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Electrical and humidity-sensing properties of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole doped with both KOH and K_2CO_3 salts

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ABSTRACT

Novel impedance-type humidity sensors were made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with KOH and K_2CO_3 salts. The humidity-sensing properties of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole were improved by doping with two alkali salts (KOH and K_2CO_3), whose dissociation constants differed greatly from each other. The electrical properties of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with KOH or a mixture of KOH and K_2CO_3 were examined in detail and found to be functions of relative humidity (RH). Additionally, the effects of the salts on the sensing properties (linearity and sensitivity) were elucidated. The sensor that was made of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film exhibited favorable impedance, high sensitivity, good linearity, small hysteresis, a short response/recovery time, a weak dependence on temperature and high long-term stability over the humidity range studied. The sensing mechanism of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film was elucidated using impedance plots.

1. Introduction

Fabricating a high-performance humidity sensor is rather complicated. Such a sensor must have various properties, including a linear response, small hysteresis, high sensitivity, short response time, low power consumption, chemical and physical stability, a wide operating range of humidities and low cost. Recently, polymeric sensors have attracted considerable interest for their ability to measure humidity because they are light-weight, flexible, and low-cost, and they have a large surface area. Polypyrrole (PPy) and its composites are the most attractive conducting polymers for use in humidity sensors owing to their remarkable mechanical and electrical properties, ease of synthesis and favorable environmental stability [1–9].

Recently, N-substituted pyrrole derivatives have become increasingly important because they have become associated with a wide range of pharmacological and biological activities [10,11]. The most common methods for synthesizing N-substituted pyrrole derivatives involve the Paal–Knorr ondensation reaction of 1,4-diketones with amines using various catalysts such as *p*-toluenesulfonic acid [12], silica-supported antimony(III) chloride [13], polystyrene-supported $GaCl_3$ [14] and β-cyclodextrin [15]. Our previous work [16] described the fabrication of humidity sensors from 1-(4-aminophenyl)-2,5-dimethyl-1H-pyrrole and 1-(4-nitrophenyl)-2,5-dimethyl-1H-pyrrole films that were themselves fabricated using a Paal–Knorr reaction in an aqueous medium using β-cyclodextrin as a catalyst. Au nanoparticles (AuNPs) were added to the 1-(4-nitrophenyl)-2,5-dimethyl-1H-pyrrole film to reduce its high resistance at low humidity, favoring its practical application.

Some polymers that are doped with inorganic salts (polymer-salts) reportedly act as humidity sensors because inorganic salt dopants improve the sensing properties of polymer-salt complexes. Typical examples are poly(propargyl alcohol) that is doped with sulfuric acid [17,18], poly(*p*-diethynylbenzene-co-propargyl alcohol) that is doped with iron trichloride [19], poly(2-acrylamido-2-methylpropane sulfonic acid) that is doped with alkali salts [20] and poly(divinylbenzene) that is doped with LiCl [21]. Recently, Jiang et al. [22] fabricated a humidity sensor based on a conducting polymer (Pebax 2533) that was doped with LiCl using an electrospinning method. To the best of our knowledge, no humidity sensor that is based on N-substituted pyrrole derivatives that are simultaneously doped with two salts with greatly different dissociation constants has yet been fabricated. This work fabri-

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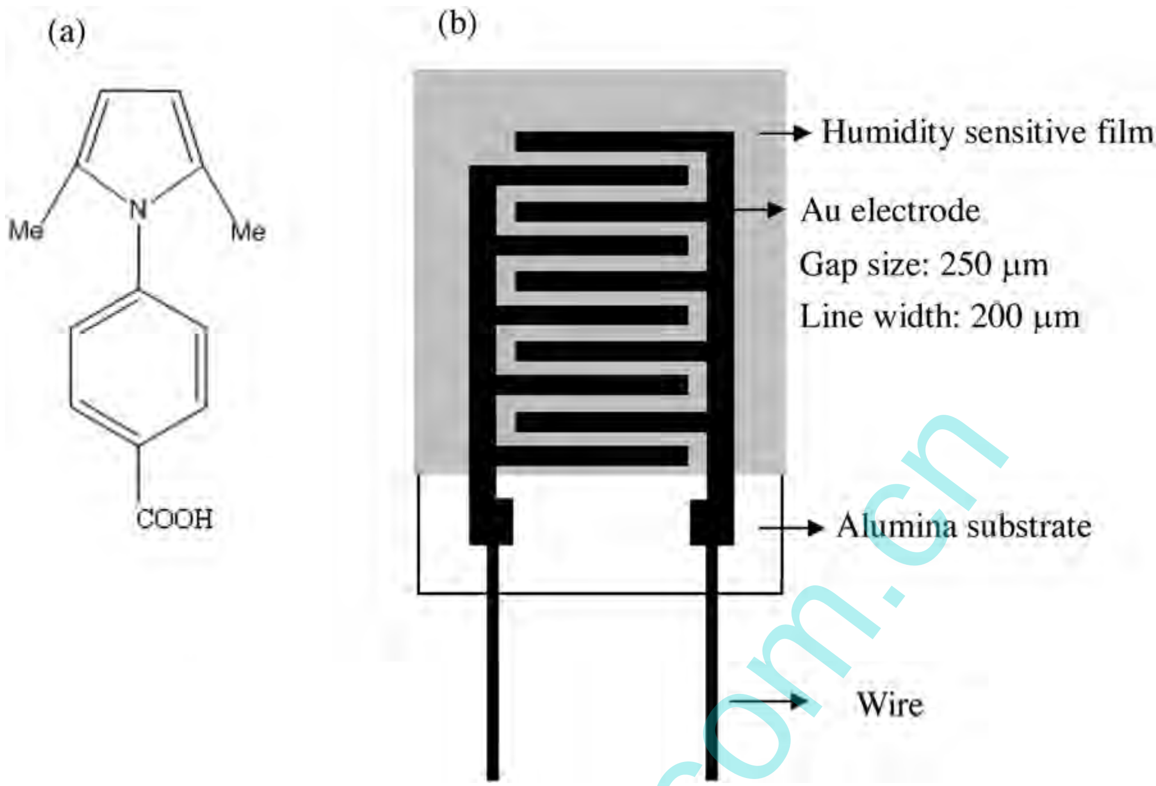

Fig. 1. (a) Chemical structures of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole; (b) structure of humidity sensor.

Table 1
Sensitivity and linearity of humidity sensors that were made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole differently doped with KOH and K_2CO_3 salts.

Sample number	Doped KOH (M)	Doped K_2CO_3 (M)	Impedance (MΩ)[a]	Sensing curve	
				Sensitivity (log Z/%RH)[b]	Linearity (R^2)[c]
1	0	0	223	−0.0059	0.8965
2	0.01	0	200	−0.0694	0.8656
3	0.1	0	0.036	−0.0268	0.8025
4	0.2	0	0.0085	−0.0191	0.7082
5	0.1	0.1	0.091	−0.0296	0.8444
6	0.1	0.2	0.244	−0.0351	0.9259
7	0.1	0.5	1.2	−0.0452	0.9311
8	0.1	1.0	45.6	−0.0555	0.9459

[a] Impedance was obtained at 20% RH.
[b] Sensitivity was defined as the slope of the logarithmic impedance versus relative humidity plot in the range 20–90% RH.
[c] Linearity was shown as the correlation coefficient of the logarithmic impedance versus relative humidity plot in the range 20–90% RH.

cates and characterizes impedance-type humidity sensors that are based on 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole films whose ionic conductivity is modified by simultaneously doping with KOH and K_2CO_3, which have differing dissociation constants. The process described herein for fabricating impedance-type humidity sensors is simple and reduces labor cost. The electrical properties of the composite 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts films were studied as functions of RH, with special emphasis on sensitivity and linearity. The films were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Complex impedance spectra were used to elucidate the role of ions in the conductance of the composite film of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts composite film. The humidity-sensing characteristics of the film, including sensitivity, hysteresis, response time, recovery time, effect of ambient temperature and long-term stability, were also studied.

2. Experimental

2.1. Materials

2-5-Hexanedione (Sigma-Aldich), 4-aminobenzoic acid (Sigma-Aldrich), β-cyclodextrin (TCI) and polyvinylpyrrolidone (PVP, average mol wt. 40,000, Sigma-Aldich) were used without further purification. All used deionized water (DIW) was prepared using a Milli-Q Millipore (Bedford, MA, USA) purification system, and the resistivity of water was above 18.0 MΩ cm^{-1}.

2.2. Preparation of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole using Paal–Knorr reaction

The preparation of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole was prepared using the method in the literature [15]. 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole was synthesized by mixing 2-5-hexanedione (0.6 mmol), 4-aminobenzoic acid (0.5 mmol) and β-cyclodextrin (10 mol%) in H_2O (3 mL), and then

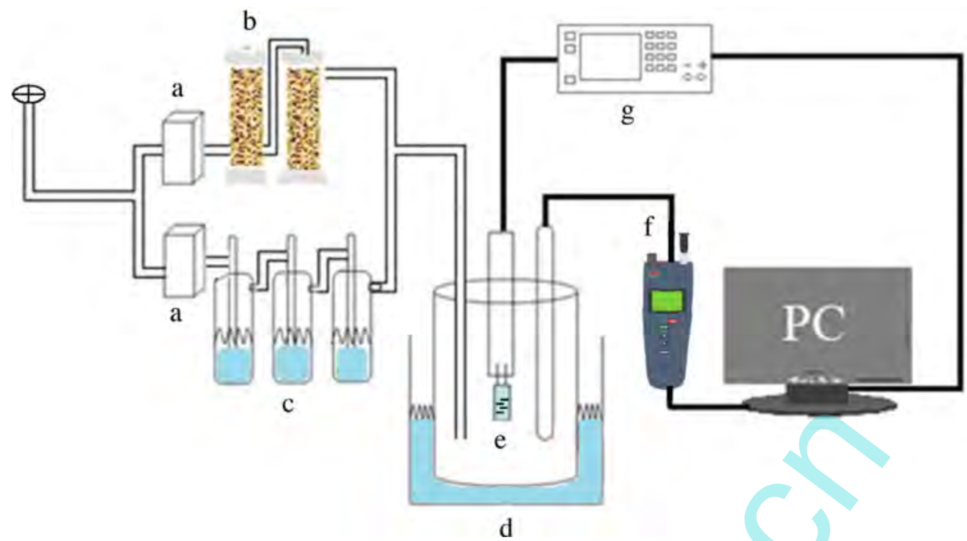

Fig. 2. Schematically plots the impedance measurement of sensors and the humidity atmosphere controller. (a) mass flow controller; (b) molecular sieve and desiccating agent; (c) water; (d) controlled temperature detection chamber; (e) humidity sensor; (f) hygrometer; (g) LCZ meter.

stirring the mixture for 24 h at 60 °C. After the reaction had run to completion, the aqueous phase was extracted using ethyl acetate. Fig. 1(a) plots the chemical structure of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole. Yield 90%; ^{1}H NMR ($CDCl_3$) δ 8.229–8.216 (d, J = 7.8, 2H, ArH), 7.336-7.323 (d, J = 7.8, 2H, ArH), 5.940 (2H, pyrrole), 2.067 (6H, Methyl) (presented in Fig. S1).

2.3. Fabrication of humidity sensors

Fig. 1(b) schematically depicts the structure of the humidity sensor. The interdigited gold electrodes were made on an alumina substrate by screen-printing method. The precursor solution of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts was prepared by adding the two inorganic salts into 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole solution at the compositions given in Table 1, with a small amount of PVP as an interface modifier. Then, 20 μL of the precursor solution of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts was drop-coated onto alumina, which were then thermally treated at 60 °C for 0.5 h in air.

2.4. Instruments and analysis

The surface microstructure of the thin film that was coated on an alumina substrate was investigated using a scanning electron microscope (SEM, Hitachi, TM3030Plus) and an atomic force microscope (AFM, Ben-Yuan, CSPM 4000) in tapping mode which the horizontal and vertical resolution are 0.26 and 0.10 nm, respectively. Structure of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole were verified by infrared spectrometer (Nicolet 380) and NMR. The impedance of the sensor was measured as a function of RH using an LCR meter (Philips PM6306) in a test chamber under the conditions of a measurement frequency of 1 kHz, an applied voltage of 1 V, an ambient temperature of 25 °C. As shown in Fig. 2, a divided humidity generator was used as the principal facility for producing the testing gases. The required humidity was produced by adjusting the proportion of dry and humid air generated by the divided flow humidity generator under a total flow rate is 10 L/min. The model of two mass flow controller's (Hastings) and flow display power-supply used is the Protec PC-540 manufactured by Sierra Instruments Inc, as described elsewhere [23]. The RH values were measured using a calibrated hygrometer (Rotronic) with an accuracy of ±0.1% RH.

3. Results and discussion

3.1. Characterization of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts composite films

3.1.1. Microstructure of surface

Fig. 3 presents the AFM images of the films of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole, 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with KOH and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with both KOH and K_2CO_3 on alumina substrates. The root mean square (RMS) roughness of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film, the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film that was doped with KOH and the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film that was doped with both KOH and K_2CO_3 were 63.4, 2.53 and 1.82 nm, respectively. Both 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film doped with KOH and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film doped with both KOH and K_2CO_3 exhibited smooth surfaces with similar values of roughness.

Fig. 4 presents SEM images of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film, the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film doped with KOH and the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film doped with both KOH and K_2CO_3. The surface of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole was rough and the film had a dendrite structure (Fig. 4(a)). Both the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film doped with KOH and the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film doped with both KOH and K_2CO_3 had smoother surfaces than did the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film.

3.1.2. IR spectra

Fig. 5(a) shows the FT-IR results of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole. The characteristic vibrations of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole included a peak at 3380 cm^{-1} attributable to the O—H stretching vibration, a peak at 1723 cm^{-1} attributable to the C=O stretching vibrations, peaks at 1600, 1499, 1250–1000 and 770–700 cm^{-1}, corresponding to the aromatic C—C stretching, C—N stretching of the pyrrole ring, aromatic C—H in-plane bending and

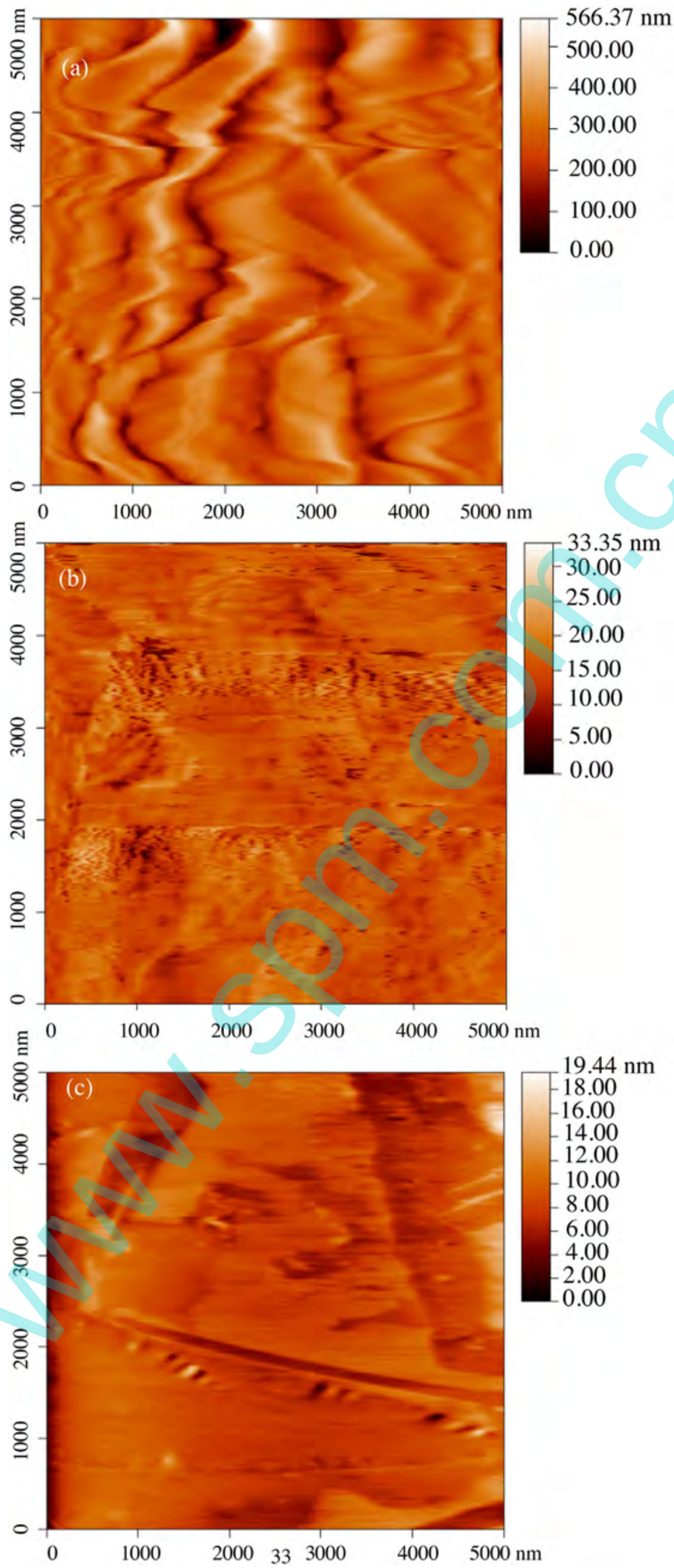

Fig. 3. AFM images of (a) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole; (b) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with KOH and (c) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with both KOH and K_2CO_3.

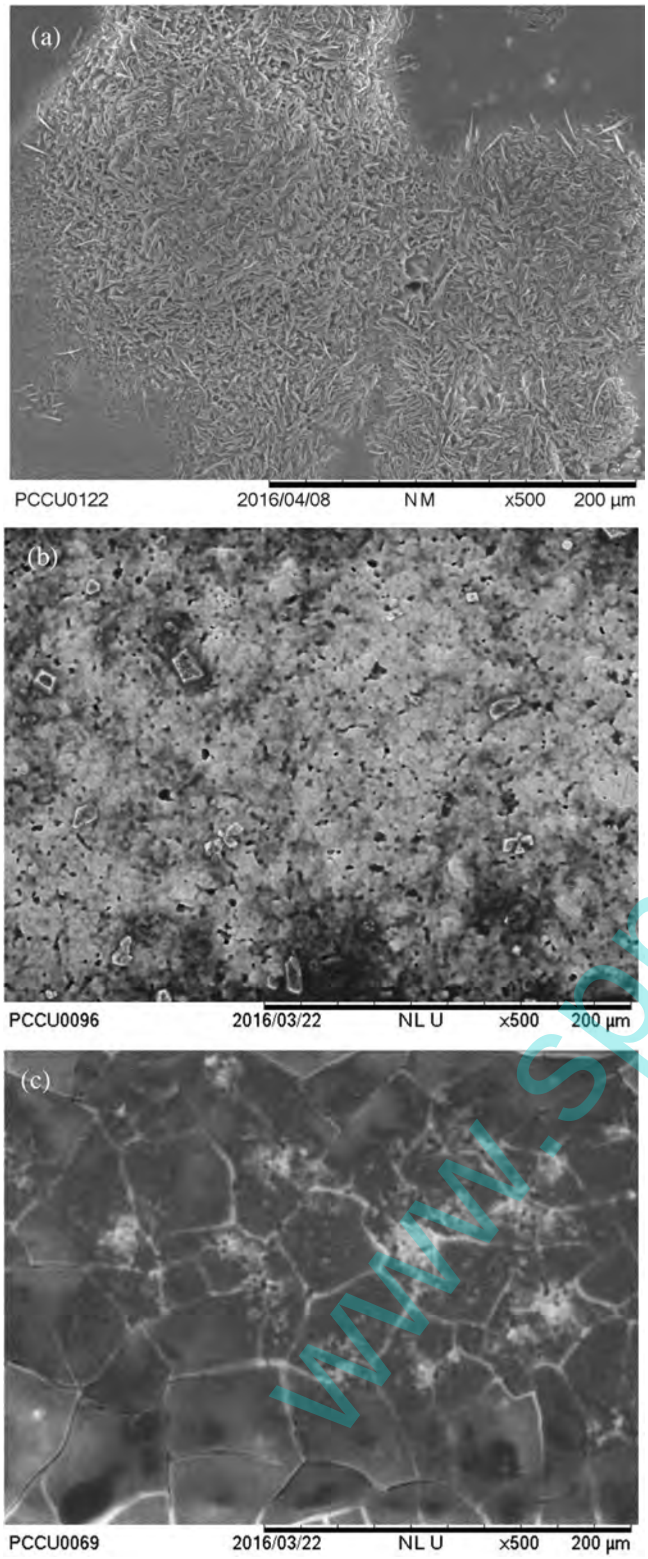

Fig. 4. SEM images of (a) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole; (b) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with KOH and (c) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with both KOH and K_2CO_3.

aromatic C—H out-of-plane bending, respectively. These results confirm that the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole was successfully synthesized by Paal–Knorr reaction. After formation of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 polymer-salts no new peak was observed (Fig. 5(b)), indicating that the salts did not destroy the structure of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole.

3.2. Electrical and humidity-sensing properties of humidity sensors made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts composite films

3.2.1. Alkali salts of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole composite

Fig. 6 plots the impedances of the alkali salts in the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole composite film as functions of relative humidity. The measurements were made at 25 °C, an AC voltage of 1 V, and a frequency of 1 kHz. The 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film (sample 1), (inset in Fig. 6), exhibited only a small change in impedance over the range of humidities studied, because its impedance was so high. To reduce this high impedance and to improve the sensitivity and linearity of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film for practical use, a composite material of alkali salts and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole was prepared. The impedance value of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salt varied with the species of salt, following the order K salt < Na salt < Li salt. This order is the same as that of equivalent conductance of the corresponding alkali ions at infinite concentration. Therefore, the ions dominated the electrical conduction of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts. The sensitivity of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts composite films exceeded that of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film, perhaps because alkali salts are strong electrolyte, the dissociation of ions increased, presenting a high charged density on 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-salts composite films, and thereby improved the sensitivity of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film. Moreover, the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole doped only with KOH had a highest conductance but lower sensitivity and linearity than those of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole doped only with LiOH or NaOH. In order to get higher sensitivity and better linearity of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH composite film in a wider humidity range, the optimum doping of KOH and the adding of both KOH and K_2CO_3 salts were investigated.

3.2.2. 1-(4-Carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole doped with single KOH

Fig. 7 plots the effect of amount of added KOH on the impedance of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH composite film as a function of relative humidity, and Table 1 summarizes the results concerning sensitivity (defined as the slope of the logarithmic impedance (log Z) as a function of%RH), linearity (given by a correlation coefficient that is defined as the R-squared value of the fitted line from 20 to 90% RH) and impedance. The impedance decreased as the amount of KOH dopant increased (samples 2–4). Both sensitivity and linearity decreased as the amount of KOH dopant increased. Sample 2 had the highest impedance (about 200 MΩ) at low humidity (20% RH), making it unsuitable for use at low humidity. When the amount of added KOH exceeded 0.1 M (samples 3 and 4), almost no impedance change was observed with RH in the range of 60–90% RH because the KOH was completely dissociated in a highly humid atmo-

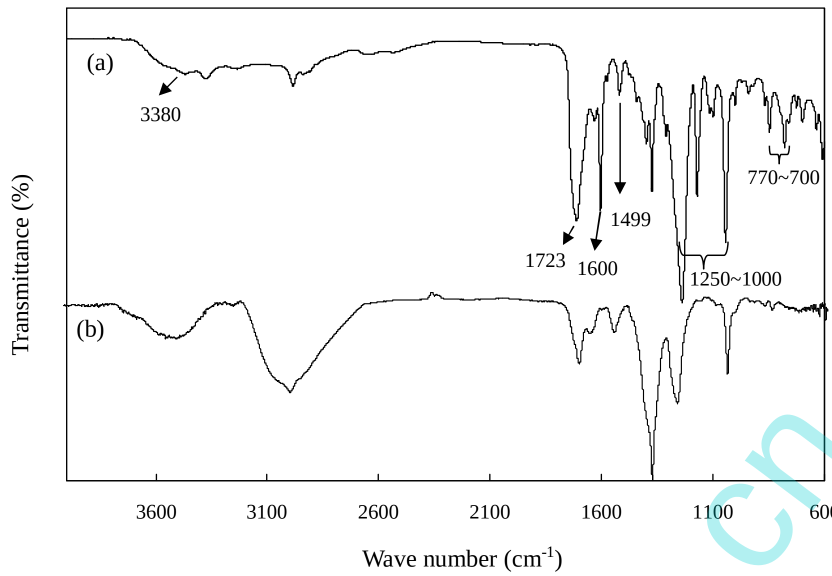

Fig. 5. IR spectra of (a) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole and (b) 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with both KOH and K_2CO_3.

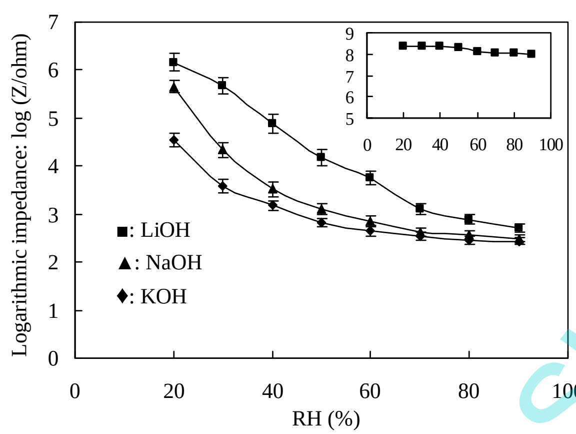

Fig. 6. Impedance versus relative humidity for humidity sensors that were made of alkali salts in 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film, measured at 1 V, 1 kHz and 25 °C. Inset: impedance versus relative humidity for 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film.

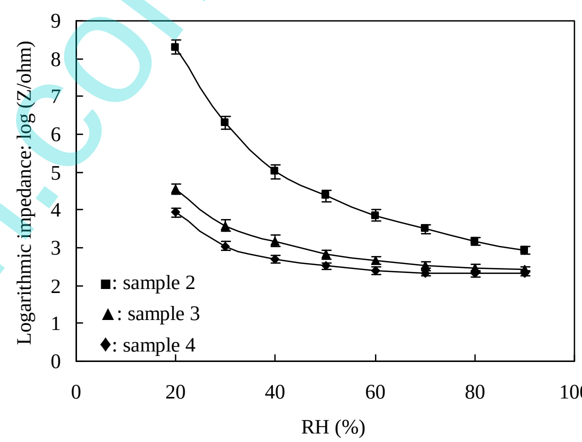

Fig. 7. Impedance versus relative humidity for humidity sensors that were made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole doped with various amounts of added KOH.

sphere. The poor sensitivity and linearity of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH composite film (sample 3) was improved by further doping of K_2CO_3.

3.2.3. 1-(4-Carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole simultaneously doped with two salts (KOH and K_2CO_3)

Fig. 8 plots the variations in impedance with%RH of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole that was doped with both KOH and K_2CO_3; Table 1 presents the results concerning the sensitivity, linearity and impedance of humidity sensing using these materials. Both sensitivity and linearity increased with the amount of added K_2CO_3 (samples 5–8). The formation of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 polymer-salts increased the impedance of the film over a wide range of RH, suggesting higher sensitivity, and improved linearity of the response curve. The impedance values increased with increasing the dosage of K_2CO_3 because of aggregations of ions at high concentrations [24]. Additionally, as described in Section 3.1.1, the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film had a rougher surface than did the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 films. Therefore, the fact that the sensitivity of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH and 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 films exceeded that of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film was related not to surface morphology, but to the fact that the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film was doped with salts, increasing the local polarity by the dissociation of ions, causing water molecules to be more strongly adsorbed, improving the sensitivity of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole film. Sample 8 had the higher impedance (about 45.6 MΩ) at low humidity (20% RH) than that of sample 7, making it unsuitable for use at low humidity. Therefore, the sensing mechanism and humidity-sensing properties of sample 7 were studied because the sample 7 had the acceptable sensitivity (slope = −0.0452 log Z/%RH) and linearity (R^2 = 0.9311) over the humidity range 20–90% RH, and a favorable impedance value (1.2 MΩ at 20% RH) for practical use at low humidity (Table 1).

3.2.4. Complex impedance

Impedance spectroscopy is a powerful method for elucidating the conduction mechanisms of humidity sensors. Therefore, the obtained impedance plots were used to identify the mechanism of conduction in the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film. Fig. 9(a)–(d) present the obtained complex impedance spectra of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film at various humidities. The impedance measurements were made at frequencies from 50 Hz to 100 kHz, relativity humidities from 20 to 90% RH, an AC voltage of 1 V and a temperature of 25 °C. In the impedance spectra, Z_r is the real part of the impedance Z, which is plotted on the real axis, and Z_i is the imaginary part of Z, which is plotted on the imaginary axis. At low humidity (20% RH), a semicircular impedance plot of the film was obtained. This film was modeled as an equivalent parallel circuit that included a resistor and a capacitor, as proposed elsewhere [25–27]. As RH increased to 40–70% RH, an inclined line appeared on the impedance plot at low frequencies whose length increased with RH. The plot of impedance finally became a straight line at 90% RH. The straight line represents Warburg impedance, which was established by the diffusion of ions across the interface between the electrode and the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film [25–28]. Therefore, firstly, upon the adsorption of water, a thin liquid layer forms around the polymer chains or fills the openings in sensing polymer films through capillary condensation or swelling. The adsorbed water improves the electrolytic dissociation of the inorganic salts in the polymer-salts complexes. Finally, the water acts as a plasticizer, which increasing the mobility of the dissociated ions (K^+ and H_3O^+). Therefore, the dissociation and activity coefficient of the inorganic salts help to explain the variations in conductance that was observed upon doping with KOH and K_2CO_3. KOH is well known to have a very high dissociation constant (6.63×10^{10}) [29,30], so KOH is dissociated completely at high humidity. The dissociation constant (1.50) of K_2CO_3 is lower than that of KOH [29,30], so K_2CO_3 does not dissociate completely at low humidity. Therefore, incorporating both KOH and K_2CO_3 into 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole-based composites is important for the detecting humidity over a wide range.

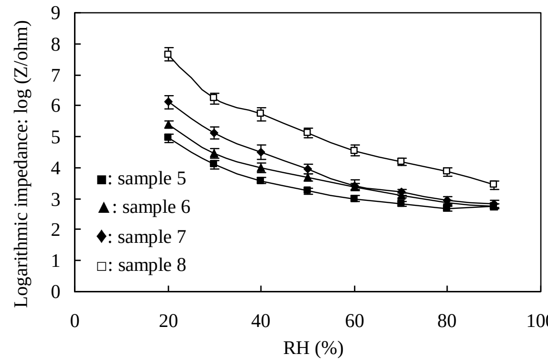

Fig. 8. Impedance versus relative humidity plots for humidity sensors that were made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole co-doped with KOH and K_2CO_3 at different dosages.

3.2.5. Humidity-sensing properties

Fig. 10 plots the log-impedance of the humidity sensor versus RH. The measurements were made at 25 °C, an AC voltage of 1 V, and a frequency of 1 kHz. The open symbols in the figure represent measurements made during desiccation, while the solid symbols represent those made during humidification. As RH increased from 20 to 90% RH, the impedance fell from 10^5 to 10^3 Ω and the curves exhibited a satisfactorily linear relationship ($Y = -0.0452X + 6.5181$; $R^2 = 0.9311$) between log-impedance and RH. The hysteresis (between humidification and desiccation, measured over an RH range of 20–90%) was less than 2.9% RH. Fig. 11 plots the log-impedance of the humidity sensor versus

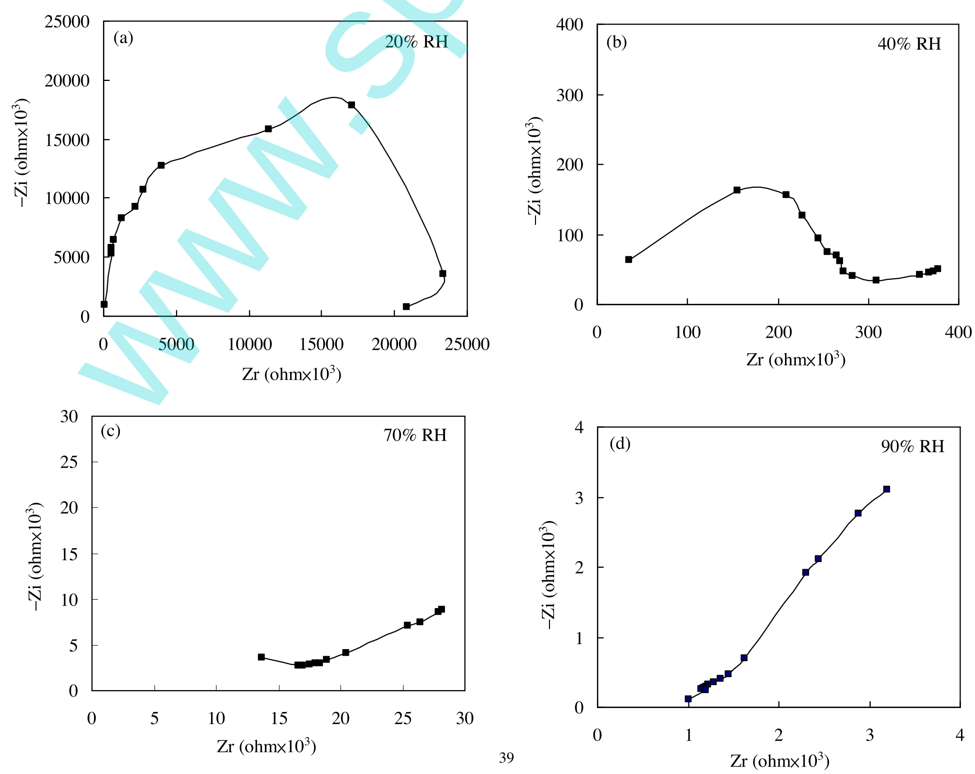

Fig. 9. Complex impedance plots of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film at (a) 20% RH; (b) 40% RH; (c) 70% RH and (d) 90% RH.

Table 2
Humidity sensor performance of this work compared with the literatures.

Sensing material	Working range (%RH)	Sensitivity (log Z/%RH)[a]	Hysteresis (%RH)	Response time (s)	References
N-substituted pyrrole[b]/KOH/K_2CO_3	20–90	0.0452	<2.9	56	This work
AuNPs/N-substituted pyrrole[c]	30–90	0.0743	<1	52	[16]
TiO_2 NPs/polypyrrole	30–90	0.0306	<3	40	[2]
PAMPS[d]/NaCl/K_2CO_3	20–90	0.0260	<8	60	[31]

[a] The sensitivity shown as the slope of the sensing curve in the working range.
[b] 1-(4-Carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole.
[c] 1-(4-Nitrophenyl)-2,5-dimethyl-1H-pyrrole.
[d] PAMPS: poly(2-acrylamido-2-methylpropane sulfonate).

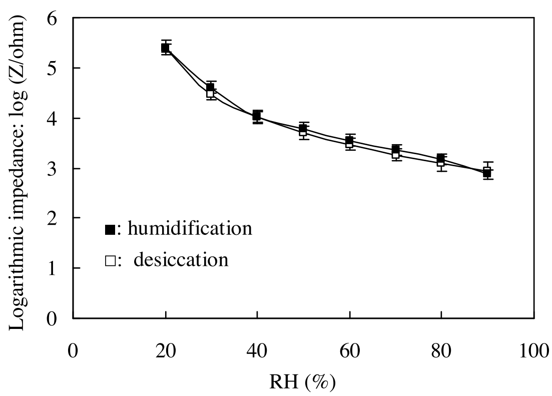

Fig. 10. Impedance versus relative humidity for sample 7, measured at 1 V, 1 kHz and 25 °C.

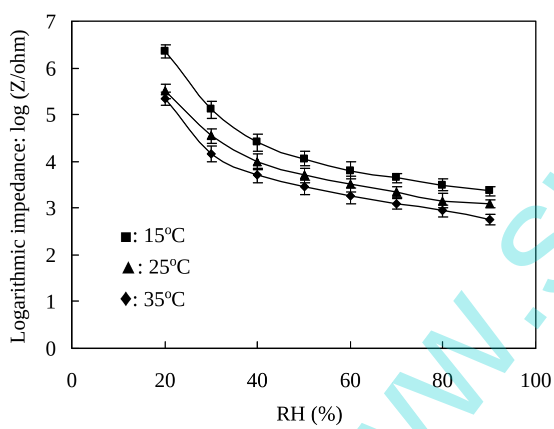

Fig. 11. Impedance versus relative humidity for sample 7 at various temperatures, measured at 1 V and 1 kHz.

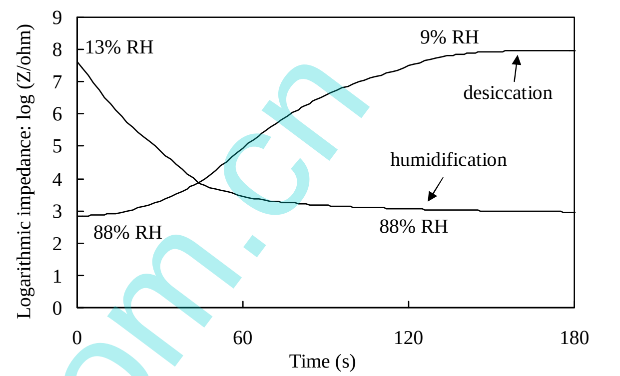

Fig. 12. Response-recovery properties of sample 7, measured at 1 V, 1 kHz and 25 °C.

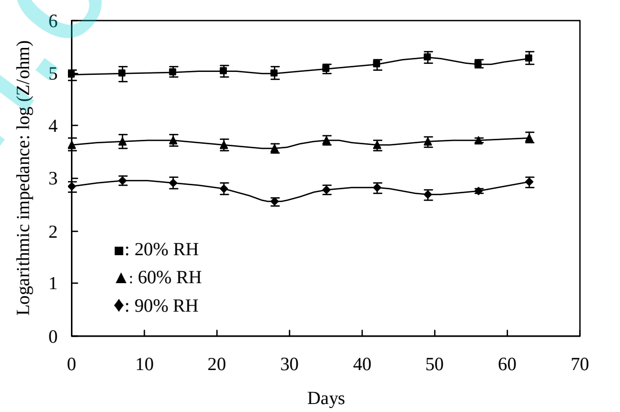

Fig. 13. Long-term stability of sample 7, measured at 1 V, 1 kHz and 25 °C.

temperature. As the temperature increased, the RH characteristic curve shifted to lower impedance. The mean temperature coefficient at 15–35 °C was −0.08% RH/°C over the humidity range 20–90% RH. The temperature-dependent nature of impedance may be compensated by designing a temperature sensor on the module. Fig. 12 plots the response and recovery of the humidity sensor, measured at 25 °C and 1 kHz. The response time ($T_{res.95\%}$) is defined as the time required for the impedance of the sensor to change by 95% of the maximum change following humidification from 13 to 88% RH. The recovery time ($T_{rec.95\%}$) is defined as the time required for the sensor to recover 95% of the maximum change in impedance following desiccation from 88 to 9% RH. The response time ($T_{res.95\%}$) and recovery ($T_{rec.95\%}$) time of the sensor were 56 and 115 s, respectively. Fig. 13 plots the long-term stability. The impedance of the humidity sensor did not vary significantly for at least 63 days at tested RH values of 20, 60, and 90% RH. Table 2 compares the humidity sensing properties of the presented humidity sensor with those in our earlier studies [2,16,31]. The developed humidity sensor that was made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 exhibited a wider range of working humidities than the sensor that was made of AuNPs/1-(4-nitrophenyl)-2,5-dimethyl-1H-pyrrole. AuNPs/1-(4-nitrophenyl)-2,5-dimethyl-1H-pyrrole had a higher sensitivity than that of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 but it had high impedance (about 55.2 MΩ at 30% RH), making it unsuitable for use at low humidity (<30% RH). Moreover, the humidity sensor that was made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 was more sensitive than the sensors that were made of TiO_2 NPs/polypyrrole or poly(2-acrylamido-2-methylpropane sulfonate)/NaCl/K_2CO_3.

4. Conclusions

By simultaneously doping the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole with KOH and K_2CO_3, its humidity sensing properties (sensitivity and linearity) were markedly improved.

For practical use over a wide range of humidities, two inorganic salts with different dissociation constants had to be incorporated: KOH completely dissociated at high humidity, whereas K_2CO_3 did not dissociate completely at low humidity. Therefore, these ions contribute to the conductivity of the 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film. The humidity sensor that was made of 1-(4-carboxylic acid phenyl)-2,5-dimethyl-1H-pyrrole/KOH/K_2CO_3 composite film exhibited good sensitivity and acceptable linearity ($Y = -0.0452\ X + 6.5181$; $R^2 = 0.9311$) between logarithmic impedance (log Z) and RH in the range 20 to 90%, negligible hysteresis (within 2.9% RH), a short response time (56 s), a short recovery time (115 s), and good long-term stability (63 days at least), measured at 1 V, 1 kHz and 25 °C. The effect of temperature between 15 and 35 °C on the response was −0.08% RH/°C at 20 to 90% RH.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2016.09.027.

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