Flexible screen-printed temperature sensor based on Mn-Co-Ni metal oxide powder filled PVB polymer

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Abstract

There has recently been renewed interest in wearable devices and electronic skin because of the demand in real-time monitoring of human body temperature. This work developed a flexible paper-based temperature sensor by screen printing technology. The sensing layer is composed of Mn-Co-Ni metal oxide powders filled with Polyvinyl butyral (PVB). The flexible temperature sensor shows extremely high sensitivity ($3.14\% ^\circ\text{C}^{-1}$) at human body temperature (25 to 45°C). It also exhibits excellent durability (less than 0.25%) during the long-term aging tests, which indicates that the flexible temperature sensor has great potential in wearable devices and electronic skin.

1 Introduction

The past decade has been the rapid development of Internet of Things (IoT) technology. It is expected that billions of devices will be integrated into the Internet [1] and the sensors are the vital element in Computer-Human Interaction (CHI) technology[2]. As an essential physiological parameter, the temperature is one of the critical indicators of health system evaluation. So real-time monitoring of human body temperature is of great significance in the field of health care. Most of the traditional temperature sensors, such as the mercury thermometer and infrared thermometer, are difficult to perform effective long-term detection of the human body. Therefore, flexible temperature sensors with ultra-thin thickness, low modulus, light weight, high flexibility and stretchability have attracted widespread attention [3]. Jin Jeon reported a flexible wireless temperature sensor based on the nickel-filled binary polymer PEO/PE composite, with a sensitivity of $0.3\text{V}/^\circ\text{C}$ at the temperature of 35 to 42°C [4]. Qingxia Liu developed a high-performance flexible temperature sensor consisting of polyethyleneimine/reduced graphene oxide bilayer and the sensitivity in the temperature range of 25 to 45°C is $1.30\% ^\circ\text{C}^{-1}$ [5]. Jin Pan reported a flexible temperature sensor array with polyaniline/graphene-polyvinyl butyral film, which shows a sensitivity about $1.20\% ^\circ\text{C}^{-1}$ at the temperature range of 25 to 80°C [6]. Guanyu Liu reported a flexible temperature sensor based on graphene oxide and the sensitivity of the sensor is $0.6435\% ^\circ\text{C}^{-1}$ over the temperature range of 30 to 100°C [7]. Wen-Pin Shih reported a graphite-based flexible temperature sensor array of polydimethylsiloxane composites. The sensitivity is 0.042K^{-1} and 0.286K^{-1} when the volume fraction of graphite is 25% and 15%, respectively [8]. Most of the flexible temperature sensors use graphene or metal powder as sensor materials. These materials are expensive and the sensitivity coefficient is no more than $1.3\% ^\circ\text{C}^{-1}$, which is challenging to satisfy the demand of human real-time temperature monitoring.

In this paper, a flexible temperature sensor with high sensitivity and low-cost was developed on the paper substrate through a screen-printing method. Polyvinyl butyral (PVB), Mn-Co-Ni metal oxide powder, and silane coupling agent (KH550)[9] were used as the adhesive, temperature sensing material, and surfactant respectively. Mn-Co-Ni metal oxide is a kind of negative temperature coefficient thermistor with a spinel structure, which has the characteristics of high sensitivity, excellent reliability, and low cost. In addition, the temperature coefficient of resistance (TCR) is usually ten times higher than that of other

temperature sensors [10]. The composition of the flexible temperature sensor was characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The morphology was obtained by scanning electron microscope (SEM). The most attractive performance of the sensor is the high sensitivity of $3.14\% ^\circ \text{C}^{-1}$ between 25 to 45°C , which is much higher than that of the graphene composites temperature sensor ($1.3\% ^\circ \text{C}^{-1}$). Further durability tests in long-terms temperature and mechanical aging prove that the flexible temperature sensor has great potential in the health care field.

2 Experiment Details

2.1 Preparation of Mn-Co-Ni metal oxide powder

The Mn-Co-Ni metal oxide powder was prepared by the co-precipitation method. 1 mol of $\text{Ni}(\text{NO}_3)_2$ (99%, Aladdin), $\text{Mn}(\text{NO}_3)_2$ (99%, Aladdin), and $\text{Co}(\text{NO}_3)_2$ (99%, Aladdin) were accurately weighed according to the stoichiometric ratio of 1.8:0.3:0.9. All the chemicals were analytical grade and used as received without further purification. Appropriate amounts of $\text{Ni}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ were dissolved in 500 ml of deionized water by constant stirring. 3 mol of ammonia water was added as the precipitating agent. The precipitate was filtered and dried at 150°C for 24 h. The obtained samples were grinded into powders and the powders were annealed at 1000°C for 2 h in air.

2.2 Preparation of the flexible temperature sensor

PVB (99%, Aladdin) and ethanol (99%, Aladdin) were accurately weighed at a mass ratio of 3:7. The reagents were all added to the beaker and heated to 200°C in order to dissolve the PVB in the ethanol, and then mixed with a magnetic stirrer for 30 minutes to form a transparent paste. The MCN powder, PVB solution and γ -aminopropyltriethoxysilan(KH550, CHINA)were respectively weighed in different proportions, and the ratios are given in Table 1. Then, mixing them in a defoaming mixer (THINKY ARE-310, JAPAN) at a rate of 2000 r/min for 10 minutes to obtain a black ceramic slurry. The flexible film was printed by the screen printer (AT-25PA Dongyuan, China). The ethanol organic reagent was volatilized by drying at 50°C for 2 hours. Ag slurry was plated on both ends of the flexible film to make the electrode.

2.3 Characterization of the flexible temperature sensor

The structure of the inorganic phase was tested by the X-ray diffraction (D8 ADVANCE Bruker, Germany). The functional groups of the organic phase were tested by the Fourier transform infrared spectroscopy (WGH-30/30ABruker, Germany). The surface structure and element distribution of the flexible film were observed by scanning electron microscope (SUPRA 55VP Zeiss, Germany). The conductivity of the film at different temperatures was measured on the probe station (SM-4, SEMISHARE ELECTRONIC CO., LTD).

Table 1 Flexible film formulation.

Content	Ceramic powder	PVB solution	KH550
20%	2g	7g	1g
30%	3g	6g	1g
40%	4g	5g	1g
50%	5g	4g	1g

3 Results And Discussion

Figure 1 shows the structure of the proposed temperature sensor, which consists of a paper substrate, PVB-MCN sensing layer, and Ag electrode. The flexible film can be printed on the fiber paper[11] substrate by the screen printing, and then the wires are printed on the film to prepare a flexible temperature sensor. It can be seen that the flexible temperature sensor is simple in structure and convenient to manufacture, which is suitable for mass production.

3.1 Structural analysis

Figure 2(a) shows the phase structure of the flexible films at different contents. It can be seen that the pure phase ceramic powder has a distinct spinel structure. With the decrease of solid content, the intensities of all diffraction peaks tend to weaken, which indicates the decrease of the inorganic phase.

Figure 2(b) shows the FTIR spectra of the flexible film at different contents. It can be seen that the absorption peak of the organic functional group appears at different positions, where characteristic peak at 3458 cm^{-1} is attributed to the functional group from the silane coupling agent and hydroxyl groups on the surface of the ceramic particles. The absorption peak at 3390 cm^{-1} corresponds to the NH groups from the silane coupling agent while the CH_2 groups at positions 2960, 2930, and 2850 cm^{-1} are functional groups from the carbon chain in silane coupling agent and PVB. The peaks at 1557 and 1106 cm^{-1} are attributed to the bonds between the silane coupling agents. The absorption peak at 1641 cm^{-1} corresponds to the carbon-oxygen bond formed during the dehydration condensation reaction between PVB and the ceramic particle. And the carbon-nitrogen double bond at 992 cm^{-1} corresponds to the chemical bond formed between silane coupling agent and PVB, which confirms that the silane coupling agent indeed played the role of adhesion. The absorption bands between 2000 and 2230 cm^{-1} correspond to the diamond substrate in the instrument. All the vibration peaks gradually decrease with the increase of the amount of the ceramic particles, which proves the decrease of the organic phase.

Figure 2(c) shows the reaction mechanism between different components. Ceramic particles have a strong tendency to aggregate because of the high surface energy [12] and the aggregation of ceramic particles will dramatically reduce the mechanical properties of flexible films. Therefore, it is necessary to do chemical modification of the ceramic for improving the dispersion performance. The silane coupling agents with polar groups at one end of the molecule can react with the hydroxyl groups of the ceramic particles while the groups at the other end can crosslink with organic polymers. γ -aminopropyltriethoxysilane (KH550) is often used in the surface modification of inorganic particles [13]. The silanol groups at one end of the silane coupling agent undergo a hydrolysis polycondensation reaction with the hydroxyl groups on the surface of the ceramic particles, forming a carbon-oxygen bond. While, the organic group at the other end of the silane coupling agent reacts with the organic functional group of the PVB, forming a carbon-nitrogen double bond. The bond bridge which formed between ceramic particles and PVB by adding silane coupling agent can help the coupling process between them.

3.2 Microstructure analysis

Figures 3a) b) c) d) shows the microstructure of flexible films. It can be seen that the size of the ceramic particles is about 4 to 5 μm with a narrow distribution. As the solid content increases, the density of the ceramic particles increases significantly. Fig. 3e) shows the element distribution of the flexible films. It can be seen that all the elements are distributed uniformly and the ceramic particles are homogeneously mixed with the PVB without visible agglomeration, which proves the high uniformity of the flexible film. Although small portions of the silane coupling agents were used as the surfactant, the distribution of the silicon element is uniform, indicating that the silane coupling agent is distributed on the surface of the ceramic particles and the PVB molecule. Fig. 3f) is the microstructure model of the flexible film. This further approves that it can effectively improve the bonding strength between ceramic particles and PVB by adding the silane coupling agent.

3.3 Electrical performance and application

Figure 4a) b) c) d) show the relationship between resistivity and temperature of flexible films. It can be seen that as the temperature increases, the resistivity shows a downward trend, and all of the flexible films exhibit a negative temperature coefficient (NTC). MCN powder is a semiconductor material with a spinel structure, which is very sensitive to temperature. When the external temperature rises, the carrier transport efficiency in the semiconductor is much improved, thus the material resistance decreases rapidly. The sensitivity of the flexible film can be calculated by the formula (1).

$$\text{TCR} = (R - R_0) / (R_0 \cdot \Delta T) \quad (1)$$

It can be seen from Table 2 that the flexible film has a high-temperature coefficient of resistance (greater than $3.1\% \text{ C}^{-1}$) in the temperature range of the human body. Furthermore, the flexible film still exceeds a temperature coefficient of resistance of $1.4\% \text{ }^\circ\text{C}$ at the wide temperature range from 25 to 80 degrees Celsius. At the same time, there is no significant hysteresis during cooling and heating.

It can be seen from Fig. 4a) that in the flexible film with a solid content of 20%, the resistivity at room temperature is as high as $2.8 \text{ G}\Omega$. With the increase of the inorganic phase, the resistivity gradually decreases to $56 \text{ M}\Omega$. Figure 4e) is an Arrhenius diagram of the flexible films. It can be seen that there is a linear relationship between resistivity and temperature for all of the flexible films and the resistivity increases as the solid content increases. It was found that compared with the 20% solids flexible film, the 30% solids flexible film has lower resistivity and better temperature dependence, which is beneficial to convert temperature signals into electrical signals. At the same time, the mechanical properties of flexible films with a solid content of 30% are better than the flexible films with a solid content of 40% and 50%. Therefore, the flexible film with a solid content of 30% is considered to have the most practical value.

In order to further study the practicality of the flexible film with a solid content of 30%, five temperature cycling tests were performed in the human temperature range ($30\text{--}40^\circ\text{C}$), and the average change rate was found to be less than 0.15%. Figure 4g) shows that the flexible film of 30% solids was aged for 1000

minutes at the temperature of 40 to 80° C. It was found that the flexible film has excellent temperature stability (0.1266% at 40° C, 0.1364% at 50° C, 0.1422% at 60° C, 0.1646% at 40° C). This is because the spinel structure only shows lattice relaxation at 200° C or higher, which is much lower than the human body temperature range. Figure 4h) shows the resistance change after bending for 1000 times at different angles. It is found that the resistance change of the flexible film during the folding process is negligible (0.2366% at 30 °, 0.2054% at 60 °, 0.1814% at 90 °, 0.1434% at 120 °).

Table 2 The TCR,B value and activation energy of flexible temperature sensor.

content	TCR _{25/45} (%)	TCR _{25/75} (%)	B _{25/75} (K)	Ea(eV)
20%	3.153	1.811	4906	0.4233
30%	3.142	1.557	3129	0.2700
40%	3.136	1.645	3591	0.3099
50%	3.115	1.713	4034	0.3481

4. Conclusion

This work developed a flexible temperature sensor of MCN powder filled PVB with the silane coupling agent as the surfactant. It can be conveniently printed on a paper substrate by screen printing technology. SEM and EDS found that the MCN ceramic particles were uniformly dispersed in PVB, which was beneficial to obtain high-quality flexible films. The 30% solid content flexible film has a temperature coefficient of resistance of $3.14\% \text{ } ^\circ\text{C}^{-1}$, B_{25/75} value of 3129 K, activation energy of 0.27 eV in the human body temperature range (25 to 45° C). The resistance drift rate does not exceed 0.1646% in 1000 minutes of temperature aging, and the resistance drift rate does not exceed 0.2366% after 1000 times bend, which shows that the flexible temperature sensor has great potential in wearable devices and electronic skin.

5 Declarations

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Figures

Figure 1

a) Screen printing schematic. b) Schematic diagram of the temperature sensor structure. c) Photograph of the temperature sensor in a bent state.

Figure 2

a) XRD pattern of the flexible film. b) Infrared spectrum of the flexible film. c) Bonding process between different components in the flexible film.

Figure 3

a) b) c) d) SEM images of different solid content flexible membranes. e) Mapping of a 20% solids flexible film. f) Structural model of the flexible film.

Figure 4

a) b) c) d) The relationship between temperature and resistance (within heating and cooling) of sensors with different solid contents in the range of 25–75 $^{\circ}\text{C}$. e) The Arrhenius diagram of the sensor in the range of 25–75 $^{\circ}\text{C}$. f) Repeat cycle test temperature between 30 and 40 $^{\circ}\text{C}$. g) Continuous resistance change rate measurement for 1000 minutes at 5 temperature values (40, 50, 60 and 70 $^{\circ}\text{C}$). h) Resistance change of the sensors at 1000 cycles of bending at 30 $^{\circ}$, 60 $^{\circ}$, 90 $^{\circ}$, 120 $^{\circ}$ bending angle.