

HUMIDITY SENSING PROPERTIES OF PLASTICIZED CA-NH₄BF₄-PEG₆₀₀ THIN FILMS

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ABSTRACT

The fabrication of resistive-type humidity sensor based on CA-NH₄BF₄-PEG₆₀₀ plasticized polymer electrolytes film was prepared by using dip-coating method on a glass substrate. The electrical properties of the film are examined as a function of relative humidity (R.H) to clarify its potential as a humidity sensor. The sensor well-responded towards humidity showing that the resistance drops with the increase in relative humidity, thus confirmed that the resistive-sensor exhibits humidity-sensitive property. The sensor element has also been characterized in terms of the effect of applied frequency in the range of 100 Hz to 10 kHz. The values of resistance show the decrement with increasing in frequency. Apart from frequency dependence, the measurement has also been carried out at different temperature elevation between 30°C and 50°C. The value of resistance decreases with increasing temperature as a result of ion mobility enhancement at higher temperature. The temperature dependence of resistance obeys Arrhenius law and the activation energy decreases with increasing in relative humidity. These entire behaviours can be explained by the conduction process occurred in CA-NH₄BF₄-PEG₆₀₀ films.

Keywords: Dip-coating method; Plasticized polymer electrolytes; Resistive-type humidity sensor

INTRODUCTION

Humidity sensors have become increasingly important for a wide range of applications such as environmental humidity for air conditioning, meteorological services, electronic processing, etc [1,2]. Generally, a good humidity sensor has to fulfil the following requirements to satisfy the widest range of applications including high sensitivity, high accuracy, good linearity, large operating range of humidity and temperature, a short response time, good reproducibility, small hysteresis, good durability and long life, high resistance against contaminants, negligible temperature dependence, and low fabrication cost [3]. Commonly, there are two categories for the humidity sensors, which are capacitive type and resistive type [2]. These two sensors are depending on whether the sensor is designed for changes of capacitance measurements or resistance measurements. The introduction of polymer-based humidity sensors has captured more attention due to their interesting electrical properties, low cost, simple fabrication and high sensitivity [4-6]. However, the polymeric humidity sensitive materials are soluble in water, and their sensing properties are soon deteriorated under high humidity [7]. Yet, the intrinsic impedance of polymer as such cellulose derivatives is so high, thus exhibits very low ionic conductivity [8]. Therefore, it is necessary to modify the sensor's material so that it can be a promising material in the application of humidity sensor. This present work concerns on resistive type humidity sensor based on polymer electrolytes composed of cellulose acetate (CA) as host polymer, ammonium tetrafluoroborate (NH_4BF_4) as dopant salt, and polyethylene glycol (PEG_{600}) as plasticizer. Besides that, the sensor performance was also evaluated.

EXPERIMENTAL

Cellulose acetate (CA) with 39.8wt. % acetyl content obtained from Sigma-Aldrich has been used as a host polymer. Ammonium tetrafluoroborate (NH_4BF_4) and polyethylene glycols 600 (PEG_{600}) procured from Fluka were used as dopant salt and plasticizer respectively. Acetone was obtained from UNIVAR, Australia was employed as a solvent. The polymer electrolytes of CA- NH_4BF_4 - PEG_{600} as the sensor material were prepared by dissolving of 1.0 g of CA in 25 ml acetone for several hours until homogenous solution was obtained. The solution was then mixed with 0.333 g (25wt. %) of NH_4BF_4 and 0.507 ml (30wt. %) of PEG_{600} . The mixtures were then vigorously stirred until the salt and plasticizer completely dissolved. The prepared solution was deposited on a glass substrate of 7.5 cm x 2.5 cm in size by dip-coating method, followed by drying at ambient temperature, 30°C in the fume hood for a couple of days to obtain a smooth layer of thin film. Using the standard electrode template, the interpenetrating finger electrodes separated by 2.0 mm were coated on the prepared samples using sputter coating equipment (K550X Sputter Coater) (Figure 1). The resistance measurement of the sensor was performed in SH-221 Bench-Top Type Temperature & Humidity Chamber which the relative humidity is ramped from 40% RH to 90% RH at 1.0 V using HIOKI 3532-50 LCR Hi-tester in the frequency range between 100 Hz and 10 kHz at the temperature range between 30°C and 50°C.

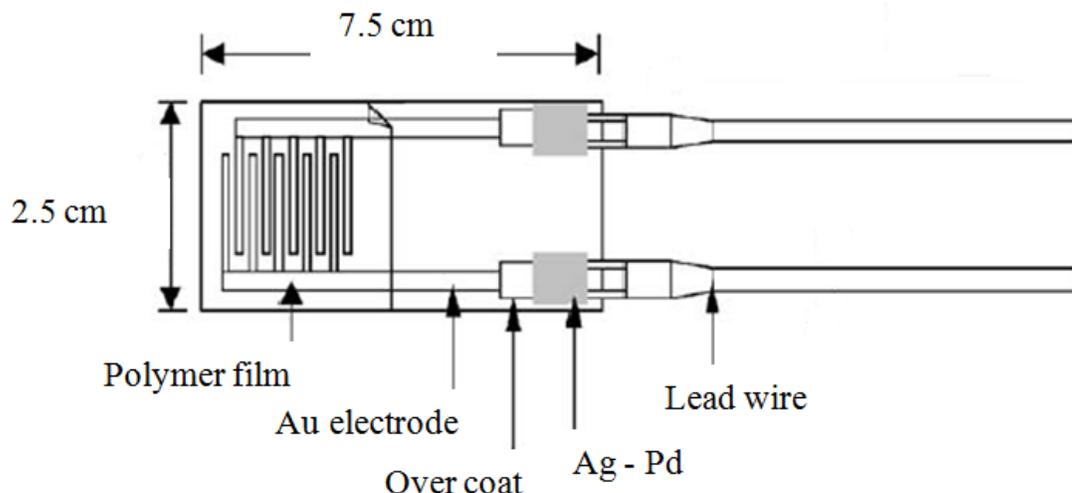


Figure 1: Schematic view of resistive-type humidity sensor

RESULTS AND DISCUSSION

Figure 2(a) shows the variation of conductivity as a function of NH_4BF_4 concentration at room temperature. The conductivity increases up to $2.18 \times 10^{-7} \text{ S cm}^{-1}$ when 25wt. % of NH_4BF_4 is added and then decreases with increasing salt concentration. The increase in conductivity in the first region is due to ion dissociation [9-11] while ion aggregates takes place in region II caused the conductivity to drop [12,13]. In order to enhance the electrical conductivity of the highest conducting sample in the CA- NH_4BF_4 system, plasticizers are added as shown in Figure 2(b). The conductivity of this system increases with increasing PEG₆₀₀ concentration and reaches maximum value of $1.41 \times 10^{-5} \text{ S cm}^{-1}$ at 30wt. % PEG₆₀₀ and then decreases with further addition of PEG₆₀₀. Plasticizers help to enhance amorphous regions in the polymer matrix in which the ions are expected to be more mobile [12,14]. Regions I, II, III and IV represent ion dissociation, partial formation of ion pairing, redissociation of ion-pairs and ion aggregation, respectively [13]. Finally, the sensory performance was evaluated by using the best conductivity sample of plasticized CA- NH_4BF_4 -PEG₆₀₀ as a membrane in humidity sensor.

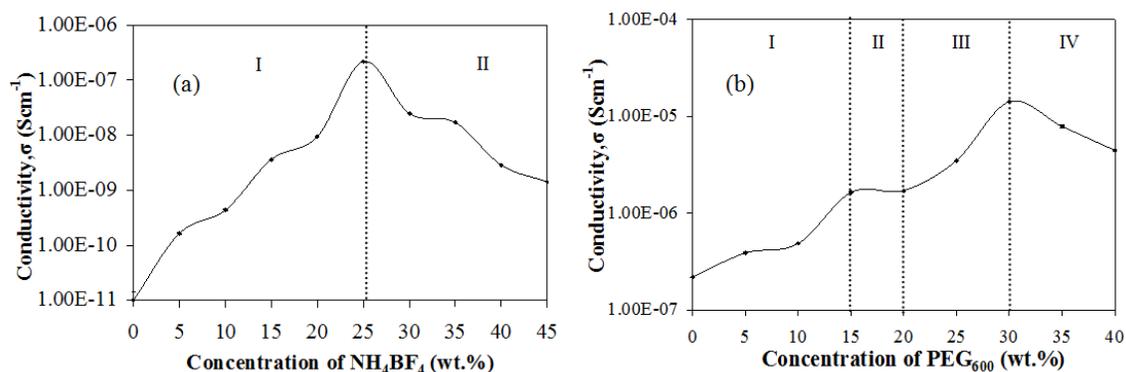


Figure 2: Conductivity at room temperature of (a) CA-NH₄BF₄ thin film (b) CA-NH₄BF₄-PEG₆₀₀ thin film

Figure 3 represents the curves of the resistance versus % R.H as a function at various temperatures at a voltage of 1 V for resistive-type sensor with a frequency of 100 Hz, 1 kHz and 10 kHz. Measurement of resistance is performed at temperature of 30°C, 40°C and 50°C as shown in the figures. The sensor response is highly dependent on the ambient temperature [15]. It can be observed that the resistance of the sensor decreased with temperature elevation as a result of enhanced ion mobility at higher temperature [7,16]. This result is also in accordance with the previous report [17], confirming that the decrease in resistance as the temperature rises is due to the thermal activation of the segment motion in polymer chains. More energy was provided for the motion of ions at higher temperature caused the resistance of the film decreased [18].

The temperature dependence of impedance at constant % R.H would give important information about the ion hopping transport inside the polymer and activation energies. Rubinger et al. [2] in his work has obtained Arrhenius activation with decreasing impedance with temperature, followed by an increase of the impedance at high temperatures due to the dehydration of the polymer film. As shown in Figure 4, similarly we found that the plots of log resistance against 1000/T between 40 and 90% R.H followed the Arrhenius equation with straight line plots. It is observed from the plots that the slopes of straight lines decrease with increasing % R.H from 40 to 90% as shown in Figure 4 (a) and (b) for the frequency of 100 Hz and 1 kHz, respectively. Meanwhile at 10 kHz as shown in Figure 4 (c), the slope of straight line increases at % R.H from 40 to 50%. Beyond 50% R.H, the slope starts to decrease. From the Arrhenius plot of resistance, the activation energy E_A is obtainable as shown in Figure 5, within investigated % R.H according to the equation $R=R_0 \exp (E_A / kT)$, where R is the parallel resistance, R_0 is the pre-exponential factor, k is Boltzman constant and T is the absolute temperature [16,19].

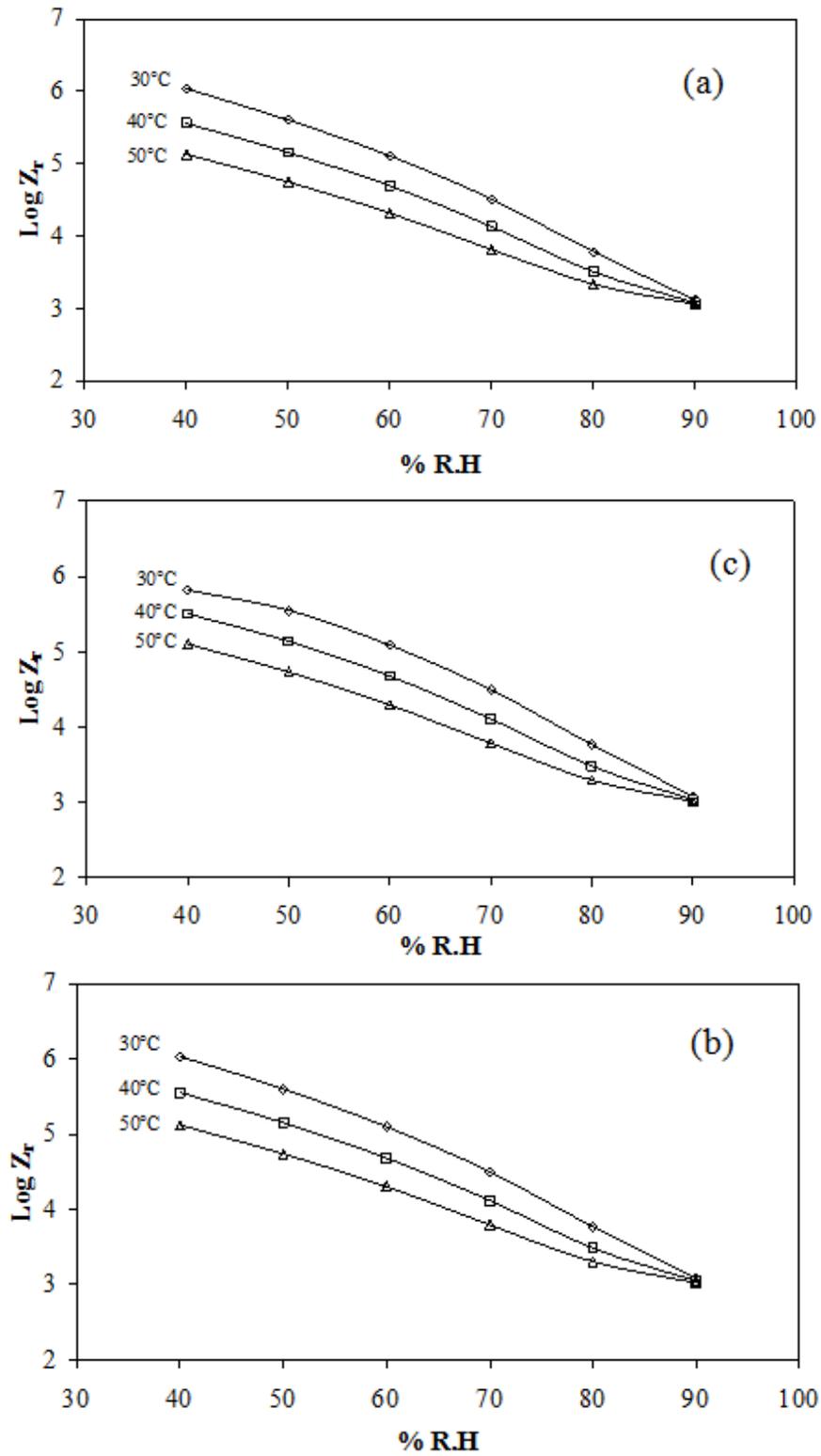


Figure 3: The resistance dependence on the relative humidity at frequency of (a) 100 Hz, (b) 1 kHz and (c) 10 kHz

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Figure 5 shows the plots of activation energy, E_A versus % R.H at three frequencies, viz. 100 Hz, 1 kHz and 10 kHz. It is observed that the E_A for the sensor decreased from 0.89 eV to 0.06 eV with an increase in relative humidity from 40% to 90% at frequency 100 Hz and 1 kHz. These entire behaviours can be explained by the conduction process occurred in CA-NH₄BF₄-PEG₆₀₀ films. At frequency 10 kHz, E_A seems to increase from 0.69 eV to 0.80 eV at 40% to 50% R.H, and then the E_A decrease continuously with rising of % R.H until 90% R.H with the minimum E_A value is 0.07 eV. The higher the frequency is, the more energy gained by water molecules to vibrate, and the frequency affected more at low humidity rather than the high one. The highest E_A occurs at 50% R.H is may be caused by the water molecules absorbed by the sensor has clogged the ionic mobility in CA-NH₄BF₄-PEG₆₀₀ films, which in turn decreases the conductivity. The water molecules absorbed at low humidity level are immobile [20], and the used of high frequency would not be quite sensitive for molecule water to vibrate since the optimum frequency is around 100 Hz to 1 kHz.

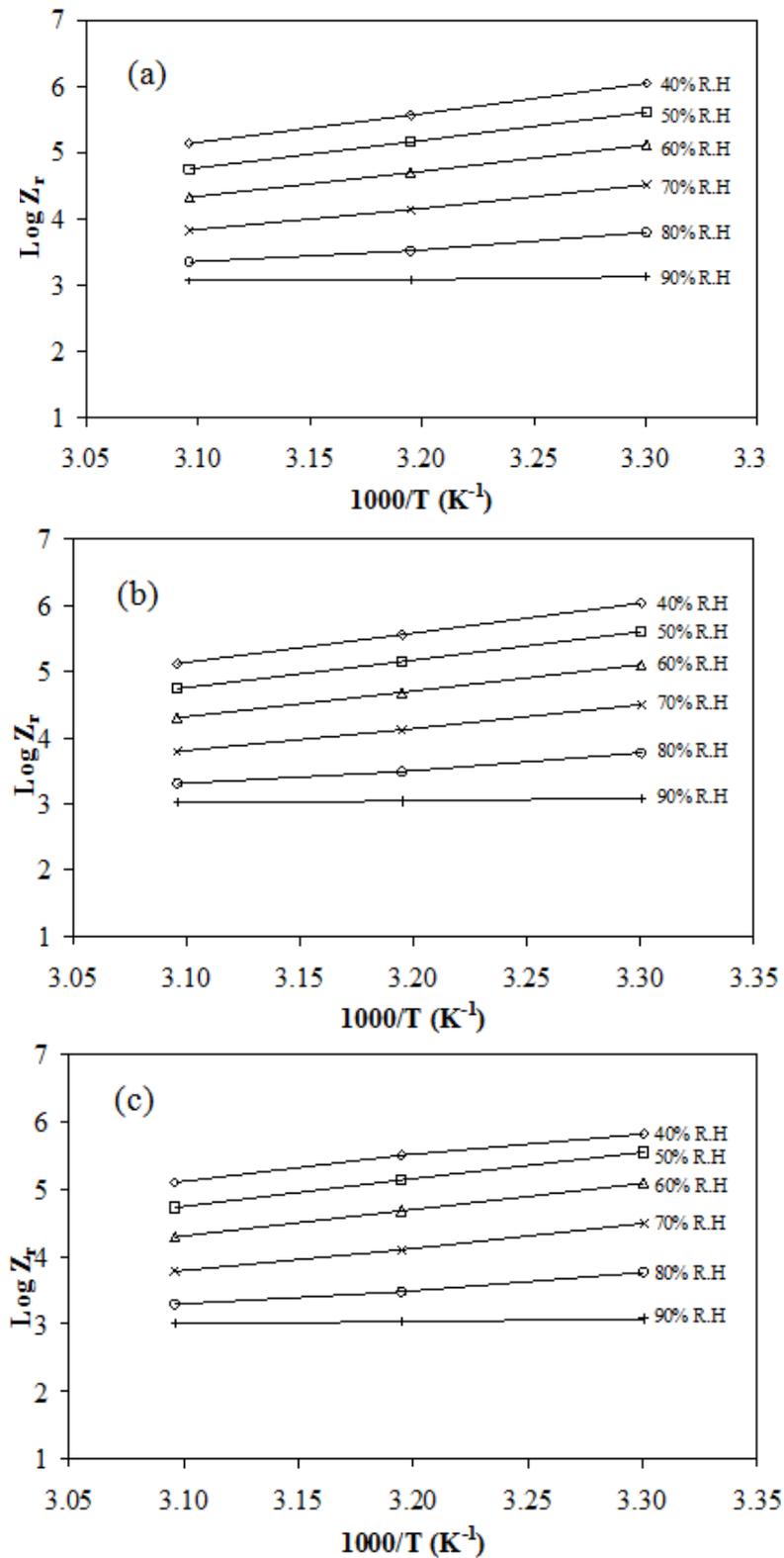


Figure 4: The temperature dependence of resistance at frequency of (a) 100 Hz, (b) 1 kHz and (c) 10 kHz

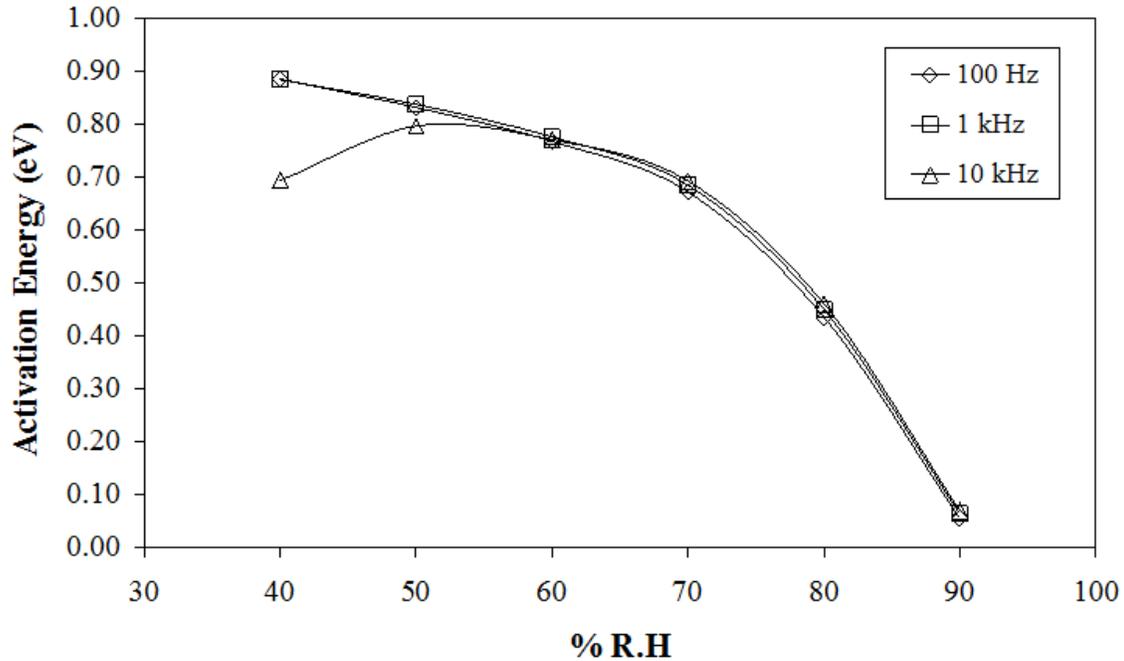


Figure 5: Activation energy for conduction as a function of relative humidity at different frequency

CONCLUSIONS

Resistive-type humidity sensor based on plasticized CA-NH₄BF₄-PEG₆₀₀ was successfully fabricated by using dip-coating method. The sensor resistance was found to respond well to R.H with a relatively good linearity and quite sensitive, though it depended on the applied frequency. The effect of applied frequency on resistance proved that the frequency influenced more at low R.H rather than high R.H. The temperature dependence of resistance obeys Arrhenius equation and the corresponding activation energy decreased as the R.H going higher at the frequency of 100 Hz and 1 kHz. The conduction process occurs inside the humidity sensor reveals that the effect of R.H at low humidity level is relatively less than the one at high R.H.

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