

# **WATER ACTIVATED IONIC CONDUCTION IN CROSS-LINKED POLYELECTROLYTES**

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## **Abstract**

The electrical properties of polyelectrolytes depend on the water concentration of the environment. The behaviour of both conductance and capacitance caused by variations in relative humidity and temperature was investigated by impedance spectroscopy for humidity sensors based on an interpenetrated network of a polymer and a polyelectrolyte. The results were interpreted on the base of the Langmuir and Kelvin equations and two different sensing mechanisms were highlighted for low and high water content.

*Keywords:* Humidity sensors; Ionic conduction, Interpenetrated polymer networks; Cross-linked polyelectrolytes, Chemoresistors.

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## 1. Introduction

Water is an omnipresent compound, it is necessary for life, but it also influences many physical properties of materials. Thus, the measurement of water content is a very common practical issue in all human activities. The determination of humidity level can use many different techniques such as chilled mirror, quartz crystal microbalance and surface acoustic wave. Also many water sensitive chemoresistors and capacitive sensors have been developed by using ceramic or polymeric materials [1]. The operation mechanism of capacitive sensors is based on the variation in dielectric constant of the sensing material with the amount of sorbed water; thus, hygroscopic insulating polymers have been used for this kind of devices [2,3]. On the other hand, chemoresistors are built with materials that change their conductance with water content, such as conjugated polymers [4,5], polymer electrolytes [6,7] or polyelectrolytes [8,9].

The electrical conduction in polymer electrolytes and polyelectrolytes is due to the ion motion that occurs in a kind of liquid solution produced by water sorption into the polymer capillaries and follows an Onsager-type equation [10-12]. Some uncertainty in that model could arise in the low humidity range, also because of the reduced conductivity exhibited by those materials at low water contents.

The aim of the present paper is the modelling of the ionic conduction in a cross-linked polyelectrolyte through a more refined inspection of the system behaviour in the low humidity range, in order to satisfactorily complete the previous investigations on this matter.

## 2. Experimental

Sintered glass substrates with two interdigitated gold electrodes on their surface were used as transducer supports. The interdigitated electrodes were constituted by two 600- $\mu$  m wide main tracks connected with 12 and 13 fingers, respectively. The fingers were 2.6 mm long, 32  $\mu$  m wide and 1  $\mu$  m thick; the gap between consecutive fingers was 40  $\mu$  m. The cell constant in a 0.1 mol L<sup>-1</sup> KCl water solution was 0.30 cm<sup>-1</sup>. The supports were dipped once or twice in a

dimethylsulfoxide solution containing 1,4-dibromobutane and poly(4-vinylpyridine) (P4VP) at a molar ratio of 2/1, diethylenetriamine and poly(glycidyl methacrylate) (PGMA) at a molar ratio 1/2, and having a 2/1 mass ratio of P4VP and PGMA. After the dipping, the transducers were heated at 90 °C for 10 h to give a solid film of interpenetrated polymer network (IPN), approximately 1 μ m and 2 μ m thick for one-layer and two-layer devices, respectively [13]. The resulting transducers were then encapsulated in ethylcellulose to protect the sensing material.

P4VP was obtained by polymerisation of 4-vinylpyridine with 2,2'-azo-bis(isobutyronitrile) (AIBN) in CHCl<sub>3</sub> at 60°C for 19 h and, then, precipitated by adding anhydrous ethyl ether. PGMA was obtained by polymerising glycidyl methacrylate in a benzene solution with AIBN as an initiator at 60°C for 4 h, followed by precipitating in methanol and purifying by repeated dissolving in acetone and precipitating in methanol.

The electrical characterization of the transducers was performed by means of impedance spectroscopy. The impedance measurements were carried out with a Solartron Frequency Response Analyser model 1255, coupled with a Solartron Impedance Interface model 1294, in a frequency range from 1 Hz to 1 MHz, with 1 V sinusoidal voltage amplitude and 0 V bias applied. The impedance spectra were fitted by Z-plot software (Scribner Associated) by using an equivalent circuit with a capacitor in parallel to a resistor followed, when needed, by a Warbourg element [10,12]. The errors on conductance ( $\sigma$ ) and capacitance (C), coming from the fitting process, were within 5%. The impedance spectra were taken both at constant temperature (25°C) in the range of RH from 1% to 80%, and at constant relative humidity (RH) values (12% and 75%) in the temperature range from 0°C to 70°C. In the first case, different RH environments were obtained, with an uncertainty within 0.5% RH, by a Humidity Generator model HG-1 from Michell Instruments Ltd. In the latter case, saturated LiCl and NaCl aqueous solutions were used to obtain environments with constant RH in a sealed bottle immersed in a water-glycol thermostat (Haake G/F3), while changing the temperature.

The response speed of the transducer was evaluated by recording the variation of the impedance module vs. time after extraction of the transducer from air with 75% of RH to the room atmosphere (35% RH).

### 3. Results and Discussion

The impedance module of the transducers quickly follows the change of RH and the equilibrium conditions to the new environment are promptly attained, without significant differences between the transducers with one or two IPN layers (Fig. 1). The following evaluation of the transducer electric properties was carried out after the equilibrium was reached to avoid the effects of sorption kinetics.

The conductance at room temperature of the transducers vs. RH is displayed in Fig. 2. In the semi-logarithmic plot, both samples show a rough linear trend with a change of the slope at about 30% RH, suggesting different conduction mechanisms for low and high humidity. A similar behaviour has already been observed [14,15], but never investigated.

The same behaviour of conductance occurs for capacitance (Fig. 3). However, differently from conductance data, the slope in the range below 30% RH was lower than that observed at higher RH values. On the other hand, the change of slope does not depend on the number of IPN layers even if the sample with two layers showed both higher conductance and capacitance than that made with one layer only.

Different processes occur in the interaction between humidity and the IPN. When water vapour is sorbed into the pores of the solid polyelectrolyte [15], it condenses on their surfaces, rich in polar sites. The Langmuir equation describes the adsorption of a gas, water vapour in this case, on condensed matter surfaces:

$$\theta = \frac{bP}{1+bP} \quad (1)$$

where  $\theta$  is the fraction of the surface covered by water,  $P$  is the water pressure on the surface and  $b$  is a factor which depends on the Gibbs function of the adsorption process, that is, on the binding strength of the adsorbate to the surface of the solid. It is worth noting that RH is directly

proportional to the activity of water in the gas phase, that is, at ordinary constant pressure, it is proportional to the partial pressure of water. This intimate adsorption causes an interaction of water with polar sites and ions on the surfaces of the pores, throughout the bulk of the polymer film. This mainly affects the electrical properties of the material at low RH. Moreover, depending on the vapour pressure and the pore size, a vapour/liquid phase equilibrium occurs in the pores as described by the Kelvin equation:

$$\ln(P_s/P_{0s}) = -2V_m\gamma / rRT \quad (2)$$

where usually  $P_s$  is the saturated vapour pressure in a bubble of radius  $r$ ,  $V_m$  is the molar volume of water,  $\gamma$  is the liquid surface tension,  $T$  is the absolute temperature,  $R$  is the universal gas constant and  $P_{0s}$  is the vapour pressure for a planar surface ( $r=\infty$ ) of the liquid. In the pores, the condition for the capillary condensation is that the radius of a pore has to be smaller than the radius computed with the Kelvin equation. Consequently, the condensation into the pores occurs also when the external RH is lower than 100%. Therefore, by increasing RH at constant temperature, moisture suction gradually occurs in the capillary pores, starting from the smaller ones, causing a plunging of the polymer chains in a liquid phase.

The electrical conduction is related to the ion mobility. In dry polyelectrolytes, the charge carriers are blocked in the ionic couple. Consequently, conductance and capacitance are very low. However, the electrical response improves when water interacts with the ions, owing to a decrease of the free energy barrier between two adjacent ion sites. At low RH the pores mainly contain vapour phase and adsorbed water, so ion motion is related to an activated process by which adsorbed water breaks the ionic interaction between ions and related counterions bound to the polymer chain, in a kind of solvation-desolvation mechanism. Therefore, the slope of  $\sigma$  vs. RH diagram (Fig. 2) is related under this condition to the progressive decreasing of the average energy of the ion-counterion interaction which affects the free activation energy associated with the ion hopping between two adjacent low energy sites (both ionic or dipolar). On the other hand, the slope of  $C$  vs. RH in the semi-logarithmic diagram (Fig. 3) at low humidity is probably mainly due to the

spreading and thickening of the adsorbed layer of water on the pore surface. By increasing RH, a condensation of water into the pores gradually occurs and, as a consequence, the dielectric constant of the IPN increases leading to a higher slope of the  $\log C$  vs. RH plot in the high RH region. The formation of a sort of liquid electrolytic solution into the pores of the IPN leads to an electrical conduction mechanism which can be described by an adapted Onsager equation [10,12,16]. For ion exchange resins, it has been demonstrated that the activity of water in a solution of cross-linked polyelectrolytes depends on the degree of cross-linking [17,18] that could be related to the average pore size. Moreover, at about 30% RH, i.e. the humidity value marking the boundary between low- and high-RH conduction mechanisms (Figs. 2 and 3), the oblique line related to the Warburg component started being visible in the Nyquist plots. It is worth noting that the component of the Warburg impedance is usually detectable in the liquid phase and it is due to diffusive processes at the electrodes.

The electrical properties of the transducers were also investigated as a function of temperature at constant RH. Fig. 4 shows the semi-logarithmic plots of conductance vs. reciprocal absolute temperature for the transducers exposed to 12% and 75% RH. In both cases, the data can be fitted by two lines. At low temperature a liquid phase leads to the formation of a sort of electrolytic solution in the pores and the electrical conduction occurs as above described. As  $\ln(P_s/P_{0s})$  depends on  $-1/T$  (Eq. 2), the liquid/vapour equilibrium is reached by increasing the temperature and the mechanism of charge transport changes, occurring, in the high temperature range, through thin adsorbed layers in the pores filled with water vapour [19]. Moreover, by increasing RH from 12% to 75%, the saturation pressure of water in the pores increases, and the region of the slope change shifts to higher temperatures (Fig. 4), in agreement with Eq. 2. This behaviour and the cross-linked nature of the IPN exclude that the change of the slopes in Fig. 4 could be related to the polymer glass transition .

The C vs. T plots displayed in Fig. 5 are consistent with the  $\sigma$  vs. 1/T plots (Fig. 4). In fact they show maxima located at temperatures roughly in the same regions where the slopes change in Fig. 4. The capacitance increases significantly approaching the maxima, conceivably because the water cloud around ions, characteristic of the liquid electrolytic phase, gradually becomes less compact, making the dipoles more easily oriented with the oscillating electric field. When the increase of the temperature induces the formation of the saturated vapour in the IPN, the liquid solution vanishes leaving a thin electrolytic film adherent to the pore surfaces, and the capacitance of the material drops down. Also this result strengthens the hypothesis of two working regimes for polyelectrolyte-based sensors: (i) the hopping regime at low humidity and high temperature; (ii) the electrolytic regime at high humidity and low temperature. The capacitance maximum (Fig. 5) represents the boundary region between the two different working regimes. The free activation energy for the hopping charge transport process is due to the ion-ion interaction and is lowered by adsorbed water molecules. The comparison between the hopping free energy for 12% and 75% RH cannot be evaluated from the slopes of the plots reported in Fig. 4 because of the difference in the number of percolation paths at the two humidities. The effect of temperature in the electrolytic regime is due to the ion mobility into the pores filled with the electrolytic solution, and it is described by the Onsager equation. Accordingly, just in the temperature region close to the maximum of the C vs. T plots, the  $\sigma$  vs. 1/T plots change their slopes, as above described.

#### **4. Conclusions**

The logarithm of both conductance and capacitance of IPN based humidity sensors was found to be linearly dependent on RH at room temperature, with a change of slope at about 30% RH, not affected by the thickness of the IPN film. This indicates that charge transport occurs with two different mechanisms, depending on the amount of water sorbed by the IPN film that determines the state of water inside the polymer pores. The behaviour of conductance and capacitance with temperature, at constant RH, confirms this hypothesis. In particular the

capacitance-temperature plots show a maximum at the borderline between the two mechanisms. Though IPN polyelectrolytes are not suitable for the realization of capacitive humidity sensors, they are promising materials for fast and sensitive humidity sensing chemoresistors.

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## Biographies

**Nadia Camaioni** received her degree in physics from Bologna University on 1985. She was appointed research scientist in 1996 at the *Istituto per la Sintesi Organica e la Fotoreattività* (ISOF) of the *Consiglio Nazionale delle Ricerche* (CNR) in Bologna (Italy). Her scientific research interests include electroactive organic materials, optoelectronic properties of conjugated organic materials, molecular electronics, sensors and plastic solar cells.

**Giuseppe Casalbore-Miceli** received his degree in chemistry from Bologna University on 1965. He is currently retired but he was a research scientist at ISOF-CNR since 1967. His activity was devoted to organic electrochemistry, electrochromic devices, humidity sensors and materials for photovoltaic applications.

**Yang Li** received his Ph.D. degree in polymer chemistry and physics from Zhejiang University (China) on 2000. He has been working in the Department of Polymer Science and Engineering, Zhejiang University since 2000 and was appointed associate professor in polymer science on 2002. His research interests include polymer materials and organic/inorganic composites for chemical sensors.

**Mu Jie Yang** was graduated from Zhongshan University (China) on 1963. She has been working in Zhejiang University since 1963. She was promoted to full professor in polymer science on 1992. Her research interests are functional polymers with optical and electrical characteristics.

**Alberto Zanelli** received his degree in chemistry on 1993 and MS degree in Analytical Chemistry on 1996, both from Bologna University. He was appointed research scientist at ISOF-CNR on 2002. His research deals with the electrochemistry of conducting polymers, polymer-based sensors, organic photovoltaic devices, organic electronics, polymeric supercapacitors, lithium-polymer batteries and organic electrochromic devices.

### **Figure captions**

Fig. 1. Impedance variation at 1 kHz of the transducers with one ( $\square$ ) or two ( $\circ$ ) layers of IPN passing from 72% RH to 35% RH at room temperature.

Fig. 2. Semi-logarithmic plot of conductance vs. RH for the transducers with one ( $\square$ ) or two ( $\circ$ ) layers of IPN at room temperature.

Fig. 3. Semi-logarithmic plot of capacitance vs. RH for the transducers with one ( $\square$ ) or two ( $\circ$ ) layers of IPN at room temperature.

Fig. 4. Semi-logarithmic plot of conductance vs.  $1/T$  at constant RH for the transducer with one layer of IPN.

Fig. 5. Plot of capacitance vs.  $T$  at constant RH for the transducer with one layer of IPN.

Fig. 1

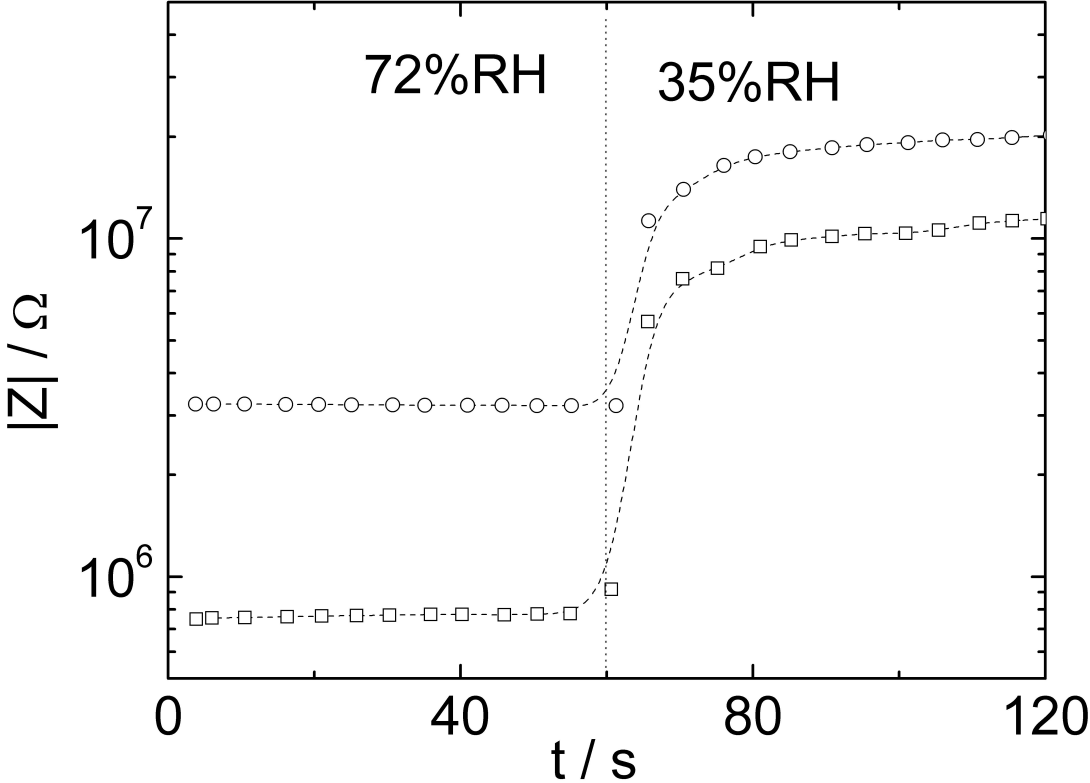


Fig. 2

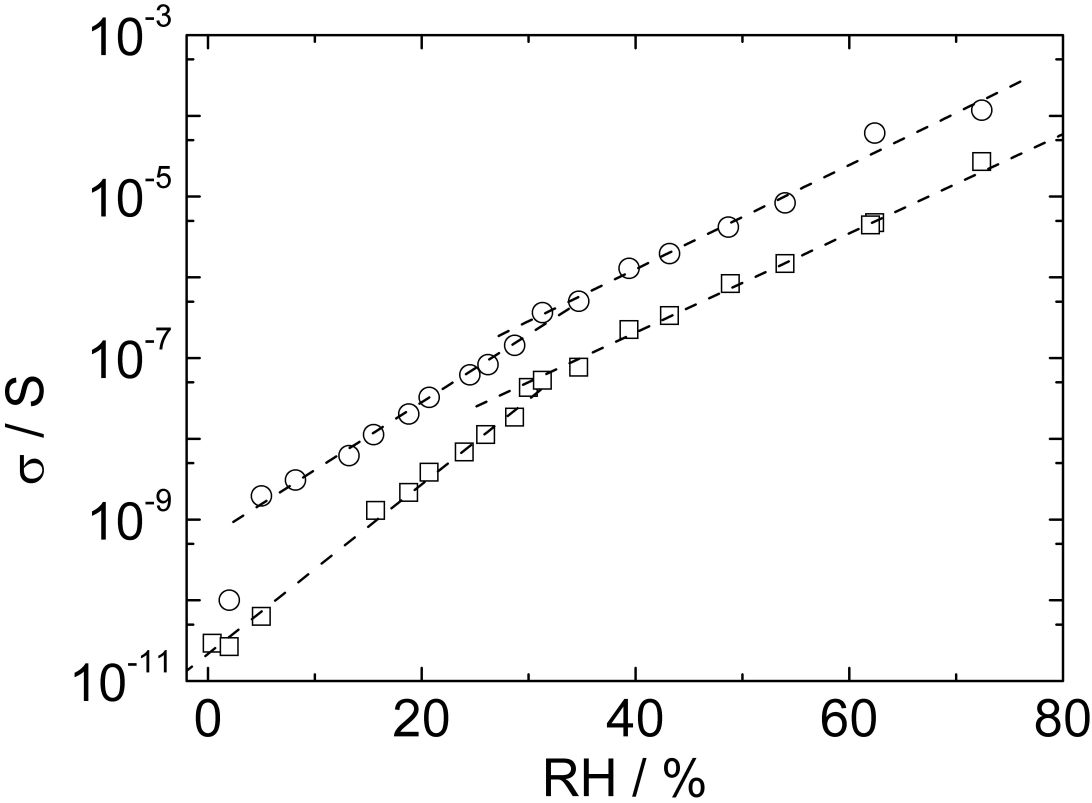


Fig. 3

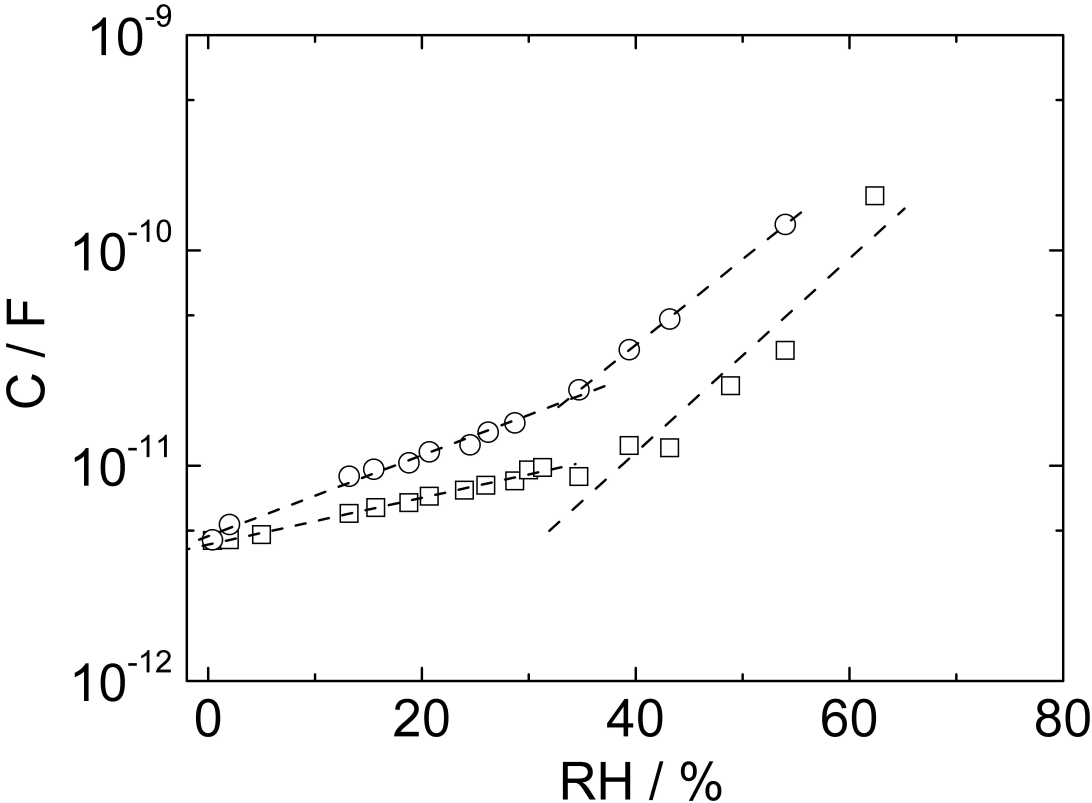


Fig. 4

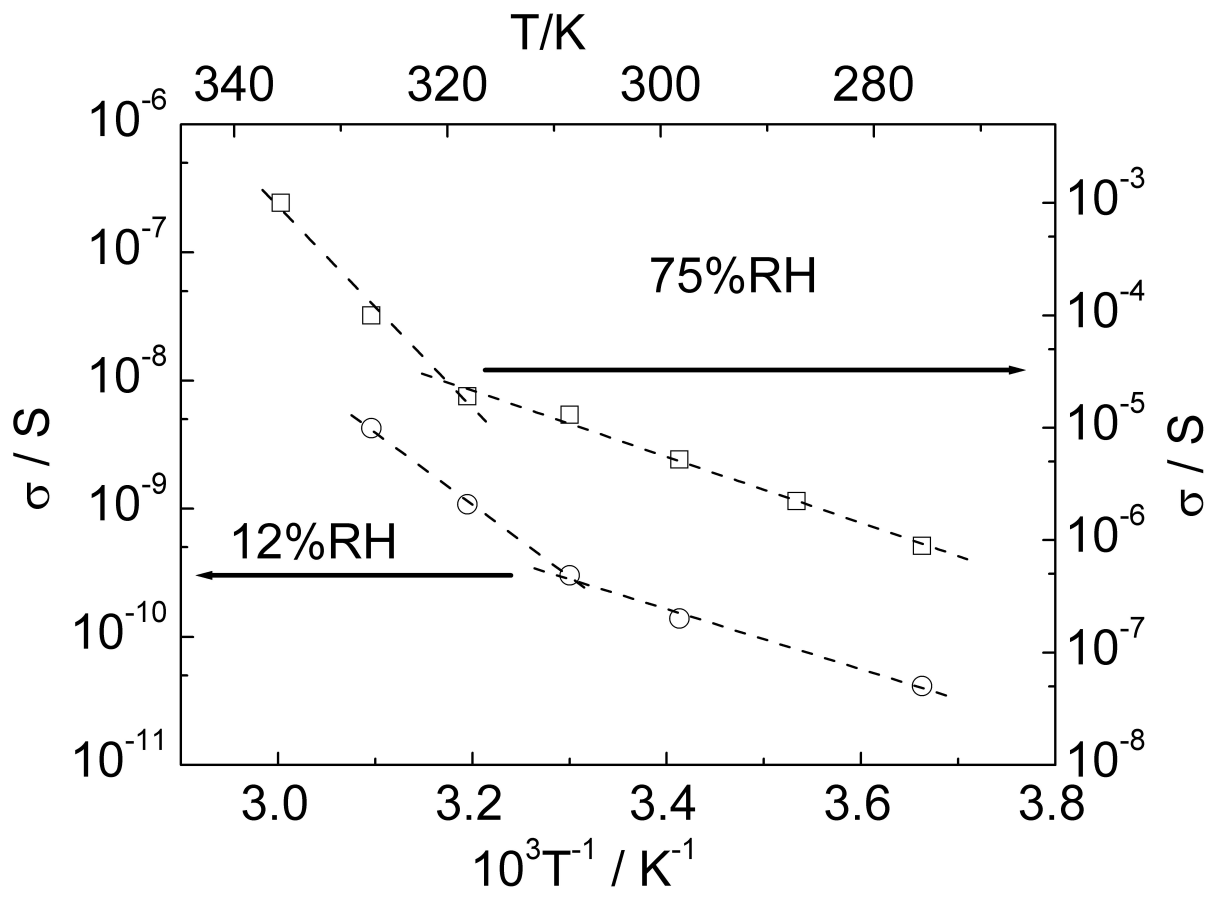


Fig. 5

