复阻抗法分析聚吡咯材料的湿敏特性

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摘要: 通过延长聚合时间到 96 h 合成了一种对湿度敏感的聚吡咯材料. 采用红外(IR)光谱, X 射线衍射(XRD)和扫描电子显微镜(SEM)的方法对合成的材料进行了表征. 测量了基于该材料的湿敏元件的湿度特性, 并且得到了在 20 Hz–100 kHz 频率范围内的复阻抗谱图. 基于测量结果讨论了该材料制备的湿敏元件的湿度敏感机制. 通过对复阻抗谱的分析研究了该湿敏元件的工作机理并且分析了参与导电的粒子.

关键词: 聚吡咯; 湿敏元件; 复阻抗

中图分类号: O646; O694

Complex Impedance Analysis of the Humidity Sensing Properties of Polypyrrole

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Abstract: Polypyrrole was obtained by chemical synthesis. The extension of polymerization time to 96 h produced a polypyrrole that was suitable for absorbing moisture. The structure and morphology of polypyrrole were characterized by infrared (IR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Properties of this humidity sensor were investigated and complex impedance plots were obtained from 20 Hz to 100 kHz. The sensing mechanism was discussed based on test results. Using complex impedance analysis we studied the working principle of the humidity sensor and confirmed the identity of the conductive particles.

Key Words: Polypyrrole; Humidity sensor; Complex impedance

Humidity is ever-existing in our environment, and its monitoring and control have been of great concern in industrial and agricultural production, environmental protection, meteorology, etc.^[1–5]. More attention has been paid on humidity sensors in electronic control systems^[6–10]. Therefore, the relative humidity measurements have been extensively studied and remarkable progress has been achieved^[11]. Based on the widely applications of humidity sensors, different humidity sensors are popularly studied. Various kinds of materials can be used as humidity

sensing materials, such as ceramics^[12], polymer^[13,14], and some composite materials^[15,16]. The humidity sensors can be divided into resistive and capacitive types according to the working principle of the sensor. In recent years, polypyrrole (PPY) has been reported by many authors, due to its excellent properties both in humidity sensor^[17–19] and gas sensor^[20,21]. Compared with other polymer materials, PPY has high conductivity, small humidity hysteresis, and good linearity. PPY also has more environmental stability and quick response-renew property than inorganic materials.

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We made a resistive-type humidity sensor based on PPY, and studied PPY's humidity sensing properties related on polymerization time before^[22]. It was found that the humidity sensing properties could be improved greatly by extending polymerization time. In this paper, we analyze the complex impedance plots to study the humidity sensing property of PPY.

1 Experimental

1.1 Growth of PPY

PPY was obtained by chemical synthesis. Pyrrole (Alfa Aesar, 98%) was distilled under reduced pressure before use. Anhydrous ethanol (Beijing Chemical Plant, A.R.) was used as a solvent for the PPY synthesis. A hydrated ferric chloride ($\text{FeCl}_3 \cdot \text{H}_2\text{O}$, Beijing Chemical Plant, 98.5%) was used as an oxidant for chemical polymerization of PPY. The main process was as follow: 3.4 mL of pyrrole was dissolved into 25 mL of ethanol and stirred for 10 min. 25 mL of $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ ethanol solution was added dropwise to the ethanol solution of pyrrole. The mixed solution was magnetic stirred for 96 h at room temperature. The resulted solution was filtered and washed three times with ethanol, then dried in a vacuum box overnight.

1.2 Methods of characterization

The X-ray power diffraction (XRD) patterns were collected on a Siemens D-5005 diffractometer (Siemens AG, Karlsruhe, Germany) using $\text{Cu-K}\alpha$ radiation at 40 kV and 30 mA. Infrared spectra were taken on a Perkin-Elmer series with a resolution of 4 cm^{-1} . The samples were prepared in a form of KBr pellet, the thickness of the pellet was about 1.3 mm. Each spectrum was collected at room temperature under atmospheric pressure. The morphology of products was characterized by a JEOL JSM-6700F field emission scanning electron microscope (SEM). The humidity sensing property was tested by the ZL-5 model LCR analyzer (Shanghai Instrument Research Institute, China).

1.3 Humidity sensor fabrication

The PPY powder was mixed with ethanol to form paste, and then the paste was screened on the Al_2O_3 substrate with 5 pairs of interdigitated electrodes. The structure of the humidity sensor was showed in Fig.1. The electrical signal was applied on the sensing film by the interdigitated electrodes. The device was dried under an infrared light, and then the protective film

Fig.1 Top-view and cross-view of the humidity sensor

Fig.2 IR spectrum of polypyrrole (PPY) material

was coated on it. A humidity sensor was obtained by the method above. The humidity environments were achieved using super saturation aqueous solutions of different salts (LiCl , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, NaCl , KCl , and KNO_3) in closed glass vessel at room temperature, which yielded 11%, 33%, 54%, 75%, 85%, and 95% relative humidity (RH), respectively.

2 Results and discussion

2.1 Structure and morphology

Fig.2 shows the IR spectrum of PPY. All the characteristic peaks of PPY were obtained in the IR spectrum. The peak at 786 cm^{-1} is characteristic of the C—H out-of-plane bending mode. The band assigned to the C—H in-plane deformation vibration of pyrrole rings appears at 1050 cm^{-1} . The bands observed at 1474 and 1189 cm^{-1} represent the C—N stretching vibration. The peak at 1555 cm^{-1} comes from the C=C stretching vibration. The weak band around 1705 cm^{-1} is normally attributed to the C=O stretching vibration, which suggests that the pyrrole rings are slightly over oxidized^[23,24]. The bands at 1295 and 925 cm^{-1} may be assigned to the doped bands. Fig.3 shows the XRD pattern of PPY. As can be seen, there is a broad feature centered at $2\theta=25.7^\circ$ for the curve, which can be assigned to the interchain spacing of PPY. The results are similar to the literature^[23]. SEM images are shown in Fig.4. As can be seen, the average size of the PPY particle is about 500 nm.

2.2 Humidity sensitive property

Fig.3 XRD pattern of PPY material

Fig.4 SEM image of PPY material

Fig.5 shows the results of the humidity sensor working at different relative humidities and different frequencies. The testing results showed that operation frequency influenced the impedance values very much. From the relationship between the impedance and relative humidity under 0.05, 0.1, 1, 10, and 100 kHz, we found that 0.1 kHz was an optimal operation frequency. The impedance curve had the best linearity. So we choose 0.1 kHz as the operation frequency for the humidity sensor based on PPY.

2.3 Complex impedance analysis

In order to find out the working principle of the humidity sensor based on PPY, we got the complex impedance plot at different relative humidities. The six complex impedance plots at different humidities are shown in Fig.6. We changed the frequency range from 20 Hz to 100 kHz and the relative humidity range from 11% RH to 95% RH at room temperature. It can be seen clearly from the figure that at low relative humidity a part of semicircle is observed in complex impedance plots (Fig.6 (a)). With increasing the relative humidity (about 33% RH), the

Fig.5 Humidity sensitive properties of PPY at different frequencies

incomplete semicircle increases and becomes a semicircle (Fig. 6(b)). Fig.6(a, b) is considered to be the complex impedance of the PPY material itself. At low relative humidity the vapor was little, and ionization rarely occurred. The current was mainly contributed by the electron transition, because impurity may be brought into this system during the material synthesis processes. Barriers and traps must exist, so current will be occurring under the applied outside electric field. Therefore, the semicircle was considered to be the electron conduction. We considered that intrinsic materials' electron mainly contributed to the conduction in low relative humidity environments.

When the relative humidity range reaches 54% RH, the complex impedance plots consist of two parts: a semicircle at high frequency and a straight line at low frequency (Fig.6(c, d, e, f)). H^+ and H_3O^+ can travel through the proton exchange mechanism. The transfer process of proton in the system of PPY can be explained in a simple form as shown in Fig.7.

Fig.6 Complex impedance plots obtained in the frequency range from 20 Hz to 100 kHz at different relative humidities

Fig.7 The transfer process of proton in the system of PPY

When H^+ and H_3O^+ ions take part in conduction, the straight line will be observed on the complex impedance plots. We can also obtain the conductivity of the humidity sensor from the complex plots. As reported in literature^[25], the arc at high frequency intersection with real axis has relationships with the total resistance of sensing materials. And the conductivity is inversely proportional to the resistance. From the plots, we can see the resistance reduced sharply with the humidity grown and the conductivity increased oppositely. Therefore, we considered that the straight line was mainly considered to be the contribution of H^+ and H_3O^+ ions to the conduction in high relative humidity environments.

From above analyses, the complex impedance plots embody the internal conductive changes of the humidity sensor. So measuring the complex impedance plots at different relative humidity conditions are very significant. From the analysis of the complex impedance plots, the sensing principle of this material is electron and ion conductivities at low and high relative humidities, respectively.

3 Conclusions

A humidity sensor based on PPY was obtained and the humidity sensitive properties were studied. The structure and morphology of PPY were characterized by means of IR, XRD, and SEM, respectively. The humidity sensitive properties were studied at different frequencies and complex impedance plots were obtained. According to the complex impedance analysis we studied the working principle of the humidity sensor.

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