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Proton motion in a polyelectrolyte: a probe for wireless humidity sensors

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Abstract
Low-cost passive wireless electronic sensor labels glued onto packages are highly desirable since they enable monitoring of the status of the packages for instance along the logistic chain or while stored at a shelf. Such additional sensing feature would be of great value for many producers and vendors, active in e.g. the food or construction industries. Here, we explore a novel concept for wireless sensing and readout, in which the humidity sensitive ionic motion in a polyelectrolyte membrane is directly translated into a shift of the resonance frequency of a resonance circuit. Thanks to its simplicity, the wireless sensor device itself can be manufactured entirely using common printing techniques and can be integrated into a low-cost passive electronic sensor label.

Keywords: Humidity Sensor, Polyelectrolyte, Printed Electronics, Wireless Sensor, Resonance, Packaging
1. Introduction
Low-cost passive wireless humidity sensors introduced as electronic sensor labels, which can be embedded into or added onto a vast array of goods or items, are demanded by the packaging industry, logistic companies and warehouses, and relates to storing and handling issues of a wide range of application areas (e.g. for the construction industry, electronics packaging and quality control of food during storage and transportation) [1-4]. A wireless sensor is composed of an antenna and a sensor device. For convenience, the reader should be a handheld electronic device comprising an antenna and an electronic chip that includes circuitry for analyzing the sensor signal. For a wireless electronic sensor label it is desired that the output sensor signal is translated into a frequency shift rather than a modulation of the signal amplitude since the latter is particularly difficult to readout without any reference readout, due to that the reading distance becomes a parameter that affects the overall signal level. This can be achieved by using a LC resonance sensor in which the resonance frequency varies with the measured unit, e.g. the humidity level. A schematic illustration of an inductively coupled humidity sensor system is given in figure 1. In this system the sensor label is powered by the remote reader via the alternating magnetic field sent from the reader antenna and captured by the sensor inductor. The impedance of the sensor label is reflected to the reader device enabling the resonance frequency of the sensor label, corresponding to the humidity level, to be readout with the reader device, i.e. the humidity level is readout in a wireless fashion without the need of a battery on the electronic sensor label.

In general, humidity sensors are divided into relative humidity (RH) sensors and absolute humidity sensors depending on their difference in measurement units [5]. Further, the ones that are based on electrical impedance changes are commonly divided into two different types, resistive- and capacitive-type sensors [6]. The resistive-type sensors are based on a
change of the real part of the impedance of the sensing material with a change in the surrounding humidity while the capacitive-type sensors are based on a change of the imaginary part of the impedance. The most common capacitive-type humidity sensors use a dielectric material as the active sensing material included in an interdigitated electrode configuration [7, 8]. Absorption of water into the dielectric layer changes its permittivity, thus modulating the capacitance (and the resonance frequency if incorporated into a LC resonance sensor) [9-11].

Figure 1. Schematic illustration of an inductively coupled sensor system for wireless humidity sensing. The sensor system consists of a flexible passive electronic sensor label that is powered remotely via the alternating magnetic field sent from the reader antenna. The impedance of the sensor label is reflected to the reader device enabling the humidity sensitive resonance frequency of the sensor label to be readout at the reader side. Thus, the humidity level surrounding the electronic sensor label can be readout wirelessly without the need of a battery on the sensor label.

Polyelectrolytes represent a family of solid-state electrolytes in which ionic charges are carried by the polymer chains while the counter-ions are condensed around the polymer chains. Polyelectrolytes are normally hygroscopic materials that can dissociate into ions upon water absorption. Because of these properties, polyelectrolyte films have mainly been considered for resistive-type humidity sensors [5, 12]. However, various relaxation mechanisms (e.g. dipolar and ionic relaxations as well as double-layer formation when sandwiched between two metal electrodes) take place in the polyelectrolyte at different frequency ranges [13, 14]. Although absorption of water is known to significantly affect the frequency range of those relaxation mechanisms [12], to the best of our knowledge nobody has used ionic motion as the sensing probe for wireless humidity sensing.
In this work, we demonstrate that low frequency relaxation phenomena in solid electrolytes can be used as the sensing mechanism in a wireless humidity sensor system. The RH dependence on the real and the imaginary parts of the total impedance of an 80 nm thin solid-state polyanionic polyelectrolyte named poly(styrenesulfonic acid) (PSS:H, figure 2a), sandwiched between two titanium electrodes forming a vertical capacitor structure (figure 2b), was analyzed with impedance spectroscopy at different levels of the RH (10% to 90% RH). This polyelectrolyte capacitor, corresponding to the humidity sensitive part, was then connected to an additional capacitor and an inductor to form a resonance circuit from which the humidity level was readout wirelessly by monitoring the resonance frequency.

2. Experimental
The sensor capacitors were manufactured by spin-coating a thin film (80 nm) of PSS:H onto a global titanium electrode, previously vacuum deposited onto a silicon wafer. The PSS:H solution, provided by AGFA-Geveart, was further diluted with deionized water and then filtered using a glass microfiber filter (GMF) membrane whose pore’s diameter was about 1 μm. After deposition, the polymer film was annealed under vacuum at 110°C for 90 s. On top of the polymer film circular titanium electrodes were vacuum deposited through a shadow mask. The resulting cylindrical capacitors had a capacitor plate area of approximately 7 x 10^{-4} cm².

The polyelectrolyte capacitors were characterized by impedance spectroscopy with a high resolution dielectric analyzer (Novocontrol Technologies GmbH). The amplitude of the ac voltage was 0.1 V and the frequency was scanned from 1 MHz to 100 Hz. Each measurement was conducted at different levels of the RH using a Challenge 160 environmental chamber.
(Angelantoni Industries). The temperature was held constant at 20°C while the RH was varied from 10% to 90% RH in steps of 10% RH. The capacitors responded rapidly to changes in the RH (~1 min), but to ensure that the absorbed water was equilibrated with the vapor phase, the impedance measurement at each RH level was recorded 30 min after the RH value was set to a specific level. The impedance characteristics of the polyelectrolyte capacitors were recorded on the form $Z = Z_{\text{Re}}(f) + jZ_{\text{Im}}(f)$, where $Z_{\text{Re}}$ and $Z_{\text{Im}}$ represent the frequency ($f$) dependent real and imaginary parts of the total impedance $Z$.

![Chemical structure of PSS:H and schematic of humidity sensitive capacitor](image)

*Figure 2. a) The chemical structure of PSS:H in its protonated (left) and deprotonated (right) form. b) Schematic illustration of the humidity sensitive capacitor, an 80 nm thin layer of PSS:H sandwiched between two titanium electrodes.*

The wireless readout was achieved using a reader antenna connected to an E4407B spectrum analyzer (Hewlett Packard). The output signal (2 mW) of the spectrum analyzer was sourcing the reader antenna, which was physically separated from the sensor circuit with an air gap of 1 cm. The reader antenna consisted of an antenna coil ($L_R$) connected in series with a resistor ($R_R = 1 \Omega$), while the sensor circuit was composed of a coil ($L_S$), a capacitor ($C$) and the polyelectrolyte capacitor ($Z$) connected in parallel, see figure 3. Since the impedance of the secondary side circuit (the sensor circuit) will be reflected to the primary side (the reader) [15], the resonance frequency of the sensor circuit can be wirelessly readout utilizing the reader antenna. This was done by analyzing the frequency response of the reader antenna using the spectrum analyzer. The reader and sensor coils were fabricated by hand and their inductance values were estimated experimentally to be $L_R = 35 \mu\text{H}$ and $L_S = 8 \mu\text{H}$. The value
of the additional capacitor in the sensor circuit was \( C = 6.6 \, \text{nF} \). The measurements performed on the sensor circuit involved the same equipment and followed the same procedure as described for the measurements performed on the polyelectrolyte capacitors to control the RH. To ensure that the observed shift of the resonance frequency originated only from the polyelectrolyte capacitor, the other circuitry of the sensor circuit was placed outside the climate chamber.

![Figure 3. Electrical circuits of the humidity sensitive resonance circuit and the reader setup.](image)

*Figure 3. Electrical circuits of the humidity sensitive resonance circuit and the reader setup. The reader setup, \( L_R = 35 \, \text{μH} \) and \( R_R = 1 \, \text{Ω} \), was separated from the sensor via an air gap of 1 cm. In the sensor circuit, with \( L_S = 8 \, \text{μH} \) and \( C = 6.6 \, \text{nF} \), the impedance element \( Z \) (\( Z = Z_{\text{Re}} + jZ_{\text{Im}} \)) corresponds to the polyelectrolyte-based capacitor, an 80 nm thin layer of PSS:H sandwiched between two titanium electrodes. The sensor is powered by the reader via inductive coupling. The impedance of the sensor is then reflected to the reader resulting in that the resonance frequency of the sensor, which corresponds to the measured humidity level, can be analyzed at the reader.*

### 3. Results and discussion

When a dc voltage is applied to the polyelectrolyte capacitor, electric double-layers are built up at the polyelectrolyte/metal electrode interfaces. Mobile protons (\( \text{H}^+ \)) in the polyelectrolyte layer migrate towards the negatively charged metal electrode while the immobile polyanions (\( \text{PSS}^- \)) remain close to the positively charged metal electrode. In the case of an ac voltage applied across the polyelectrolyte capacitor, the polarization characteristics of the polyelectrolyte capacitors depend on the frequency of the voltage [13, 14]. In the frequency range of this study, 100 Hz to 1 MHz, two different relaxation phenomena can be identified by analyzing the real and the imaginary parts of the impedance.
The real ($Z_{\text{Re}}$) and the imaginary ($Z_{\text{Im}}$) parts of the impedance of the polyelectrolyte-based capacitor are given as functions of frequency for different RH levels (10% to 90% RH) in figure 4. Clearly, both $Z_{\text{Re}}$ and $Z_{\text{Im}}$ are functions of the frequency and the RH. $Z_{\text{Re}}$ starts to show RH dependence at frequencies above 800 Hz while $Z_{\text{Im}}$ starts to show RH dependence at considerably higher frequencies (~60 kHz). Note that $Z_{\text{Im}}$ at 30% and 50% RH and at 70% and 90% RH, respectively, are close to indistinguishable. At 10% RH $|Z_{\text{Im}}| = |Z_{\text{Re}}|$ at ~12 kHz. This frequency, here called the transition frequency, represents the transition between the two relaxation mechanisms. Below the transition frequency $|Z_{\text{Im}}| > |Z_{\text{Re}}|$, thus indicating a dominant capacitive character of the impedance. The high value of the imaginary impedance found in this low frequency region, corresponding to a large effective capacitance ($C_{\text{Eff}} \sim 20 \, \mu\text{F cm}^{-2}$ at 100 Hz, $C_{\text{Eff}} = [2\pi f |Z_{\text{Im}}|]^{-1}$), is associated with the formation of electric double-layers at the polyelectrolyte/metal electrode interfaces [14, 16]. Above the transition frequency $|Z_{\text{Re}}| > |Z_{\text{Im}}|$, i.e. the impedance acquires a dominant resistive character. This originates from dissociated protons migrating away from the polymer chains in the oscillating electric field [14]. This is referred to as ionic relaxation. The transition between these two relaxation mechanisms is suddenly shifted to significantly higher frequencies above 50% RH (see inset figure 4b). Above 100 kHz, $|Z_{\text{Re}}| > |Z_{\text{Im}}|$ between 10% and 50% RH while $|Z_{\text{Im}}| > |Z_{\text{Re}}|$ at higher RH levels, which means that the resistive part of the impedance dominates in dry conditions while the capacitive part dominates at humid conditions. Hence, the polyelectrolyte capacitor cannot be classified as a capacitive-type sensor nor as a resistive-type sensor, but rather as a hybrid of the two types: here referred to as an impedance-type sensor.
Figure 4. a) The real and b) the imaginary parts of the impedance of the polyelectrolyte capacitor (an 80 nm thin PSS:H layer sandwiched between two titanium electrodes) versus the frequency at different levels of the RH (presented in steps of 20% RH between 10% and 90% RH for clarification). The impedance data represents the average of three polyelectrolyte capacitors. The inset in b) shows the evolution of the transition frequency, representing the frequency where $|Z_{\text{Im}}| = |Z_{\text{Re}}|$, versus the RH (no data could be extracted for 90% RH due to experimental limitations, the upper frequency limit of the measurement setup was 1 MHz).

To complete the sensor and obtain a humidity sensitive resonance circuit, an inductor ($L_S$) was added in parallel to the polyelectrolyte capacitor. An inductor in the form of a circular loop antenna with $L_S = 8 \, \mu\text{H}$ was used in our study. Planar inductors with such inductance value can be manufactured using low-cost and high volume manufacturing techniques today [17, 18]. Adding a capacitor ($C = 6.6 \, \text{nF}$) in parallel to the polyelectrolyte capacitor and the coil ($L_S$) shifts the resonance frequency range of the sensor circuit to the specific RH sensitive frequency region and creates a more well-defined resonance peak. The addition of the capacitor ($C$) in parallel to the polyelectrolyte capacitor resulted in a more pronounced
capacitive behavior of the impedance characteristics of these two capacitive elements alone. The imaginary part of this impedance was higher than the real part independently of the frequency and the RH. The imaginary part showed a weak RH dependence above 20 kHz while the real part showed a clear RH dependence above 4 kHz. The electrical circuit of the resulting sensor circuit is given in figure 3 together with the circuit of the reader setup. As a consequence of the inductive coupling between the two coils the impedance of the sensor circuit will be reflected to the reader circuit, resulting in that the resonance frequency of the sensor circuit can be wirelessly readout at the reader side.

The configuration of the sensor circuit results in that a change in $Z_{Re}$ and $Z_{Im}$, of the polyelectrolyte sensor capacitor, influences the resonance frequency. The resonance frequency of the resulting sensor circuit is RH dependent giving the highest resonance frequency for the driest conditions, see figure 5. The resonance frequency is about 665 kHz at 10% RH and decreases in a non-linear fashion down to 468 kHz at 90% RH. Three different regimes of the resonance frequency are observed: (i) between 10% and 50% RH the resonance frequency decreases slightly (from 665 kHz to 639 kHz, corresponding to a sensitivity ($S$) of 0.65 kHz/% RH assuming a linear dependence in this regime), (ii) between 50% and 70% RH the resonance frequency drops drastically (from 639 kHz to 504 kHz) and defines the most sensitive region for the sensor with $S = 6.75$ kHz/% RH; and (iii) above 70% RH the resonance frequency continues to decrease (from 504 kHz to 468 kHz at 90% RH) with $S = 1.80$ kHz/% RH. Hence, the sensitivity of the sensor is not constant versus the RH. This can be explained from previous observations and models for proton transport in solid electrolytes. In a dry film protons are localized by electrostatic interaction in proximity to the sulfonate groups of the polyanions. Upon absorption of water, hydronium ions ($H_3O^+$) are formed that screen this electrostatic interaction [19]. This results in lower activation energy
for proton transport [20]. The conductivity mechanism at relatively low concentrations of hydronium is likely taking place as “vehicular” transport, in which proton migration is assisted by translational dynamics of larger species, ”vehicles”, [21] here identified as H$_3$O$^+$. This mechanism of proton transport is likely the origin of the moderate increase of the transition frequency in the 10% to 50% RH region (figure 4b) as well as the first plateau, in the same RH range, of the resonance frequency of the sensor circuit (figure 5). Between 50% and 70% RH, a drastic change of the transition frequency and the resonance frequency are observed. At those hydration levels, the amount of absorbed water is large enough to provide percolation paths, in which proton transport takes place via hopping between absorbed water molecules. This mechanism is frequently termed as the Grotthuss mechanism or structure diffusion [22]. At higher humidity levels, the transition frequency is expected to saturate since the proton mobility is known to reach a maximum at high humidity levels [19]. This could however not be observed since the upper frequency limit of the experimental setup was 1 MHz.

![Figure 5. The resonance frequency of the polyelectrolyte-based sensor circuit, readout wirelessly, versus the RH. The symbols represent the average of three sensors and the error bars represent min and max values.](image)

Compared to other humidity sensor technologies, the performance of the sensor circuit reported here is somewhat different. Polymer-based capacitive-type humidity sensors, for which a change in the RH is associated with a change in the permittivity of the polymer dielectric, usually exhibit a linear response of the capacitance with the RH [23]. LC circuits
based on such capacitive-type sensors, together with a coil, have been demonstrated previously [9-11]. The humidity sensitive resonance frequency of those sensor circuits was readout in a wireless fashion. The wireless sensors reported in [10] displayed a linear evolution of the resonance frequency versus the RH, but had a similar sensitivity ($S = 4-16$ kHz/% RH) as the sensor circuit reported here ($S = 6.75$ kHz/% RH between 50% and 70% RH). Humidity sensors based on other technologies and materials, e.g. thin films of aluminum oxide [24] and nanowires [25], display very good sensor characteristics. However, these sensors are not passively operated, can not be readout in a wireless manner and are not compatible with low-cost manufacturing techniques. Since the sensor circuit presented here is compatible with low-cost and high volume manufacturing techniques, new potential applications can be targeted that previously has been too expensive. For instance, sensors can be permanently mounted inside walls or beneath floors in houses for wireless monitoring of eventual leakage or moisture problems. The large shift of the resonance frequency between dry and humid conditions can be used for such dry/wet sensors. In addition, drying processes inside materials, e.g. drying of concrete [26], can be monitored due to the high sensitivity between 50% and 70% RH.

4. Conclusions
A thin polyelectrolyte proton membrane sandwiched between two electrodes constitutes the sensor device for wireless humidity sensing. The microscopic mechanisms that are responsible for the humidity sensing are due to the proton motion within the membrane, either migration away from the polymer chains (resistive character) or accumulation along the metal surface within electric double-layers (capacitive character). Those two events overlap such that both the real and the imaginary parts of the impedance vary with the relative humidity. As a consequence, when a polyelectrolyte is used as the “dielectric medium” in a capacitor
structure, the device is neither a pure resistive-type sensor nor a pure capacitive-type sensor. Instead, we call it an impedance-type sensor. The achievement of wireless sensing by connecting an inductor to this impedance-type sensor via an additional component provides direct translation of the humidity dependent proton motion into a shift in the resonance frequency of the sensor circuit used. The impedance-type sensor circuit is a simple device that can be integrated into a low-cost passive electronic sensor label that can be manufactured using common printing technologies of today.

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Xavier Crispin is Associate Professor in Organic Electronics at the Department of Science and Technology, Linköping University, Sweden, since 2004. He received his M.Sc. in Chemistry in 1995 and his PhD in Chemistry in 2000, both degrees from the University of Mons-Hainaut in Belgium. From 2000 to 2004, he was Assistant Professor in Surface Physics and Chemistry at Linköping University. Today, he is supervising the research focused on solid-state electronics within the group of Professor M. Berggren.