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Electrical Properties of Woodceramics - Humidity Sensor

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Electrical properties of woodceramics (WCMs hereafter), particularly humidity and temperature dependence of electrical resistivity, have been evaluated. Relative humidity dependence of the electrical resistance shows an excellently linear relationship in the range 15 - 70%RH measured, where ionic and electronic conduction exist simultaneously. Donor-type levels of 0.05 eV and 0.01 eV have been deduced from the temperature dependence (100 - 370K) of the electronic conduction measured in vacuum. Time constants of 12 -20 min have been obtained by measuring time response when exposed to water vapor. A prototype humidity sensor has been demonstrated here with its circuitry. The excellent linearity of WCMs on the humidity is prominent advantages for a new humidity sensor.

Key words: woodceramics, humidity sensor, porous carbon, electrical properties, time dependence

1. INTRODUCTION

Sensing and controlling environmental humidity is receiving a great attention for industrial processes and also human comfort. In recent years the use of humidity control systems has increased in the quality control of production processes and a wide variety of industries, such as electronic devices, precision instruments, textiles, foodstuffs, automobiles, medical equipments, agriculture, and also in many domestic appliances for living environment. A large number of ceramic, polymeric, and composite sensors have been investigated as sensing elements [1 - 5]. Since each of these have advantages and limitations, no single device can be considered to be universally applicable as a humidity sensor.

Ceramic humidity sensors have shown advantages over polymer sensors in terms of their mechanical strength, resistance to chemical attack, and their thermal and physical stability [3, 5]. Polymers are inherently less robust than ceramics, and are limited to lower temperatures in usage with slow response, long-term drift, and hysteresis. Woodceramics are new porous ceramic materials and have recently shown a strong promise of constituting the next generation of industrial materials [6, 7]. Woodceramics (WCMs hereafter) are drawing particularly strong attention as ecomaterials of low cost with the prominent characteristics of lightness, hardness, porosity, corrosion resistance, and heat resistance; which are obtained by sintering woody materials impregnated with phenolic resin forming glassy carbon. It is noteworthy that WCMs can be fabricated from waste papers, sawdusts, telephone books and so on, thereby WCMs are environment conscious materials designed for minimizing the environmental impacts. In order to overcome the problems of carbon materials like charcoals, i.e. fissures and warps, WCMs have been greatly reinforced mechanically by impregnating wood with phenolic resin to form glassy carbon after sintering, retaining several of charcoal properties such as porosity, lightness, and so on.

In this paper we report on the electrical properties of woodceramics, particularly humidity and temperature dependence of electrical resistivity. Time response of WCMs with exposure to water vapor has been discussed and also a prototype humidity and temperature sensors with their circuitry have been fabricated and demonstrated.

2. EXPERIMENTAL

Medium-density fiber board (MDF hereafter) made from pinus radiata was used to manufacture WCMs. The MDF was impregnated with phenolic resin using an ultrasonic impregnation system [7]. After the impregnated MDF was dried at 135°C, it was sintered at 650°C in a vacuum furnace to produce WCMs. During the sintering the phenolic resin changes into glassy carbon, thereby reinforcing the cell walls of wood cellulose. The glassy carbon has superior properties of corrosion resistance, mechanical strength, and suppresses the fissures and warps, which are problems in case of charcoals.

The crystallographic properties of the WCMs were obtained by a standard X-ray diffraction technique using CuK_a radiation at 30 kV. Fluorescence X-ray spectroscopy were performed using Rh tube at 50 kV to obtain chemical composition of WCMs. After cutting the WCMs to desired size, aluminum or gold was evaporated in vacuum onto the WCMs to form ohmic contacts as electrodes for measuring electrical characteristics. Electrical and humidity measurements for WCMs were performed in the chamber equipped with the Peltier stage to control the specimen temperature. Electrical resistivity were measured by flowing a constant DC current of 1 mA between two electrodes and detecting potential yielded.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns for the WCM specimens sintered at 650°C, indicate that WCMs consist of polycrystalline compounds of $C_6H_9O_6$ and $C_4H_6O_6$, although all the diffraction peaks have not been present. This is in agreement with the reported results [8 - 11] attributed to structural changes. The carbonization of cellulose, i.e. a main constituent of wood, yields the formation of condensed aromatic ring structures [8, 9]. In addition, the condensed aromatic ring structures are also formed by the carbonization of phenolic resin, forming glassy carbon [10, 11] as a result of the elimination reaction of methane and hydrogen.

3.1 Temperature dependence of electrical resistance

Temperature dependence of the electrical resistivity have been measured at temperatures from 100 to 370K for the WCM specimens with thicknesses of 1, 3 and 5 mm (cross section 6 x 8 mm^2), and are shown in Fig. 1 and Fig. 2. The resistivity decreases with increasing temperature; indicating the negative temperature coefficients.

From the results of X-ray measurements, the WCMs seem not to have the complete aromatic ring structures. Therefore, we have adopted energy band model rather than π electron model to explain the electrical properties of WCMs. In general, electronic conduction and ionic conduction exist simultaneously in porous ceramics [12]. At low humidity, electronic conduction plays a major role, while ionic conduction plays a major role at high humidity. At medium humidity, there is a transition from electronic

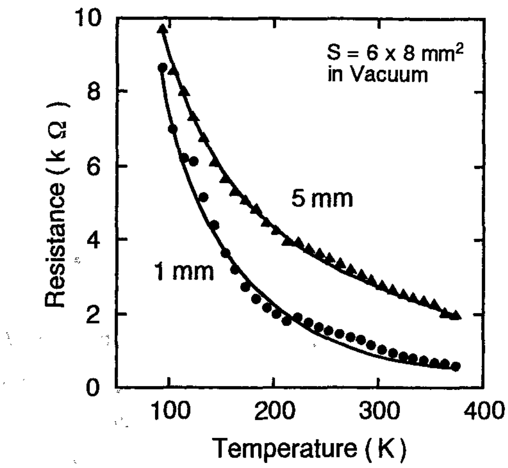

Fig. 1 Electrical resistance versus temperature for typical woodceramic specimens with thicknesses of 1 mm and 5 mm in vacuum (cross section 6 x 8 mm^2).

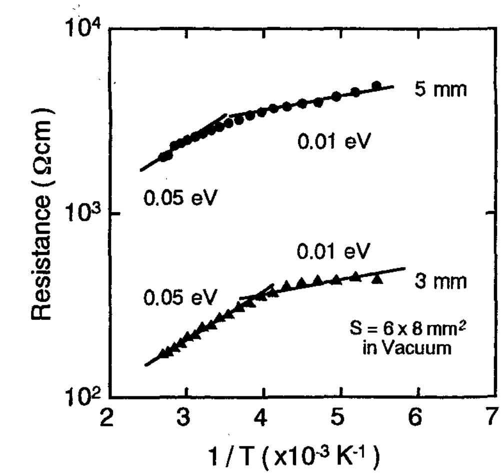

Fig. 2 Arrhenius plots of electrical resistance for woodceramic specimens with thicknesses of 3 mm and 5 mm in vacuum (cross section 6 x 8 mm^2).

to ionic conduction. Here, in order to eliminate the contribution due to ionic conduction, we have utilized vacuum (2 x 10^{-3} Torr) to measure the temperature dependence of electrical resistance of WCMs, where the conduction mechanism is limited to electronic. The resistance change when exposed to the relative humidity of 10%, is illustrated in Fig. 3, where the ionic conduction dominates over the electronic conduction. The greater the relative humidity, the less becomes the resistance magnitude. The resistance of 10%RH case in Fig. 3, is given by the sum of electronic and ionic conduction. The ionic conduction could be attributed to the proton hopping between water molecules adsorbed on the specimen surfaces of WCMs. For this humidity case of 10%RH in

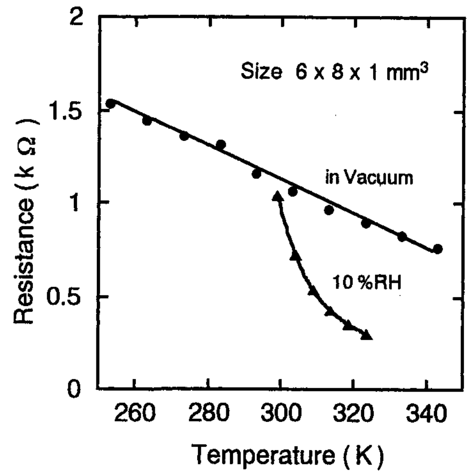

Fig. 3 Effect of temperature on the electrical resistance of woodceramic in vacuum and 10%RH atmosphere.

Fig. 3, adsorption activation energy was deduced as 0.42 eV, i.e., 40.5 kJ/mol, which is approximately equal to the heat of solidification of H_2O (41 kJ/mol) and rather less than the energy of the chemical bond (>80 kJ/mol).

The electrical behavior of WCMs is similar to n-type semiconductor. For the case of electronic conduction the trapped electrons in the sites of impurities or vacancies, are raised to the conduction band, resulting in the increased conductivity (reducing the resistivity). In fact, the fluorescence X-ray spectroscopy for the WCMs indicates the chemical composition as C:80 wt%, O: 17 wt%, Na: 2.8 wt%, K: 0.3 wt%, Ca: 0.2 wt%, Si: 0.1 wt%, and so on. Since the main constituent of WCMs is wood, the WCMs contain a variety of impurities resulting in the extrinsic material. Therefore, electron density for the WCMs n in the conduction band should be expressed by

$$n \sim \left(\frac{N_d - N_a}{2N_a}\right) N_C \cdot \exp(-E_d/kT) \quad \text{-----} \ (1),$$

where N_d is donor density, N_a acceptor density, E_d energy level of donors, N_c effective density of states in the conduction band, k Boltzman constant, and T absolute temperature. That is, the electrical conduction is governed by the impurities and/or defects in WCMs, which generate free electrons to the conduction band. From Arrhenius plots of the electrical resistivity shown in Fig. 2, the donor levels are deduced in terms of Eq. (1): 0.05 eV and 0.01 eV from the conduction band edge.

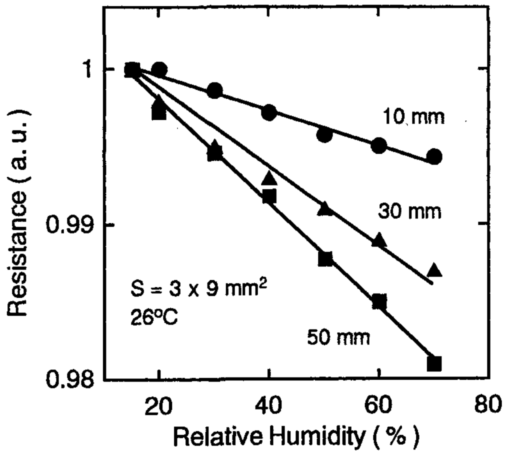

Fig. 4 Relative humidity dependence of the electrical resistance for woodceramic specimens with lengths of 10, 30, and 50 mm (cross section 3 x 9 mm²).

3.2 Humidity dependence of electrical resistance

Humidity dependence of the electrical resistance is presented in Fig. 4 for the WCM specimens with length of 10, 30, and 50 mm (cross section 3 x 9 mm²) at room temperature. The data have been taken after 5 min when the each humidity value has been obtained. The ordinate is shown here in relative resistance in order to facilitate the comparison with each other. It should be noted that the resistance change of WCMs indicates a good linear relationship with humidity, whereas other humidity sensors commercially available at the present time, show non-linearity with humidity. The linear relationship probably results from a unique structure of WCMs, since the change of resistivity on humidity is caused by the adsorption of water molecules at the porous surface: WCMs have two kinds of vacant pores, that is, (1) pores between wood fibers and (2) vessel pores. This linear relationship is contributed by the sum of electronic and ionic conduction. From the viewpoint of electronic conduction, the adsorption of water molecules on the WCM surface, could give rise to donor-like surface states [13], although the details of the process are not well understood. As a result, the resistivity decreases with humidity. On the other hand, ionic conduction refers to the enhancement of conductivity due to chemisorption, physisorption, and/or capillary condensation of water molecules within the pore structure. This leads to the dissociation of water molecules because of high local electron charge density and electro-static field, yielding hydronium (H_3O^+) and hydroxyl (OH^-) ions [3]. These ions may attach to surface at cationic or anionic sites. With application of an electric field, ions move to alternate sites, causing a reduced resistivity. Consequently, the change of electrical resistivity on humidity is the sum of both electronic and ionic conduction.

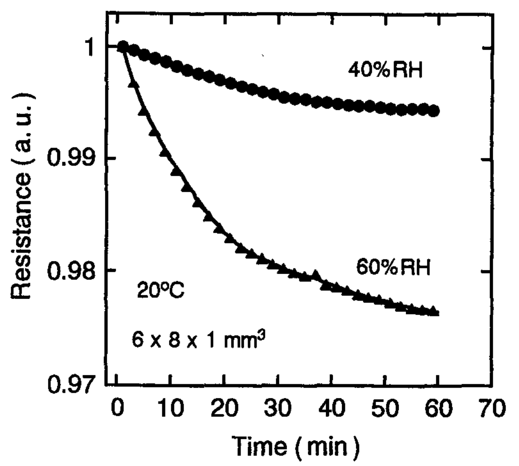

Fig. 5 Electrical resistance versus exposure time to water vapor for woodceramic specimen.

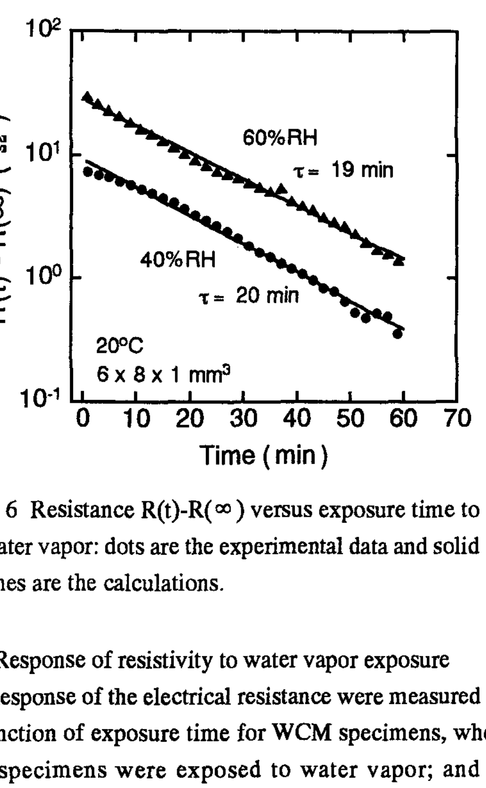

Fig. 6 Resistance R(t)-R(∞) versus exposure time to water vapor: dots are the experimental data and solid lines are the calculations.

3.2 Response of resistivity to water vapor exposure

Response of the electrical resistance were measured as a function of exposure time for WCM specimens, when the specimens were exposed to water vapor; and is presented in Fig. 5 and Fig. 6. The response of resistance *R(t)* is given by

$$R(t) - R(\infty) = R_0 \exp\left(-\frac{t}{\tau}\right) \quad \text{----- (2)},$$

where R_o is initial resistance, $R(\infty)$ resistance at exposure time $t=\infty$, and τ time constant. In Fig. 6 the dots are the experimental data from Fig. 5, while solid line are the results of curve fittings using Eq. (2). As a result of the curve fittings, time constants of 12 - 20 min are deduced for the WCM specimens with thicknesses of 1 - 3 mm (cross section 6 x 8 mm^2).

4. FABRICATION OF HUMIDITY SENSOR AND ITS CIRCUIT

In order to exemplify woodceramics as humidity sensor and temperature sensor, we have fabricated humidity and temperature detecting circuitry, which is displayed in Fig. 7 and Fig. 8. Three sensors i.e., one for humidity and two for temperature, have been used here with dimension of 6 x 8 x 30 mm: two temperature sensors are sealed with epoxy resin, nonhygroscopic material. Since temperature compensation and output circuit become simpler and inexpensive, we utilized the change of resistance rather than capacitance which requires complex circuitry. Figure 7 is an analogue circuit for humidity and provides an output voltage which is proportional to the relative humidity. The output of the humidity sensor is compared with temperature sensor in terms of bridge circuit, and then through buffer circuit the temperature correction is performed in a differential amplifier. Temperature output circuit depicted in Fig. 8 consists of operational amplifiers. A constant current of 1 mA is designed to flow through both temperature and humidity sensors. The output values of those analogue humidity and temperature detecting circuits, have been measured and are illustrated in Fig. 9 and 10, respectively. The outputs from those analogue circuits

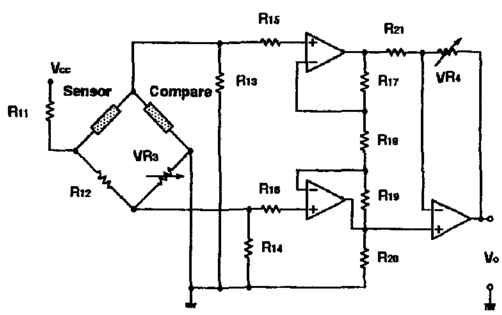

Fig. 7 Analogue circuit for detecting humidity.

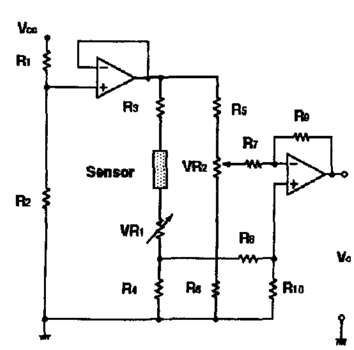

Fig. 8 Analogue circuit for detecting temperature.

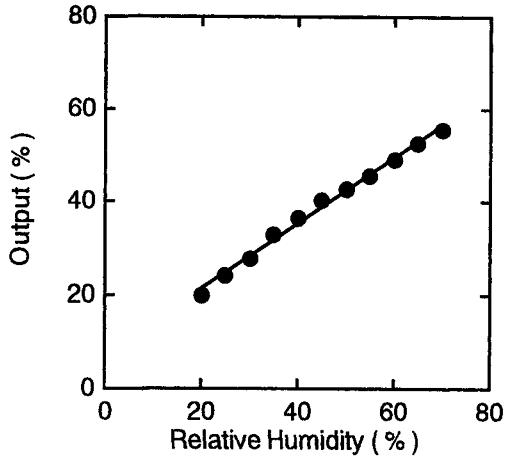

Fig. 9 Output versus relative humidity for the circuit displayed in Fig.7.

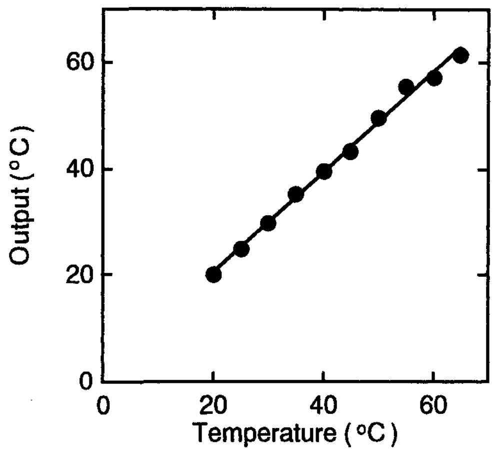

Fig. 10 Output versus temperature for the circuit displayed in Fig.8.

indicate close values with the respective relative humidity and temperature.

4. CONCLUSIONS

Electrical properties, especially humidity and temperature characteristics of woodceramics fabricated at 650°C have been evaluated. X-ray diffraction patterns show that woodceramics consist of $C_6H_9O_6$ and $C_4H_6O_6$ polycrystalline compounds. Relative humidity dependence of the electrical resistance indicates the excellent linear characteristics in the range 15 - 70%RH measured, where ionic and electronic conductions take place simultaneously. Donor trap levels of 0.05 eV and 0.01 eV from the conduction band, have been deduced from the temperature dependence in vacuum; that is, for the electronic conduction which is separated from the ionic conduction. Time constants of 12 - 20 min have been obtained from the time response measurements when exposed to water vapor.

Woodceramic is therefore a suitable candidate for use as a humidity sensor and also temperature sensor at low cost. Additional challenges remain to realize better sensitivity in practical application.

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