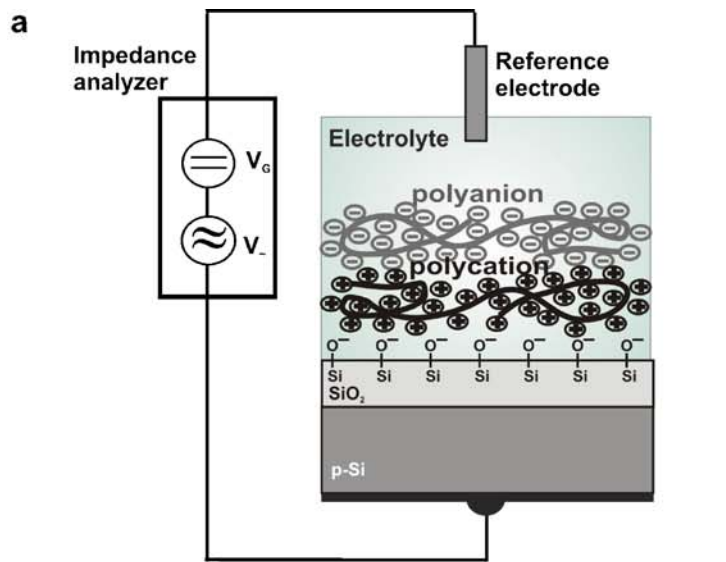
Fig. 1 Capacitive field-effect EIS structure covered with polyelectrolyte multilayers (**a**) and chemical structure of PAH and PSS (**b**) schematically; the liquid-cell AFM image corresponds to an EIS structure covered with two PE layers (**c**). Scan size is $1 \times 1$ μm. The z-axis displaying the height was scaled to 10 nm

were obtained from Sigma-Aldrich. The chemical structure of PAH and PSS is schematically shown in Fig. 1b. The PSS is a strong polyelectrolyte that totally dissociates in aqueous solutions and therefore is fully negatively charged in a wide pH range as it liberates Na$^+$ ions [24]. The PAH is a weak polyelectrolyte, and the degree of charging of its amine group depends on the pH of the aqueous solution. It is approximately fully charged at neutral and acidic solution and is neutral at a pH value above 10 [24]. Usually, the dissolution of PAH and PSS changes the pH value of the electrolyte solution (e.g. due to the partially deprotonation of the amine groups of PAH, leading to a decrease of pH). Therefore, the pH of both PAH and PSS solutions was adjusted to the same value of pH 5.4 by titrating with NaOH and HCl. Before PEM adsorption, the surface of the SiO$_2$ layer was cleaned and activated in 2% Hellmanex (Helma) aqueous solution for 10 min to increase the number of surface active groups. As in PE solution of pH 5.4 the surface of SiO$_2$ is negatively charged, we started the formation of the PEMs onto EIS sensors with positively charged PAH.

During the experiments, EIS sensors were consecutively exposed to the respective PE solution (50 μM PSS or PAH, 0.1 M NaCl, pH 5.4) for a time necessary for the adsorption of a single monolayer (usually 3–15 min), followed by rinsing in buffer solution (0.1 M NaCl, pH 5.4). These procedures were repeated until the desired number of layers was obtained (in this study, the maximum number of PE layers was 19). The thickness of the PE layer measured by imaging ellipsometry (EP$^3$, Nanofilm, Germany) was approximately 2 nm per layer, which is in good accordance with the results reported in [18, 25]. The liquid-cell atomic force microscopy characterisation of the prepared polyelectrolyte mono- and multilayers using a Digital Instrument AFM (Veeco Instruments, USA) showed that the surface roughness ($R_{ms}$) is increased with the number of adsorbed PE layers (e.g. from $R_{ms}$=2.4 nm for the second PSS2 layer up to $R_{ms}$=6 nm after the adsorption of the 11th PAH11 layer). Figure 1c exemplarily depicts a liquid-cell AFM image of an EIS structure functionalised with two PE layers.

### Measurement setup

EIS sensors covered with mono- and multilayers of positively charged PAH and negatively charged PSS have been characterised by means of constant-capacitance (ConCap) method using an impedance analyzer (Zahner Elektrik). The experimental setup used is schematically shown in Fig. 1a. For the measurements, the EIS sensor was mounted into a

Digital Instruments NanoScope
Scan size          1.000 µm
Scan rate          0.2958 Hz
Number of samples      512
Image Data          Height
Data scale        10.000 nm

10251157.001

homemade measuring cell, sealed by an O-ring and contacted on its front side by the electrolyte and a reference electrode and on its rear side by a gold-plated pin. The contact area of the EIS sensor with the solution is determined by the diameter of the O-ring and was about 0.5 cm$^2$. A conventional Ag/AgCl electrode (Metrohm, 3 M KCl) was used as a reference electrode. To achieve a preferably reproducible adsorption (and thus a reproducible sensor signal), as well as to prevent the possible effect of ion concentration and electrolyte conductivity changes due to the PE dissociation on the impedance of the whole measuring system, the pH value and conductivity of PE solutions have been controlled before and after PE adsorption with a Mettler-Toledo MPC 227 pH/conductivity meter. The measurements have been performed in a dark Faraday cage at room temperature.

For operating the EIS sensor, a dc polarisation voltage is applied via the reference electrode to set the working point of the EIS sensor in the depletion range of the capacitance–voltage curve, and a small superimposed ac (alternating current) voltage with an amplitude of 20 mV is applied to measure the capacitance of the sensor. In the ConCap mode, the capacitance of the EIS sensor is kept constant using a feedback-control circuit that allows a direct dynamic recording of potential changes caused from the adsorption of charged macromolecules as well as a continuous monitoring of the multilayer buildup [17]. For comparison, the ConCap curves of the bare EIS structures were also recorded.

The pH and ion (or salt) sensitivity of the PEM-modified EIS structures with PAH or PSS as terminating layer have been investigated in 0.1 M NaCl solutions with different pH values of 4.6, 5.6 and 7.3 and in NaCl solutions of different concentration of 1–100 mM (pH 5.6), respectively. For comparison, the pH- and ion-sensitive behaviour of bare SiO$_2$ layers has been investigated too. The EIS sensors with a SiO$_2$ layer as gate insulator show a pH sensitivity of about 39–42 mV/pH in the range from pH 4 to pH 9, which is comparable with pH sensitivity values reported in literature for a SiO$_2$ layer (typically 25–48 mV/pH) used in EIS or ISFET sensors [11, 17, 18, 26]. The ion sensitivity of SiO$_2$ layers in acidic solution (pH 5.6) was about 3–5 mV/pNa, which is comparable to values reported in [27].
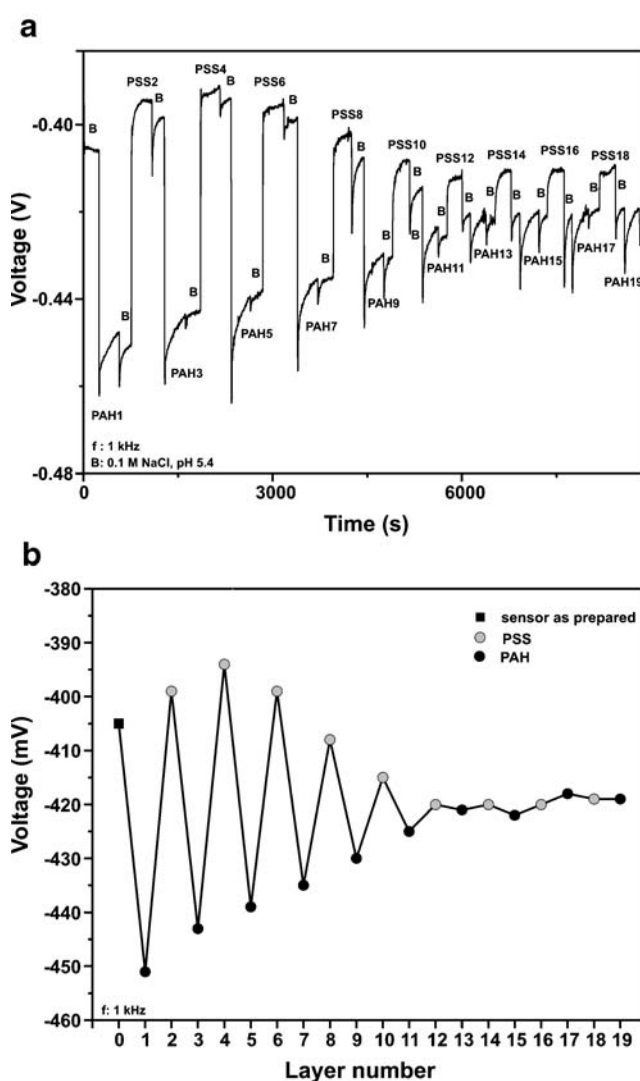
## Results

### ConCap monitoring of PEM buildup

Figure 2a shows the ConCap response of the EIS sensor before and after adsorption of each PAH and PSS layer measured at a frequency of 1 kHz. The bare EIS sensor was first equilibrated in buffer solution. As soon as a stable

sensor signal was obtained, the PAH solution was applied to the sensor, and the sensor signal was recorded for about 5 min followed by rinsing the measuring cell and the sensor surface with buffer solution and measurement in buffer solution for about 3 min. In the next step, the PSS solution has been applied to the sensor surface, and the ConCap response was recorded for about 5 min again. These procedures were repeated until the desired number of layers were adsorbed. Thus, the sensor signal was monitored continuously during the whole PEM deposition.

As it can be seen from Fig. 2a, the adsorption of each PE layer leads to alternating shifts of the sensor signal. The potential jumps observed after each rinsing step could probably be due to the removal of loosely attached PE macromolecules as well as washing the small ions out the





Fig. 2 Monitoring of polyelectrolyte adsorption: ConCap response of the EIS sensor before and after adsorption of each PAH and PSS layer measured at a frequency of 1 kHz (**a**) and potential changes in the depletion region as a function of the PE layer number (**b**). The maximum number of adsorbed PE layers was 19

multilayer, resulting in a change of an ion concentration and ion profile in the PEM. Incidentally, the direction of these shifts depends on the sign of the charge of the outermost (terminating) PE layer, resulting in a kind of zigzag curve of the signal changes as a function of the PEM number (Fig. 2b). The adsorption of PAH shifts the sensor signal towards the direction as for an additional positive charging of the $SiO_2$ surface (corresponding to a more negative sensor signal in Fig. 1 due to the feedback control in the ConCap mode) that will increase the surface potential. Consequently, the direction of the potential change after adsorption of negatively charged PSS corresponds to the case as if the $SiO_2$ surface would have been additionally negatively charged. This indicates that the molecular layer may also induce an interfacial potential change resulting in a change in the flat-band voltage of the EIS structure. Moreover, as can be seen from Fig. 2b, for up to six to seven adsorbed layers, we have not observed any distinct decrease of the potential (signal) shifts with the number of layer deposited that is in agreement with previous results [17–19].

However, for a further increase of the PEM layer number, the potential shifts have a tendency to decrease with increasing the number of PE layers. For example, potential jumps decrease from originally 40–50 mV for an EIS structure with five to seven PE layers to about 10–15 mV and several millivolts for an EIS structure with 9–11 and 13–16 PE layers, respectively. A similar effect has been observed in PE-modified field-effect thin-film resistors already after the first adsorbed PE layers [21–23]. This is in contrast to electrokinetic studies such as zeta potential measurements where the potential steps remain constant over a large range of deposited layers [28]. In zeta potential measurements, the potential at the PE/electrolyte interface is measured, whereas the FEDs determine the potential changes at the PE/gate insulator interface, which strongly depend not only on the amount of surface (interface) charges of the terminating layer but also on the charge distribution and screening effects within the PEM. According to the capacitive model proposed in [21–23], the screening of PE charges by mobile ions within the PE film leads to a decrease of the signal of the FED with the number of layers deposited. Another possible mechanism responsible for the effects described above could be the ion concentration redistribution within PEM induced by the charge of the outermost layer [17–20, 29].

## pH and ion sensitivity of EIS structures covered with PEMs

Figure 3 demonstrates a typical ConCap response of EIS structures with a post-deposited PEM [with 14th PSS14 (a) and a 15th PAH15 (b) layer as outermost layer]. The measurements have been performed at a frequency of 1 kHz

in 0.1 M NaCl solutions with different pH values between 4.6 and 7.3. The PE-modified EIS sensors show a clear dependence on the pH value of the solution. The average pH sensitivity of the sensor with the PSS14 and PAH15 layer as terminating layer was about 18 mV/pH and 21 mV/pH, respectively. A slightly higher pH sensitivity of about 20 and 25 mV/pH was observed for an EIS structure with the PSS8 and PAH11 terminating layer, respectively. Thus, the pH sensitivity slightly depends on the sign of charge of the terminating layer (the difference between the pH sensitivity of the sensor with PAH and PSS as terminating layer was about 3–5 mV/pH) as well as on the number of adsorbed PE layers. These experiments confirm the high permeability of the PAH/PSS system for protons that is in
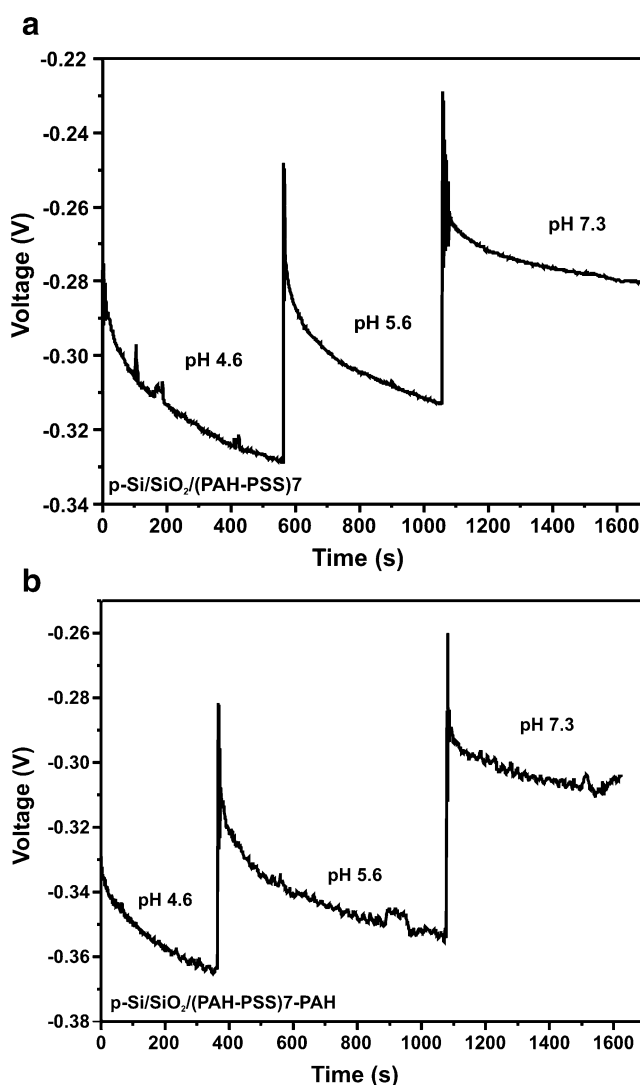


Fig. 3 pH sensitivity of post-deposited PEMs: ConCap response of EIS structure with the 14th PSS14 (a) and 15th PAH15 (b) layer as outermost layer. The measurements have been performed at a frequency of 1 kHz in 0.1 M NaCl solution with different pH values from 4.6 to 7.3

good agreement with results for a PDADMAC (poly (diallyldimethylammoniumchlorid))/PSS system [30]. On the other hand, the observed values of pH sensitivity are almost 1.5–2 times smaller than those of bare unmodified $SiO_2$ layers. The possible reason for such behaviour could be the partial screening of surface active groups of the $SiO_2$ by the first adsorbed layers of PAH. This is inconsistent with results reported in [30] where it was found that the pH sensitivity of the silicon thin-film resistor is not changed considerably by the adsorption of charged polymers.

Figure 4 shows the ConCap response of EIS structures with the fourth PSS4 (a) and an eighth PSS8 (b) layer as outermost layer measured in NaCl solutions with different ion concentrations. To avoid a possible effect of electrolyte conductivity changes on the sensor response, the measurements have been performed at a low frequency of 100 Hz. In the case of PSS as a terminating layer, with increasing the NaCl concentration, the sensor signal is changed towards the direction as for an additional positive charging



**a**

**b**

**Fig. 4** ConCap response of EIS structures with post-deposited PEMs with the fourth PSS4 (**a**) and eighth PSS8 (**b**) layer as outermost layer measured in NaCl solutions with different concentration

of the EIS sensor surface (corresponding to a more negative sensor signal in Fig. 4 due to the feedback control in the ConCap mode). These observations are in good agreement with similar measurements performed on bare Si–$SiO_2$ structures. The average ion sensitivity was about 20 and 12 mV/pNa for the EIS sensors with PSS4 and PSS8 as terminating layer, respectively. Thus, a decrease in ion sensitivity with increasing number of adsorbed polyelectrolyte layers has been observed. On the other hand, the obtained sensitivity values are much higher than those of bare $SiO_2$ layers (3–5 mV/pNa). Therefore, the ion sensitivity of the functionalised EIS sensor cannot be addressed to—or at least only to—the $SiO_2$ layer. In general, for all field-effect devices modified with charged macromolecules, the sensor signal strongly depends on screening effects in the electrolyte solution and on the charge distribution within the molecular layer. The performed experiments actually do not allow to completely understand the ion(salt)-sensitive behaviour of the PEM-modified EIS sensors as well as the basic mechanism of signal generation. One possible source of signal generation might be associated with the reduced electrostatic screening by mobile charges inside the PEM compared to the bulk medium outside [23].

## Discussion

From the experiments performed in this work as well as recently reported in [16–23], it is obvious that the consecutive adsorption of oppositely charged PE layers onto the gate surface of the FED alternately changes its flat-band voltage, thus generating a sensor signal. However, it is still under discussion which mechanism is responsible for this shift of flat-band voltage. Recently, we have proposed that a local pH and ion concentration redistribution within the PEMs could be responsible for the experimentally observed effects in FEDs induced by the adsorption of charged macromolecules [17–20]. In fact, recent investigations show that PEMs are permeable for water molecules, protons and small ions, and therefore, the charge balance in PE layers involves both polyions and small ions (see, e.g. [3, 6, 7]). Moreover, by using a pH-sensitive fluorescent dye, it was found that the pH profile and the absolute pH values inside the PE film drastically depend on the charge and hence, on the potential at the interface between the outermost layer and the electrolyte solution [31]. In addition, the ionisation, and therefore the charge of the weak PE such as PAH in the embedded layer, oscillates with the net charge of the outermost layer [32, 33]. Besides, the adsorption of the first PAH layers could also change the surface ionisation of $SiO_2$ via a charge regulation effect yielding the sensor signal.
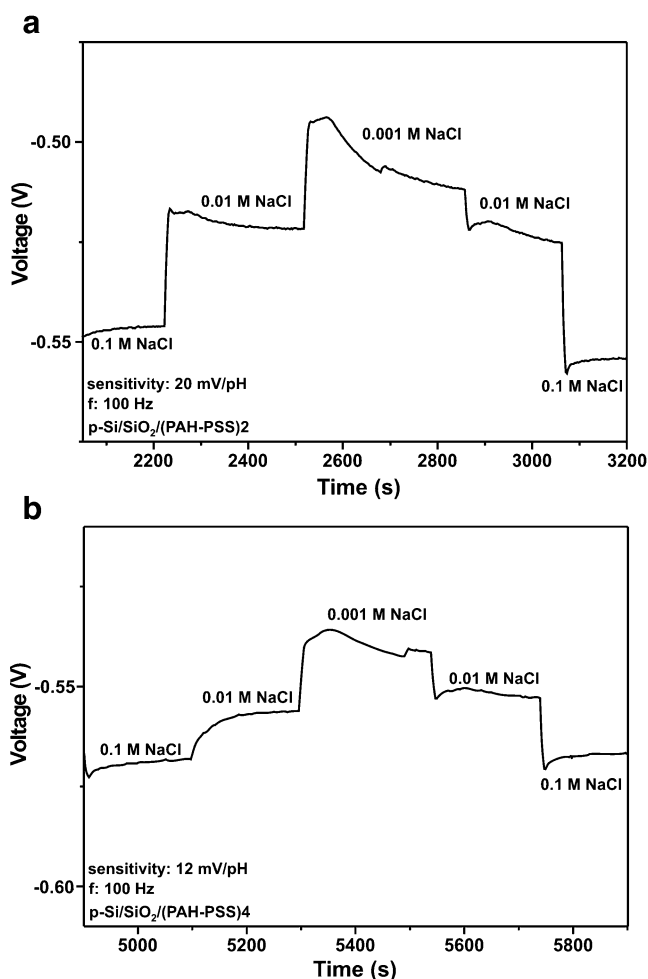
Thus, the sign and value of the charge of the outermost layer is an important parameter that controls the properties of PEMs. The local electric field emerged from the outermost PE layer can result in a redistribution of protons (ions) within the PEM, which in turns changes the local pH. Because the underlying gate insulator (in this study SiO$_2$) is known as pH-sensitive, the redistribution of protons, and therefore alternating changes in the pH profile inside the PEM after consecutive adsorption of each positively or negatively charged PE layer, can be detected with the underlying pH-sensitive field-effect transducer. An adsorption of PAH causes a decrease in pH due to the release of protons from the silanol groups of the SiO$_2$ surface. In contrast, the adsorption of PSS on a PAH-covered SiO$_2$ causes an increase in pH, which can be attributed to an increase of the protonation of PAH. The discussed mechanism predicts smaller sensor signals (lower pH change) if the measurements with PEM detection are performed in pH buffer solutions, which, in fact, has been observed in [19]. An alternative mechanism based on screening effects in PEM was proposed in [21–23] to explain the signal decrease with increasing layer number.

The mechanism of signal generation proposed in [17–20] allows further to explain the pH-sensitive behaviour of EIS sensors covered with PEMs. As it has been discussed in "pH and ion sensitivity of EIS structures covered with PEMs", the pH sensitivity of modified EIS sensors slightly depends on the type of terminating PE layer as well as on the number of adsorbed layers. This fact is a direct indication that the PEMs exhibit a high permeability for protons. Therefore, pH changes in the surrounding electrolyte will change the local pH within the PEM that will be directly detected by the underlying SiO$_2$ layer. The high permeability of PEMs for protons as compared to other ions has been discussed in [30] and explained by the Grotthuss-like mechanism of delocalised protons inside the PE films.

## Conclusions

The layer-by-layer adsorption of charged macromolecules on a field-effect capacitive EIS structure has been investigated using positively charged PAH and negatively charged PSS polyelectrolytes as a model system. Alternating shifts in the ConCap response, having a tendency to decrease with increasing the number of PE layers, have been observed after the adsorption of each polycation and polyanion layer. In addition, pH and ion sensitivity of EIS sensors covered with PEMs have been studied, and possible mechanisms of signal generation are discussed.

The performed experiments demonstrate that a buildup of PEMs can be observed by FEDs, providing an insight into their electrostatic and interfacial properties. At the same time, the deposition of PEMs with a well-defined architecture allows the adsorption of defined charges at defined distances, which successfully proves this model system for investigating the response mechanism of modified FEDs. The obtained results with EIS sensors might be very useful for studying fundamental effects induced in FEDs by molecular interactions at the solid/liquid interface and can be extended to further charged macromolecules.

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