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Characterization of capacitive humidity sensors based on doped poly(propargyl-alcohol)

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Abstract

Films of poly(propargyl alcohol) (POHP), doped with both sulphuric acid and iron trichloride, were deposited on interdigitated gold electrodes. Their electrical properties were examined as a function of percentage relative humidity. The devices showed low-frequency capacitance linearly dependent on RH% with good response time, and are proposed as possible capacitive humidity sensors.

1. Introduction

In spite of the large number of compounds investigated it is not easy to identify good materials for humidity sensor construction. The requirements for a humidity-sensing material essentially include linear response, fast response time, high sensitivity, chemical and physical stability, wide percentage relative humidity (RH%) operating range and, possibly, low cost.

Because of their low cost, stability, permeability to water and easy handling, polymers have been widely investigated as water vapour sensing materials [1–5]. The change in electrical characteristics with RH% is the principle on which many polymer water vapour sensors are based: variation of the capacitance in the case of capacitive devices [6], variation of the impedance for resistive devices [7]. The former and the latter kind of sensors are, respectively, produced with higher and lower resistance materials. To improve the performance of the devices, polymer composites and multilayer polymeric structures have been investigated, for example, a film of composite poly(*o*-aminophenol)/poly (vinylalcohol) [7], a double layer structure of polyamine/polymethylmetacrylate [8], crosslinked polyimide/fluorinated polyimide [9], composite films of poly(*o*-phenylenediamine)/poly(vinylalcohol) [2, 10], SiO_2/Nafion® composite [11] and so on.

Water is sorbed within the polymers and interacts with the polar sites [12]. At constant temperature, the amount of water sorbed by the polymer as a function of the water vapour pressure is controlled by the absorption isotherm, which can be experimentally determined by measuring the weight variation of the polymer. The water sorption changes the dielectric constant of the polymer and this is the basis of the capacitive sensors. Although the conductivity of pure polymers does not often change much with RH%, the conductivity of polymer electrolytes and polymer-salt complexes increase strongly, due to water sorption, and can be suitable for resistive humidity sensors. Nevertheless the determination of the relationship between the conductivity or the capacitance of these materials and RH% is often difficult. A rigorous treatment is very complex and the water content inside the polymer for each RH% (sorption isotherm) has to be considered, as well as the nature of the ions which transport the charge, their interaction, the dimension of the channels where the ions migrate, interface processes and many other parameters.

A simplified treatment was previously proposed in order to describe the electrical characteristics of films [13] or pressed pellets [5] of polymer electrolytes and polymer-salt complexes. The ion migration, in the presence of humidity, was considered a function of the interaction of the ions inside liquid channels formed by the swelling of the polymer matrix. A modified Onsager equation was used to describe this interaction; good fittings of the conductivity data with this equation were obtained by replacing the dielectric constant with a function which gave the best fit of the experimental capacitance values (dependent on RH%). In the case of ion conducting polymer films, the film capacitance and conductivity were obtained with impedance measurements and a sigmoidal trend with RH% was found for both quantities and for all the polymers investigated. Having obtained no linear response, other possibilities were investigated.

This paper describes the characterization of capacitive humi-sensing devices based on ion conducting polymers (polypropargyl alcohol doped both with $FeCl_3$ or sulphuric acid). Unlike in previous work, the capacitance of the whole device is considered here, instead of only that of the polymer film. The most important parameters of the devices, the sensitivity and the response time, are also reported. Further improvement may be achieved (miniaturization, for example), but in our opinion, the reported data are interesting enough to present these devices as candidates for possible technological utilisation. The main advantages are low cost, stability and large variation of the capacitance values with humidity.

2. Experimental details

2.1. *Materials*

Poly(propargyl alcohol) (POHP, Figure 1) was prepared and doped with H_2SO_4 as previously described [13] (H_2SO_4-doped POHP = H–POHP) $FeCl_3$ doped POHP (F–POHP) was obtained by adding 350 mg of polymer to 20 $cm^3$of a $FeCl_3$ solution in methyl alcohol (17.5 mg $FeCl_3$ cm^{-3} methyl alcohol). The mixture was stored at 30 °C for 24 h and the product then precipitated with acetone.

2.2. *Devices*

The devices were made by depositing $FeCl_3$-doped POHP or H_2SO_4-doped POHP on interdigitated (IDT) gold electrodes. Doped polymer powders (100 mg) were mixed with printing ink (0.01 cm^3 BASF SS777, mild product + 1 cm^3 SS719, slow) and thick films were deposited by the silk screen printing method onto IDT gold electrodes. Finally, the devices were heated at 50 °C for 5 h. The printing ink used shows very high impedance [14], no sensitivity to humidity and it does not interact with the doped polymers.

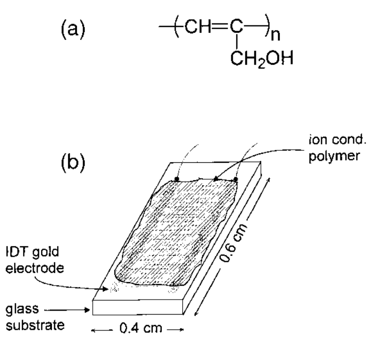

Fig. 1. (a) Formula of POHP; (b) structure of the device.

2.3. *Apparatus*

The devices were tested under dynamic conditions in a home-made cell equipped with a commercial humidity sensor (Eliwell mod. EWHS 31, humidity range 5–98%, temperature range: −10 to 70 °C). Different RH% values were obtained by bubbling dry argon in water. The analogue output of the sensor was acquired through a Keithley 2000 digital multimeter.

The current–voltage and current–time curves were recorded with a Solartron 1286 electrochemical interface. The impedance measurements were performed using a Solartron 1255 frequency response analyser coupled with a Solartron 1286 electrochemical interface. The fitting of the impedance spectra was carried out using the noniterative, nonlinear software, previously described [15]. The a.c. signal amplitude is given in the Figure captions. The resistance and the capacitance of the components associated with the various semicircles of the Nyquist plots were obtained by using the resonance formula $2\pi fRC = 1$, where f is the frequency and R and C are the resonance, resistance and capacitance, respectively. Changes in the capacitance with RH% were monitored in the time using the same Solartron 1286 + 1255 apparatus, driven by Zplot software (Scribner Associates Inc.). All the measurements were carried out at constant temperature (22 °C).

3. Results and discussion

The results presented were obtained from devices based on F–POHP and H–POHP. As already reported for analogous systems [5], at constant potential the current flowing in the device reaches a quasi steady-state value depending on the environmental RH% (Figure 2). Unfortunately, a linear or a well defined response between current and relative humidity was not observed. In fact, the current is a function of a number of factors (the interface characteristics, the rate of water absorbtion by the polymer electrolyte, the ion transport

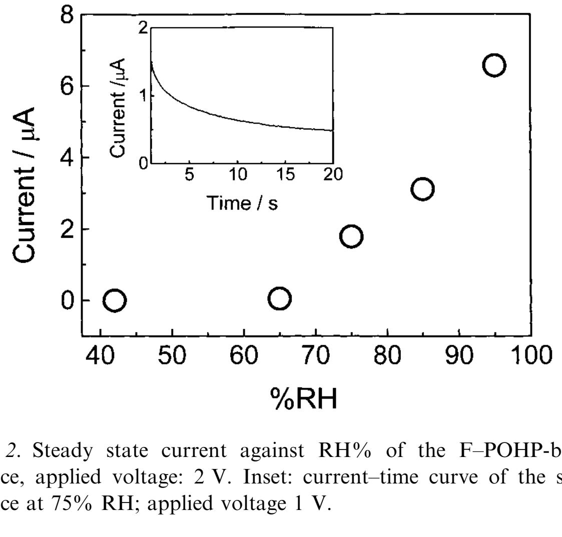

Fig. 2. Steady state current against RH% of the F–POHP-based device, applied voltage: 2 V. Inset: current–time curve of the same device at 75% RH; applied voltage 1 V.

within the polymer film) and so it is not easy to produce a resistive-type device. Thus, the possibility of using the devices as capacitive sensors was explored.

Impedance measurements, were performed at different values of RH%. Depending on the humidity, for all the devices tested (starting from the highest frequencies) the following elements can be observed (Figure 3):

(i) A semicircle due to the film impedance (sometimes not completely visible at frequencies <5 MHz) (region A in the Nyquist plot of Figure 3).

(ii) Sometimes, a second semicircle appears, partially superimposed on the Warburg impedance, connected with charge transfer at the polymer/electrode interfaces (region B in the Nyquist plot of Figure 3).

(iii) A straight line, due to the diffusion of the electroactive species (Warburg impedance), or, with blocking electrodes, to the interface capacitance in a nonhomogeneous material (region C in the Nyquist plot of Figure 3).

In general, at high amplitudes of the sinusoidal voltage, components of the total impedance, as interface processes, were more evident than at low amplitudes, while the film impedance (semicircle A, Figure 3) remained the same in all cases, as reported previously [16] for the same materials used in this work. From the analysis of the impedance spectra it was observed that the impedance of all films shows a sigmoidal trend as a function of RH%, as expected. In fact, a model for the mechanism of ion transport through this kind of doped polymer has been previously proposed [16]. It is based on the hypothesis that the ions migrate through a solution layer which grows inside the polymer because of water absorption. The growth of these liquid-like layers, affects the dielectric constant of the material. A modified Onsager equation (Equatioin 1) was used to describe the trend of the film [16] (or pressed pellet [5]) conductivity with RH%, the capacitance of the materials being dependent on the relative humidity:

$$\Sigma = a\Sigma_0 - \left\{ \frac{b}{[\varepsilon(\mathrm{RH\%})T]^{3/2}} + \frac{c}{[\varepsilon(\mathrm{RH\%})T]^{1/2}} \right\} \qquad (1)$$

where a, b and c depend on the cell size, the viscosity of the medium and universal constants. From Equation 1, it is evident that the resistance of the film ($\Sigma = 1/R$, semicircle A in Figure 3) is not a linear function of RH%. With the above equation, a very good fit of the experimental data, showing a sigmoidal trend with RH%, was obtained.

The plots of the experimental capacitance values for different frequencies, as a function of RH% for the H–POHP and F–POHP-based devices are shown in Figures 4 and 5. The trend depends, as expected, on the frequency. At high frequencies, (region relative to the capacitance of the film, semicircle A, Figure 3) the trend is again sigmoidal: a simple relationship between the capacitance and the relative humidity does not exist. The logarithmic plot is not linear and tends to a constant value both at low and high relative humidity. The prevailing processes which affect the impedance at lower frequencies (regions B and C, Figure 3) are the charge transfer across the electrode double layer and the diffusion of the electroactive species. The plots of the logarithm of the capacitance vs. RH% approximate to a straight line and the device could be used as a humidity sensor. In particular, the correlation coefficient of the plot: log(capacitance at 50 Hz) against RH% was found to be 0.99, within the range 10–95% RH.

Figure 6 shows the variation over the time of the capacitance of H–POHP and F–POHP-based devices, at low frequencies, on changing the environmental relative

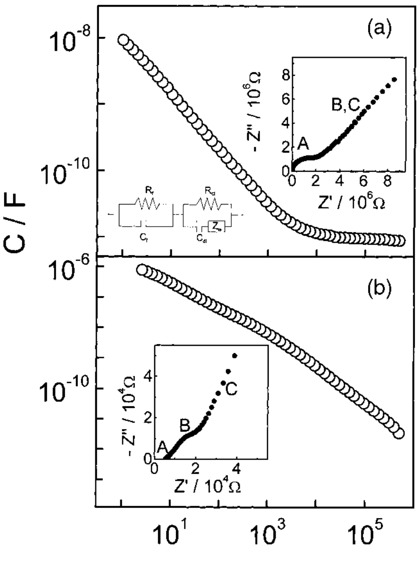

Fig. 3. (a) Capacitance against frequency and (inset) Nyquist plot of the H–POHP-based device at 46% RH. Sinusoidal voltage 1 V. Frequency range 1–500 000 Hz. Inset: equivalent circuit. (b) The same plots for the same device at 75% RH. A, B, C indicate, the regions related to the film impedance, charge transfer through the electrodes and diffusion (Warburg impedance), respectively. In the equivalent circuit R_f and C_f are the resistance and the capacitance of the film, R_{ct} and C_{dl} are the resistance of the charge transfer and the double layer capacitance at the electrodes and Z_w is the Warburg impedance.

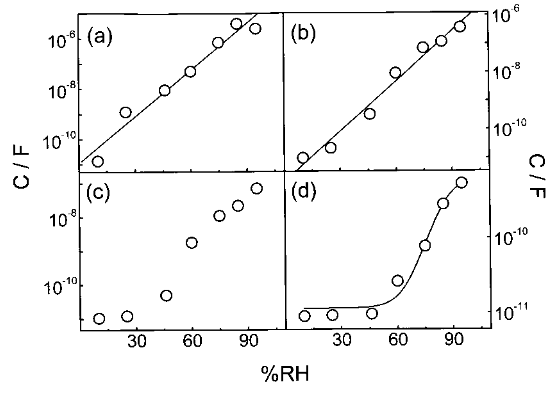

Fig. 4. Capacitance of the H–POHP-based device against RH% at different frequencies: (a) 1, (b) 53, (c) 559 and (d) 48 000 Hz. Sinusoidal voltage 1 V.

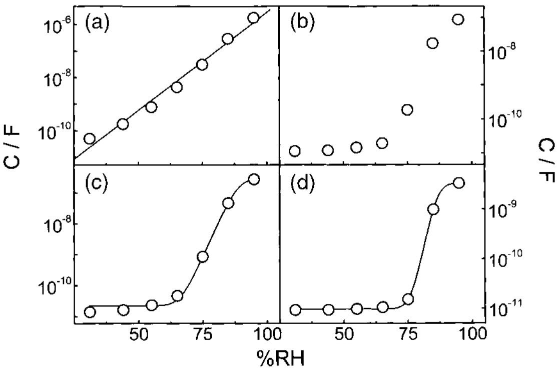

Fig. 5. Capacitance of the F–POHP-based device against RH% at different frequencies: (a) 1, (b) 53, (c) 559 and (d) 30 000 Hz. Sinusoidal voltage 1 V.

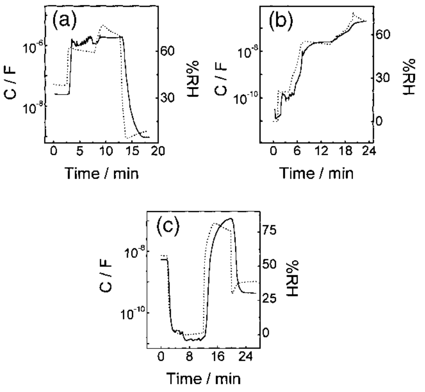

Fig. 6. Response of the H–POHP (a, b) and of the F–POHP (c) based devices used as capacitive sensors (full line) and of a commercial sensor (dotted line, see Section 2). Frequency: (a) 1, (b) 50 and (c) 1 Hz. The device was set near the commercial sensor in the measurement cell, where the humidity was changed with time.

humidity. In particular, it can be observed that the response of the H–POHP-based device is fast, considering the thickness of the films (~100 μm). Although the electrical properties of the film are not involved, in this case, in the determination of the content of water vapour in gas phase, nevertheless the thickness of the film plays an important role in reaching equilibrium conditions at the electrode/electrolyte interface.

Some specifications of the H–POHP device are summarized in Table 1.

4. Conclusions

Stable, cheap devices with good response times can be realised with acetylene type polymer electrolytes deposited onto interdigitated gold electrodes. A linear response with RH% was not easily achieved. For all the samples, a reasonably good linear relationship between the logarithm of the capacitance and RH% was attained, at frequencies where double layer processes are rate determining, The electrical characteristics of samples tested continually for five days did not change significantly. The specifications of a laboratory-made H–POHP device are reported. These results are very promising and can certainly be improved upon by optimizing the construction parameters.

Table 1. Specifications of the H–POHP based sensor

Size of device (Figure 1)	0.6 cm × 0.4 cm
RH range	10–95%
Minimum sensitivity	1.32 pF × RH% unit (RH 10%, frequency 1 Hz)
Maximum sensitivity	1.31 μF × RH% unit (RH 90–95%, frequency 1 Hz)
Response time	a delay of ~1 min with respect to the commercial sensor

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