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Effect of macrostructural control of an auxiliary layer on the CO_2 sensing properties of NASICON-based gas sensors

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A B S T R A C T

Macrostructural effects of an auxiliary electrode on the CO_2 gas sensing properties of NASICON ($Na_3Zr_2Si_2PO_{12}$) solid-electrolyte sensors were investigated. The sensor with a porous Li_2CO_3–$BaCO_3$-based auxiliary layer (mp-Sensor), which was prepared by utilizing constituent metal acetates and polymethylmethacrylate microspheres as a template, showed faster CO_2 response and recovery and smaller cross-response against humidity changes than those obtained with a dense auxiliary layer without pores (d-Sensor). The magnitude of CO_2 response of mp-Sensor was slightly larger than the theoretical one, probably due to the existence of impurities which might have reacted with CO_2 in the auxiliary layer. On the other hand, c-Sensor with a thicker and dense auxiliary layer, which was prepared by commercially available carbonates, showed smaller CO_2 response and larger cross-response to humidity than mp-Sensor and d-Sensor. Thus, the use of the porous auxiliary layer prepared by constituent metal acetates was confirmed to be effective for improving the CO_2 sensing properties along with the large CO_2 response and small cross-response to humidity.

1. Introduction

CO_2 gas is well-known as a typical greenhouse effect gas. The CO_2 concentration in the atmosphere increased steeply in the past quarter century, and the rise in global temperature and following sea-level rise are now serious issues in our world. In addition, CO_2 also affects human health [1]. On the other hand, the efficiency of photosynthesis of plants is largely dependent on the CO_2 concentration in the atmosphere, and an appropriate concentration has a positive effect on an increase in crop yields [2,3]. CO_2 concentration is generally measured by infrared-type sensors, but they cannot be used widely because of their large size and high cost. Therefore, development of low-cost portable CO_2 sensors with high sensitivity and selectivity is desired in various fields such as maintenance of living atmospheres and agricultural, biological and automobile industries. Some types of CO_2 gas sensors, such as resistive, optical, capacitive and solid electrolyte type, have been thus far studied eagerly by many researchers [3–9]. Electrochemical solid-electrolyte sensors attached with metal carbonates as an auxiliary layer atop the sensing electrode are very promising among them [6–9]. It was reported that some binary carbonates (e.g., Li_2CO_3–$BaCO_3$) as the auxiliary layer showed relatively high CO_2 sensing properties [10,11]. However, they have some problems such as poor long-term stability [12] and large cross-sensitivity to water vapor [13,14]. Those problems have been studied and improved partially by mixing some metal oxides with the binary carbonates and by selecting the material of the counter electrode [13,15–17]. However, control of the macrostructure has not been investigated well in the field of solid-electrolyte gas sensors, except for a few works by Plashnitsa et al. [18,19]. On the other hand, we have so far succeeded to develop various high-potential gas sensors by introducing well-developed sub-micron size macropores into the sensing layer [20–25]. If such macroporous structure is introduced into the auxiliary phase of solid-electrolyte sensors, various sensing properties, such as humidity effect, response and recovery speeds and CO_2 response, are expected to be improved. Therefore, effects of introduction of macropores into the auxiliary layer of NASICON solid-electrolyte gas sensors were investigated in this study.

2. Experimental

2.1. Fabrication of sensor devices

Na^+ super ionic conductor (NASICON) powder was prepared from $Si(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $PO(OC_4H_9)_3$ and $NaOC_2H_5$ by a conventional sol–gel method [14]. They were mixed in an ethanol solvent kept at ca. 70 °C for 12 h with a small amount of nitric acid as

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a catalyst and ultrapure water under a N_2 flow, and then these alkoxides were hydrolyzed in the solution. The xerogel obtained was dried at 120 °C for 24 h and then heated at 750 °C for 1 h to remove organic compounds and to get the NASICON powder. The NASICON powder obtained was pressed into a disc (10 mm in diameter) and then sintered at 1100 °C for 5 h in air.

A pair of Au electrodes was deposited on the NASICON disc by ion sputtering and then heat-treated at 600 °C for 2 h in air. A polymethylmethacrylate (PMMA, 1.5 μm in diameter) template film was covered on one of two Au electrodes (sensing electrode) by dip-coating of an aqueous PMMA suspension containing a dispersant (P123: $(EO)_{20}(PO)_{70}(EO)_{20}$, MW: 5800, EO: ethylene oxide, PO: propylene oxide). Thereafter, the template was air-dried at room temperature, allowing the PMMA microspheres to self-assemble into a 3D array by sedimentation. Subsequently, an aqueous 1.5 mol dm^{-3} acetate (CH_3COOLi:$Ba(CH_3COO)_2$ = 1:1 in molar ratio) solution as a precursor of binary carbonate (Li_2CO_3:$BaCO_3$ = 1:2 in molar ratio) was soaked into the template film, and dried in vacuo. The resultant film was fired at 500 °C for 1.5 h in air to decompose the PMMA template and to obtain a macroporous binary carbonate layer. The sensor with such a macroporous auxiliary layer will be referred to as mp-Sensor.

On the other hand, sensors with a dense auxiliary layer were also fabricated by the similar process, but without the PMMA template film. The thickness of the auxiliary layer was controlled by the number of dip-coating of the precursor acetate solution. For both mp-Sensor and d-Sensor, the thickness of the auxiliary layer was controlled to be the same.

Besides these sensors, a conventional sensor (c-Sensor) was fabricated using commercially available carbonates (mean particle size: 0.7–1 μm) as raw materials for the auxiliary layer. A pair of Au electrodes of c-Sensor was only deposited by screen-printing of Au paste. Then, the binary carbonate paste, which contained Li_2CO_3 and $BaCO_3$ powders (Kishida Chemical Co., Ltd.) in α-terpineol (Li_2CO_3:$BaCO_3$ = 1:2 in molar ratio), was also screen-printed on one of two Au electrodes and fired at 600 °C for 2 h.

The binary carbonate powders obtained were characterized by X-ray diffraction analysis (XRD, Rigaku Corp., RINT 2000) and the microstructure of the auxiliary layers of all sensors was observed by a scanning electron microscope (SEM, Hitachi Ltd., S-2250).

2.2. Measurement of CO_2 sensing properties

Sensing properties to CO_2 of the sensors were measured at 400 °C by switching the atmosphere between 500 and 5000 ppm CO_2 balanced with a synthetic air at 30 min intervals. A difference between EMF in 500 ppm CO_2 (EMF_{500}) and that in 5000 ppm CO_2 (EMF_{5000}) was defined as a gas response ΔEMF_{CO_2} ($EMF_{5000} - EMF_{500}$) in the present study. In addition, an EMF shift induced by a humidity change from 0% to 70% relative humidity (RH), ΔEMF_{RH}, was measured. RH was controlled by mixing a dry air with a wet air containing saturated water vapor at 25 °C; the wet air was prepared by bubbling the dry air through liquid water at 25 °C. The number of electrons involved with the electrochemical reaction on the sensing electrode was estimated from the EMF dependence on CO_2 concentration. 90% response and recovery times were represented by Res and Rec, respectively.

3. Results and discussions

3.1. Characterization of auxiliary layers

Fig. 1(a) shows an XRD pattern of grayish powder prepared from an aqueous CH_3COOLi and $Ba(CH_3COO)_2$ mixed solution by a sol–gel method, which was used for the auxiliary layers for mp- and d-Sensors. It is found that Li_2CO_3 and $BaCO_3$ existed as the main phases and there was no notable peaks ascribed to their oxides or hydroxides. Both Li_2CO_3 and $BaCO_3$ phases are known to exist individually at 400 °C, which was the operating temperature of the sensors in this study, as supported by the phase diagram for Li_2CO_3–$BaCO_3$ [26]. An XRD pattern of the white powder prepared from commercially available carbonates used for c-Sensor is shown in Fig. 1(b). It is almost comparable to that of the powder prepared from Li and Ba acetates, but the peaks ascribed to Li_2CO_3 were comparatively larger than those of the powder prepared from Li and Ba acetates.

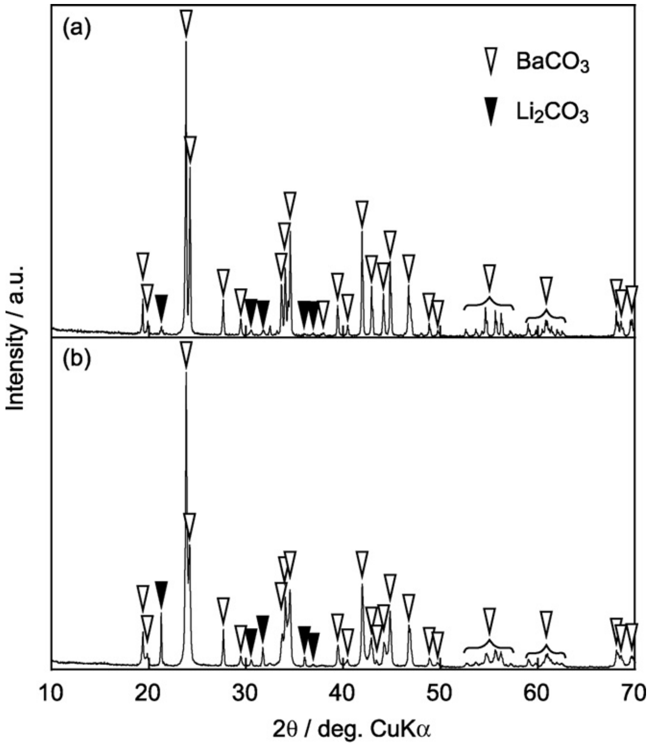

Fig. 1. XRD patterns of mixed Li_2CO_3–$BaCO_3$ binary powders prepared from (a) an aqueous CH_3COOLi and $Ba(CH_3COO)_2$ solution by a sol–gel method and (b) commercially available Li_2CO_3 and $BaCO_3$ powders.

SEM photographs of a PMMA template film fabricated on an Au electrode atop a NASICON disc are shown in Fig. 2. PMMA microspheres of 1.5 μm in diameter were closely packed on the substrate, as shown in Fig. 2(a). The thickness of the PMMA film was 10.0–11.5 μm with 8–9 layers of the PMMA microspheres which were uniformly stacked over each other, as shown in Fig. 2(b). Unfortunately, a few and much smaller PMMA microspheres with a diameter less than 500 nm were mixed as a contaminant with the generally sized PMMA microspheres used in this study.

Fig. 3 shows a porous Li_2CO_3–$BaCO_3$ binary carbonate film used as the auxiliary layer for mp-Sensor fabricated by utilizing the PMMA microsphere film as a template. Relatively uniform and well-developed porous structure with spherical macropores with a diameter of ca. 1.37 μm and a carbonate wall thickness of ca. 165 nm was observed on the surface of the auxiliary layer. The size of macropores was a little bit smaller than that of the PMMA microsphere templates (diameter: 1.5 μm). In addition, the cross-sectional view of the porous carbonate film showed that the bulk was also extremely porous, but the framework of macropores did not maintain the spherical morphology of PMMA microspheres. That is probably because the grain growth of the carbonates (especially Li_2CO_3) occurred even at 400 °C during the thermal decomposition of PMMA microspheres and acetates.