Conducting Polymer as a Humidity Sensor

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Abstract: Recently, humidity sensors have been developed rapidly and have attracted much attention in many fields such as agriculture, food safety; industrial sectors, medical treatment, research and development laboratories as well as daily life applications are reviewed and presented in this article. The Relative Humidity sensors based upon their organic and inorganic functional materials, also as conduction mechanisms and fabrication technologies. Recently, metal oxides, polymers, and carbon materials are often utilized in the planning and manufacture of humidity sensors. Correlations of electrical characteristics doped sensor materials feature of noted. The electrical properties of various sensor materials are found to vary significantly with the morphological changes, doping concentration of various materials, and film thickness of the substrate. The thick film and thin film processes either within the preparation of materials or within the choice of shape and size of the sensor structure provides advantages over other technologies. These polymer-metal-based sensors are widely used in the preparation of sensors because of their simple preparation process, low price, show faster response than other types, wide source of raw materials, and good biological compatibility.

Keywords: Conducting polymer, Sensor, Humidity Sensor, Polyaniline

1. Introduction

The word polymer designates as a large number of molecules whose structure is composed of multiple repeating units of monomer derived from a Greek word (poly means "many'' and mer means "parts"). Polymers can be categorized as Natural Polymers such as – amber, rubber, cellulose, lignin, resins, etc. Synthetic Polymers such as – polyethylene, polypropylene, polystyrene, synthetic rubber, phenol-formaldehyde, silicone, etc.. All the polymers are produced via the polymerization of small molecules known as monomers. Because of their wide range of properties, both synthetic and natural polymers play an essential role in everyday life. Generally, organic polymers are insulators but there is a group of polymers that are electrically conducting known as conducting polymers (CPs) such as – polypyrrole, polythiophene, polyacetylene, polyaniline, etc. These conducting polymers have single and double bonds alternatively containing aromatic rings. Polymers are specifically composed of elements such as carbon, hydrocarbons, nitrogen, fluorine, phosphorus, etc. that bind together and form a long chain which is called the backbone of the polymer. One or more atoms are attached to these elements with the backbone of the polymer for example Polyvinylchloride has chlorine attached to the carbon atoms in the backbone chain. The conductivity of the pure conjugated polymers is due to the existence of a conducting band. Three of the four valence electrons of conducting polymer are strongly localized which form σ bonds through sp^2 hybridization whereas the remaining one electron forms a π bond. These π bond electrons of conjugated polymers are delocalized and can move freely. However, pure conducting polymers have low conductivity which can be increased by oxidation (p-doping) or reduction (n-doping). On the basis of conductivity, materials are classified into three types as conductors, semiconductors, and insulators. A material having conductivity less than 10^{-7} S/cm is regarded as an insulator. Metals with conductivity larger than 10^3 S/cm are conductors whereas the conductivity of a semiconductor lies between 10^{-4} to 10 S/cm. The variation of conductivity also depends upon the dopants used. Generally, it is believed that polymers are electronically non-conducting and the inability of polymers to carry electricity separates them from metals

and semiconductors. CPs are similar to other organic polymers defined by sigma (σ) and pi (π) bonds. Recent research suggests that they have different promising applications [1-10] in electrochromism, organic solar cells, supercapacitors, sensors, flexible transparent displays, painting, packaging, electrical insulations, etc.

Hermann Staudinger proposed the concept of macromolecules in the 1920s and got the Nobel Prize in Chemistry in 1953 for his discoveries in the field of macromolecular chemistry [11]. The first conducting polymer, polyacetylene, was synthesized by Hideki Shirakawa, Alan Heeger and Alan Mac Diarmid and its electrical conductivity was discovered in 2000 [12-15]. One of the most attractive conjugated polymers in both non-conducting as well as conducting forms is Polyaniline (Pani). It can be prepared via polymerization using chemical oxidative or electrochemical methods. In 1935 Yasui suggested the reaction scheme of aniline using carbon electrodes [16]. In 1967, Buvet and his group proposed that PAni is a redox-active electronically conducting and can be used as electrodes for conductivity measurements [17,18].

Polyaniline (PAni) is a type of conducting polymer and has high electrical conductivity. Among the family of conducting polymers and organic semiconductors, polyaniline has many attractive processing properties. PAni has three different forms depending on its degree of oxidation state [19]; leucoemeraldine (fully reduced), emeraldine (half oxidized) and pernigraniline (fully oxidized). Emeraldine base (EB) form is highly stable at room temperature, so it is regarded as the most useful form. This form is neutral. In its doped state (i.e. protonated), it is called emeraldine salt (ES). Emeraldine salt is electrically conducting of the order of $\sim 10^{-4}$ S/m [20, 21]. Emeraldine base form has equal numbers of imine (=NH-) and amine (-NH-) sites. Protonation occurs at imine sites to form emeraldine salt (bipolarone or dicatione). Apart from oxidation levels, polyaniline forms have also been recognized by color and conductivity variation. Green protonated emeraldine salt form of polyaniline is obtained via polymerization of aniline when treated with acidic. Treatment with acids increases its electrical conductivity by 10 orders of magnitude. It can easily transform into a fully oxidized form of blue pernigraniline salt by further oxidation. In the case of electrochemical polymerization (ECP), Cyclic Voltammetry (CV) clearly shows the color-changing property from leucoemeraldine (yellow) to pernigraniline (PB) (violet) with variations in oxidation levels and from violet to yellow with variations of oxidation states.

When Polyaniline is doped with metals than its conductivity changes. The dopants are Zinc Oxide, MnO_2, GO, Bi_2O_3, etc. The properties of Zinc oxide is that it is a II-VI semiconductor with a wide direct bandgap of ~ 3.36 eV. This bandgap can be tuned between 3-4 eV using different dopants. It has a hexagonal wurtzite structure, which is most stable in ambient conditions. It has a melting point 1974°C. It is insoluble in water and soluble in acids. ZnO has an n-type character with electron mobility varying up to 2000 cm^2 /V-s. It has properties such as non-toxic, high thermal conductivity, stability, high refractive index, high transparency, high electron mobility, high breakdown voltage, low electronic noise, antibacterial properties, and UV protection, etc. Due to its extensive properties, ZnO has many applications in electronic and optoelectronic devices like solar cells, LEDs, transparent conducting electrodes, liquid crystal displays, photodetectors, and transparent photonics, light-emitting diodes, solar cells, photovoltaic devices, sensors, etc. It has also been used in other applications such as plastics, cement, batteries, paints, adhesive, rubber, glass, etc. Manganese oxide has the formula MnO_2 and has a molar mass of 86.936 g/mol. It has a tetrahedral crystal structure with a melting point 535°C. It is insoluble in water. MnO_2 is highly oxygen-deficient. Due to its attractive properties, it can be used in batteries (dry cell, alkaline, zinc-carbon). It is also used as a pigment, reagents in organic synthesis glass making, etc. Graphene Oxide (GO) also called graphitic oxide. It is a compound of carbon, oxygen, and hydrogen. GO is composed of graphite using Hummer's method or modified Hummer's method. Structure and properties depend upon the synthesis method and degree of oxidation. Graphene Oxide has layers of about 0.8 to 1.2 nm thick. GO is hydrophilic in nature. GO is an insulator or almost a semiconductor with conductivity b/w ~ 1 to 5×10^{-3} S/cm. GO when treated with hydrazine convert into graphene which has high conductivity ~ 10 S/cm and charge mobility is in b/w 0.1 to 10 cm^2 /Vs. Bi_2O_3 has four polymorphs- α, β, γ and δ with the variation of temperature. The crystal structure of α, β, γ and δ are monoclinic, tetragonal, bcc and fcc respectively. Bi_2O_3 has a melting point 817°C. α exists at room temperature whereas β, γ and δ are high-temperature phases. With the variation of temperature, the highest conductivity reported is ~ 1 S/cm. These phases can be transformed from one another. α exists at room temperature when it is heated up to 727°C it transforms into δ phase and exists in that 23 phase till its melting point 824°C. Once it is heated, during cooling δ phase can be converted into β or γ phase depending upon the cooling rate. If the cooling rate is fast it is converted into β phase at 650^0 C and converted into α monoclinic phase at 303^0 C and if the cooling rate is very slow it is converted into 639^0 C and then convert into α monoclinic phase at 500°C. Reportedly, bandgap of α form is found to be ~ 2.7 eV. It is insoluble in water and soluble in acids. In conducting polymers, doping was done by redox and non-redox doping methods. The redox doping method includes oxidation or reduction of CPs in which the number of electrons gets changed in the polymer backbone. Redox doping can further be classified in three divisions- P-type doping, N-type doping, and Doping involving no dopants- viz. photodoping and charge insertion doping [22-24]. Photodoping is a technique in which doping of CPs can be done by irradiation of polymer using photons of high energy than the bandgap of conducting polymer. Chemical and electrochemical methods are included in redox doping techniques in which either electrons are removed from the polymer backbone (p-doping) or electrons are added to the polymer chains (n-doping). A chemical method is a technique in

which a polymer is exposed to oxidizing or reducing agents whereas an electrochemical is a method in which oxidizing or reducing agents are present in the electrolyte. The non-redox method of doping is a technique in which the number of electrons attached to the polymer chain remains constant. In non- redox doping the energy level of the conducting polymer gets rearranged for e.g. Change of Polyaniline emeraldine base form to emeraldine salt form when treated with some specific acids. For Polymerization, two synthesis methods are there –

1. Chemical Oxidative method [25-27].
2. Electrochemical Polymerization method [28-30].

The Chemical oxidative method is the process in which relatively small molecules, called monomers, combine with chemicals for polymerization to produce chainlike networks. Polymerization of monomers occurs to make a product that has enhanced structure and properties that differentiate polymers from substances composed of smaller and simpler molecules. In other words, this is a process in which monomer molecules polymerized through chemical reactions to form polymer chains or 3D networks. Electrochemical polymerization (ECP) is performed in a one-compartment three-electrode connected cell. These electrodes can also be connected directly or using salt bridges. These electrodes are dipped in a solution known as electrolyte. The three electrodes are working (cathode), counter (anode), and Reference Electrodes. Polymerization occurs at the counter electrode (anode). Usually, ECP is carried out using a suitable power supply or Potentiostat that has been used to control the process. ECP is the three-step process [31]. In the first step, oxidation of monomers leads to the formation of soluble oligomers on the anode. The second is the nucleation and growth process. The second step strongly depends upon the environmental conditions and also essential for polymer growth on the electrode whereas the third step is responsible for chain propagation by polymerization. Generally, ECP occurs in an acidic medium with higher pH which is sometimes responsible for the formation of oligomeric materials.

Conducting polymers are rapidly gaining attraction in new applications areas due to their better electrical and physical properties and lower costs. Due to their processability, conductive polymers have promising applications such as displays, supercapacitors, sensors, diodes, batteries, electromagnetic shielding, etc. Another use is for absorbent coating particularly radar-absorptive coatings on stealth aircraft. But they have structural limitations like material inconsistencies, toxicity, poor solubility in solvents, cost, etc. Among all conducting polymers (CPs), polyaniline has been extensively used because of its low cost, good environmental stability, good conductivity, redox reversibility, and easy synthesis procedure. Investigation and analysis of polyaniline reveal their potential applications [32-35] in the field of sensors, electrochromic display, Schottky diodes, corrosion inhibitors, supercapacitors, rechargeable batteries, etc.

2. Sensor

A sensor is a device that detects or senses some condition or activity and responds to the information received. In other words, the sensor detects and measures input signals and converts it into electrical and optical signals. According to the international electrochemical committee, a sensor is a primary part of the measuring chain which converts input signals into output signals suitable for measurements. Classification of Sensors On the basis of the nature of signals there are Analog and digital sensors. On the basis of fabrication, it has Thick-film sensors, thin-film sensors, integrated sensors. On the basis of their operations, there are: Electrical sensors, Humidity sensors, Biosensors, Chemical Sensors, Optical Sensors.

These sensors are broadly divided into

1) Chemical Sensors
2) Physical Sensors and
3) Biosensors.

A chemical sensor is a device that works on chemical information and transforms that data into electrical or optical form. This chemical information originates from a chemical reaction or some physical property. Physical sensor provides information related to some physical properties like pressure, acceleration, mass temperature, etc. Similarly, a biosensor works with biomolecules, cells, etc.A sensor is said to be commercially utilized if it has some properties such as high sensitivity, selectivity, quick response and recovery time stability in different environments and temperature, reproducibility, reliability, broad range of measurement reliability, interchangeability, repeatability, etc.

3. Humidity sensors

Humidity is the amount of water vapor present in the environment. There are three modes of measurements of humidity: absolute, relative, and specific.Absolute humidity is the amount of water molecules present in the air measured in $gram/m^3$ or gram/kg.Relative humidity is the amount of water molecules or vapor in the air compared to the maximum amount the air can hold at a constant temperature. It is expressed in RH%. There is a limit of air to hold water vapor at a constant temperature. When this limit is reached the air is called saturated i.e. 100 RH%. RH% doesn't show the amount of water present in the air but it shows how close the air is to saturation. Specific humidity is the ratio of the mass of water vapor present in the amount of air to the mass of dry air present in the same amount or it is equal to the

mass of water vapor to the total mass of moist air. Humidity variation occurs with the variation of atmospheric temperature and pressure.

A hygrometer is a device that is used to measure humidity. Different types of Hygrometers are available in the market:

1. Dew point Hygrometer
2. Dry and wet bulb Hygrometer
3. Gravimetric Hygrometer
4. Chilled Mirror Hygrometer
5. Electronic Hygrometer

Chilled mirror method is fast and quick among all the three.

Electronic type hygrometer or humidity sensors are broadly classified into two divisions:-

1. Resistive Type
2. Capacitive Type.

Resistive type humidity sensors measure change in resistance/ impedance values with variation in RH%. The plastic or polymeric material film is used for sensing. Variation in impedance occurs due to the movements of ions. Capacitive type sensor uses plastic or polymer as a dielectric material sand-witched between two electrodes in the form of a capacitor. Variation of dielectric constant and capacitances are measured.

4. Characteristics of humidity Sensors

a) Sensitivity: The material should show high sensitivity in terms of the variation of resistance or impedance on contact with very small quantities of the gas or vapor concerned.

b) Selectivity: Some materials are equally sensitive towards relative humidity (RH%). Therefore, selectivity is an important criterion.

c) Reproducibility: The materials should sense the humidity over a large number of cycles for extended periods and the sensor should not undergo environmental degradation rapidly due to pressure, temperature, etc.

d) Cost-effective: As far as possible, a sensor should not be expensive.

e) Response and Recovery Time: It is the time taken by the sensor to measure the change in impedance while the relative humidity changes from 10% to 90% and 90% to 10% respectively.

Conducting Polymers as Humidity Sensors: Conducting polymers are basically plastics that can conduct electricity. Conducting polymers constitute a class of materials that are very promising for application in the field of humidity sensors. In general, conducting polymers could be used in all types of sensors as long as they can function at room temperature. The great advantage of conducting polymer-based humidity sensors is that they have the potential to improve properties and are sensitive to small perturbations. They also offer great design flexibility. The flexibility of polymers properties, however, depends upon doping and the introduction of functional additives. Doping in the conducting polymers is responsible for the alteration of single and double bonds in the polymer backbone chain. The primary dopants (anions) introduced during the polymerization. The nature of the anion also strongly influences the morphology of the polymer. Doping produces charge carriers due to the chemical modification of polymer structure which is responsible for improvement in electrical conductivity. In addition, anions can serve as specific binding sites for the interaction of the conducting polymer with the water molecules. They are relatively, open materials that allow the ingress of water molecules into their interior.

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