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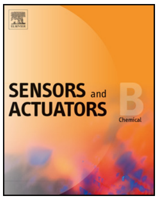

Highly sensitive humidity sensor based on lithium stabilized Na-β''-alumina: *dc* and *ac* analysis

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ABSTRACT

The humidity property of the lithium stabilized Na-β''-alumina (LSBA) sensing material was investigated in detail on a resistivity-type sensor prepared by pasting LSBA powder on a ceramic substrate with Ag interdigitated electrodes through *ac* and *dc* analysis. Results from *ac* complex impedance analysis suggested that LSBA powder based sensor was highly sensitive to humidity with a six order magnitude impedance difference as relative humidity (RH) changed from 11.3% to 93.6% and good stability in 30 days. The response time and recovery time of the sensor were short at lower RH circumstance, which were 42 s and 48 s at 52.8% RH, respectively. Evidences from *dc* variation, *ac* dielectric loss and *ac* complex impedance spectra under different RH circumstance indicated that high humidity sensitivity of the LSBA sensor originated not only from the water molecules absorbed on the surface but also from the Na^+ ions in the conduction slab of the LSBA crystal.

1. Introduction

Humidity measurement is of great importance in agricultural activities, industrial process control and our daily life [1,2]. For the increasing demanding of high-quality products and comfortable living environment, humidity sensor is gaining more and more attention. Various materials have been studied for a humidity sensor, such as organic polymers [3–6], metal oxides [7,8], and porous dielectric ceramics [9–11]. Other materials such as porous silicon [12], porous SiC [13,14], carbon nanotubes [15–17] and oxide nanowires/nanorod [18–20] can also be used. Surface feature of the material and the interaction between the water molecule and the humidity sensing material are important factors for a humidity sensor. Large surface area and good conductive capability will benefit humidity sensitivity. Recently, many studies reported improved humidity performance orignated from the large surface area of nano sized-material [21–23]. On the other hand, studies of the material modification for good conductive capability were also undergoing for a better humidity sensitivity [24–27].

Lithium stabilized Na-β''-alumina (LSBA) is known by its high sodium ion conductivity, which has been widely used in the Na-sulfur batteries and zero emission battery research activity (ZEBRA) as solid electrolyte [28–30]. Excellent ion conductivity of the LSBA ascribes to its special crystal structure. In LSBA crystal lattice, there are loose packed oxygen layers named conductive slab, and closed packed oxygen layers named spinel block in which the arrangement of the atoms is similar to the magnesium aluminum spinel. Na^+ ions locate at the conductive slab where they partly occupy and transfer among Na^+ ions sites and vacancies. There are massive defects in the conductive slab where other ions could enter and exchange with Na^+ ions, such as Ag^+, Ba^{2+}, Sr^{2+}, Nd^{3+}, Eu^{3+}, et al. [31]. Water molecule can also enter into the conductive slab and exchange with Na^+ ions. Based on these properties, it arises a consideration about the potential application of the LSBA power in humidity detection. Several studies reported interactions between LSBA and water vapor or CO_2 gas [32–35]. SAB has been explored for detection of CO_2 [36,37]. However, none of the studies investigated the possibility of LSBA for humidity detection.

In this article, a humidity sensor based on LSBA powder was fabricated. The humidity sensing properties of the LSBA powder were investigated in terms of *ac* complex impedance, *dc* variation and *ac* dielectric loss properties. Complex impedance variation, response and recovery properties with RH changes and stability of the sensor were discussed. A reasonable humidity sensing mechanism was deduced from results of *dc* variation, *ac* dielectric loss properties and *ac* complex impedance spectra of the sensor.

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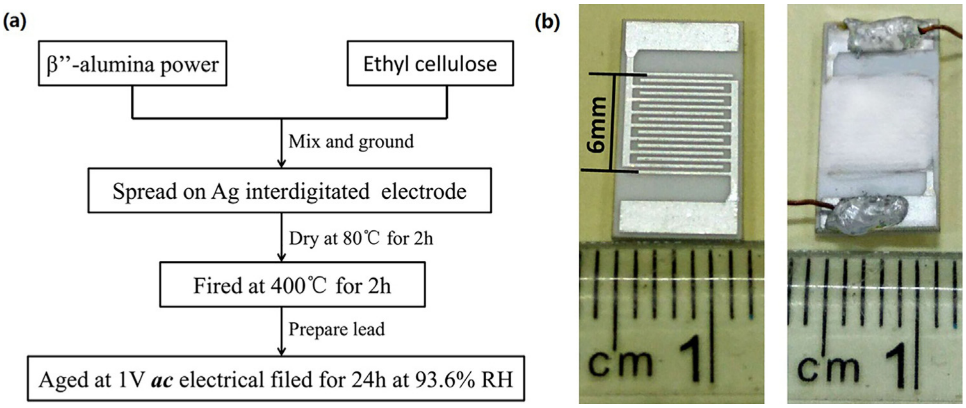

Fig. 1. The fabrication procedure of LSBA humidity sensor(a) and photos of the humidity sensor(b).

2. Experimental

Lithium stabilized Na-β”-alumina powder was synthesized by conventional solid state reaction. Bochmite (Alumina Corporation of China, Zhengzhou, China), $LiNO_3$ and $NaNO_3$ (Sinopharm Chemical Reagent Corporation, Shanghai, China) were firstly mixed according to the chemical composition of $Na_{1.67}Li_{0.33}Al_{10.67}O_{17}$ and milled for 12 h in nylon jar with ethanol as media and zirconia beads. The mixture was then dried and calcined at 1400 °C for 2 h. All reagents used are analytical-grade purity without further purification.

X-ray powder diffraction (XRD; X'pert, Philips, Eindhoven, The Netherlands) using Cu-Kα radiation (λ = 1.5406 Å, scanning rate = 0.02° $2\theta\ s^{-1}$ at 5–70°) was used to analyze the crystal structure of as-synthesized powder. The morphologies and microstructure of the as-synthesized products were examined using field scanned electronic microscopy (FE-SEM; JSM-6710F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM; Tecnai F30G, FEI, Hillsboro,OR, USA). High-resolution X-ray photoelectron spectroscopy (XPS) was used to verify the chemical composition of the powder. The XPS was performed on a spectrometer (VG ESCALAB220i-XL, Thermo-Scientific, Waltham, MA, USA) with a focused monochromatized Al-Kαradiation (E = 1486.6 eV). The *dc* variation with time was recorded on a digital source meter (2410 SMU, Keithley, Beaverton, OR, USA). The *ac* impedance spectroscopy was carried out on a precision impedance analyzer (4294A, Agilent, Santa Clara, CA, USA). The impedance data were collected and analyzed by Z-viewer software [38]. Nitrogen adsorption-desorption tests (3H-2000PS4, Beishide Ltd., Beijing, China) was used to analyze the Brunauer-Emmett-Teller (BET) surface area of the LSBA powder.

The sensor was fabricated on Ag interdigitated electrodes. Firstly, a small amount of LSBA powder was ground with ethyl cellulose in agate mortar to form humidity-sensing paste. The paste was coated onto Ag interdigitated electrode. Then, it was fired at 400 °C for 2 h and aged at room temperature with a voltage of 1 V, 100 Hz for 24 h to improve its stability and durability in 93.6% RH circumstance. The schematic of the preparation procedure and the photos of the sensor were presented in Fig. 1.

The *dc* variation with time of the sensor was measured using a programmable *dc* voltage/current generator (Keithley2410). Before the measurement, the sensor was kept in the target humidity environment for about 30 min. Then 1.0 V *dc* voltage was applied to the sensor and maintained 30 min. Discharge current-time curve was recorded when *dc* voltage was changed from 1 V to 0 V.

The humidity sensing properties of the LSBA humidity sensor were measured on an impedance analyzer. The *ac* voltage applied was 0.5 V, and the frequency varied from 40 Hz to 10 MHz. The target humidity environments were achieved with supersaturation aqueous solutions of different salts in a closed vessel, including LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl and KNO_3, which yielded 11.3%, 32.8%, 52.8%, 75.3%, 84.3% and 93.6% RH, respectively [39]. These RH levels were independently monitored by a standard hygrometer. The response time and recovery time were defined as the time spent by a sensor to achieve 90% of the total impedance change in the adsorption and desorption process [40]. The hysteresis was measured by switching the humidity sensor between the chambers of 11.3%, 32.8%, 52.8%, 75.3%, 84.3% and 93.6%RH, and then shifting back. All of the sensing measurements were carried out at a constant temperature of 25 °C with a temperature controller. The stability property of the sensor was evaluated by resistances variation of the senor every 9 days in 30 days under different RH circumstance. Impedance modulus – temperature feature of the sensor was investigated in the temperature range of 25 °C to 50 °C.

3. Results and discussion

3.1. Structure and morphology

The crystal structure of the as-synthesized powder was characterized by XRD (Fig. 2a). All diffraction can be perfectly indexed into a crystal phase of $Na_{1.67}Li_{0.33}Al_{10.67}O_{17}$ (space group: *R3m*, JCPDS:82-0462), which indicated a pure β”-alumina phase [41,42]. The diffraction peaks were intensive and narrow which suggested that the powder obtained by solid state reaction was of good crystal quality.

The morphologies and composition of the powder were observed by using SEM, EDS and TEM. As it was seen from Fig. 2b, the grain in the powder was platelet shape with a grain size of 0.5–1 μm. The atomic ratios of Al/Na was 1: 6.28 which was approximately equal to the proportions of LSBA (Na/Al = 1: 6.38). The percent of O atom was higher than that of SBA, which may be due to the absorbed CO_2 and H_2O. TEM images of the LSBA powder (Fig. 2c and d) showed that the grains appears as facets. The facets were parallel to the conduction planes, which could be confirmed by the HRTEM images. As it shown in Fig. 2d, lattice fringes distance in HRTEM image was 1.13 nm, which correspond to the (003) plane of the LSBA where Na^+ ions was located.

The XPS spectrum of LSBA powder was shown in Fig. 2e. The binding energy peaks located at 62 eV, 73 eV, 117 eV, 530 eV and 1071 eV in the fully scanned spectra were assigned to Na2s, Al2p, Al2s, O1s and Na1s, respectively. The Element Li was not detected because of the nature of the instrument. These values of binding energy coincided well with published data of SBA [43–45], which further confirmed the chemical composition and oxidation state of elements in the studied powder.

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