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Bi-electrolyte Carbon Dioxide Gas Sensor Based on Paste Sodium-Beta Alumina and Yttria-stabilized Zirconia

Hyeuk Jin Han and Chong Ook Park+

Abstract

CO_2 sensor was used only one solid electrolyte in many cases. To improve the sensing characteristics of CO_2 sensors, solid electrolyte CO_2 sensor has been developed by bi-electrolyte type sensor using Na-Beta-alumina and YSZ. However, in many further studies, bi-electrolyte type sensor was made by pellet pressed by press machine and additional treatment for formation of interface. In the aspect of mass production, using thick film and additional treatment is not suitable. In this study, CO_2 sensor was fabricated by bi-electrolyte structure which was made by an NBA paste layer deposited on YSZ pellet and fired at 1650°C for 2 hour. The formation of stable interface between YSZ and NBA were confirmed by SEM image. When the type IV electrochemical cell arrangement represented by CO_2,O_2,Pt| Li_2CO_3-$CaCO_3$||NBA||YSZ|O_2,Pt is used to measure the CO_2 concentration in air. This sensor EMF should depend only on the concentration of CO_2 by logarithmic. Also, sensor shows P_{CO_2} and EMF relationship like nerstian reaction at a temperature of 450°C.

Keywords: Gas sensors, Yttrium zirconium oxide, Na beta alumina, CO_2, Paste

1. INTRODUCTION

As the importance of controlling CO_2 increased in various technologies, the need of inexpensive CO_2 sensor with high selectivity is growing. So the development of solid electrolyte CO_2 sensor is required from the point of simplicity, low price and quantitative characteristic [1-3].

In this paper, to improve the sensing characteristics of CO_2 sensors, solid electrolyte CO_2 sensor has been developed by Bi-electrolyte type sensor using Beta-alumina and YSZ which are super ionic conductor material have applied to the solid ion device for a long time [4]. In the bi-electrolyte CO_2 sensor, a combination of Na^+ conductor of the Sodium-Beta-alumina (NBA) and Li-based binary carbonate represented by Li_2CO_3-$CaCO_3$ mixture were used as auxiliary electrode and O^{2-} conductor of YSZ was used as a reference material.

Following the Nernst equation, it reacted to CO_2 rapidly and reversibly in CO_2 concentration range 100~5000 ppm. The structure of this new type sensor was as followed.

$$CO_2,O_2,Pt|\ Li_2CO_3\text{-}CaCO_3||NBA||YSZ|O_2,Pt \quad (1)$$

However, in a further number of studies, bi-electrolyte sensor was prepared by pressing pellets and additional processing for forming an interface [5-7]. In the case of the mass production, the use of additional treatment and the pellet form is not suitable. Therefore, NBA paste was used in the process for connecting the electrolyte easily in this experiment.

2. EXPERIMENTAL

2.1 CO_2 Sensor Preparation

The YSZ (TOSOH Corporation 8 mol%) pellet was made by applying a pressure of 2 tons about 1 minute at carver uni-axial press. After the molding, it was put in a bag of rubber and removed the air for 15 minutes. It applied a pressure of 29000 psi at the CIP device (flow autoclave system). After creating a pellet, pellet was sintered at 1350°C for 8 hours. Fig. 1 shows the schematic structure of the prepared sensor.

Next, Na_2CO_3 (Aldrich) and Al_2O_3 (Aldrich) powders were weighed in a molar ratio of 1.2:11 for synthesizing Na-beta alumina. Then it was mixed ball milling in the bottle containing ethanol and zirconia ball for 1day. The resulting powder was dried

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, E4 A304, Korea Advanced Institute of Science, 291, Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea
+Corresponding author: copark@kaist.ac.kr
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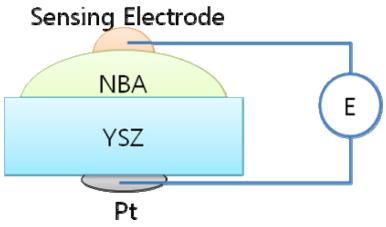

Fig. 1. Schematic structure of the CO_2 sensor.

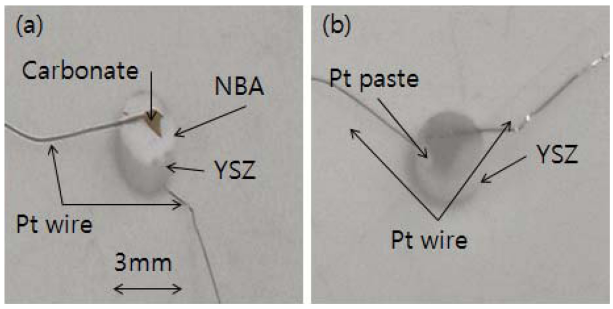

Fig. 2. Photographs of the fabricated CO_2 sensor; (a) A top view and (b) bottom view.

and calcinated at 1650°C for one day. After calcinations, the powder was crushed by ball milling for 3 days. Final powder was obtained by drying and it was identified by X-ray diffraction.

NBA paste was put on the YSZ pellet and fired at 1650°C for 2 hour. Since NBA was put on top of the YSZ by paste form, SEM photographs were taken to confirm the formation of the interface between the YSZ and the NBA.

Then Pt paste and Pt wire was put in the bottom of YSZ and heat was treated at 1000°C for 1 hour. Mixture of Au, Li_2CO_3 and $CaCO_3$ paste was deposited on the NBA and Pt wire was put together. Then it was baked at 740°C for 15 min. A view of the sensing element is shown in Fig. 2.

2.2 CO_2 Sensing Mechaninsm

The mechanism of the sensor is very similar to the operation of Na-based carbonate electrodes [8]. The reaction of sensing electrode is assumed to be as follows,

$$Li_2CO_3 = 2Li^+ + CO_2 + (1/2)O_2 + 2e^- \quad (2)$$

$$2Na^+ + O_2\text{-} = Na_2O \text{ (interface between NBA and YSZ)} \quad (3)$$

$$(1/2)O_2 + 2e^- = O^{2-}\text{(YSZ)} \quad (4)$$

The overall chemical reaction is written as

$$Li_2CO_3 + 2Na^+ = 2Li^+ + Na_2O + CO_2 \quad (5)$$

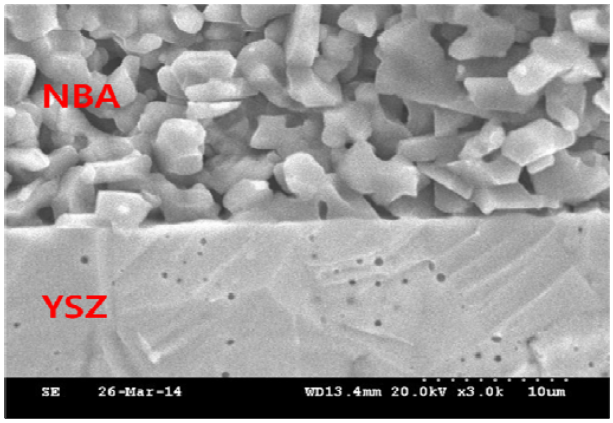

Fig. 3. Sensing performance of the CO_2 sensor (450°C).

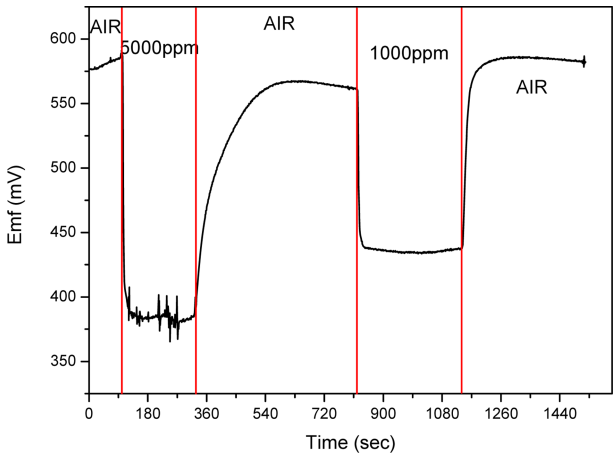

Fig. 4. Interface between NBA and YSZ.

Assumed by the constant activities of Li_2CO_3, Na^+, Li^+ and Na_2O, EMF can be expressed as

$$E=E_0-(RT/2F)\ lnP(CO_2) \quad (6)$$

The CO_2 sensing properties were examined at 450°C. As shown in Fig. 4, the sensor reacted well to changing from dry air (0 ppm CO_2) to dry 5000 ppm CO_2 and 1000 ppm CO_2. The sensor responded well to dry air at recovery state.

3. RESULTS AND DISCUSSIONS

This sensor was made by printing paste on the YSZ pellet rather than the Miura method which is classic method for joined to each other electrolyte by using Pt-wire spring system. Therefore it is necessary to confirm that interface between NBA and YSZ. As shown in Fig. 3, NBA paste film and YSZ form interface between NBA and YSZ.

Fig. 4 shows the response of the CO_2 sensor at 450°C. When the partial pressure of CO_2 is changed, the EMF changed and reaches a constant value within 200 s. The response is quite rapid because the time of 200 s is necessary to change the gas composition in the testing tube.

Sensitivity were 71.54 mV/dec at 450°C. This value shows only 1% error compare to the result of a theoretical value (71.73 mV/dec) that came out in the previous equation (6). As a conclusion, E vs. log P_{CO2} shows a linear relationship obeying the Nernst law for 450°C.

4. CONCLUSIONS

CO_2 sensor was fabricated by bi-electrolyte structure that the NBA paste painted on top of the YSZ pellet. Without any special mechanical forces, it was possible to confirm the formation of stable interface by heat treatment using a simple paste.

P_{CO_2} and EMF relationship were showed nerstian reaction with the theoretical relationship at a temperature of 450°C. It functions as CO_2 sensors in which EMF are expressed by eq. (6). Also, sensitivity Error compare to theoretical value is approximately 1%.

In the future, on the basis of this result, CO_2 sensor will produced by typecasting method because typecasting can make sensor more cheap and easy to approach mass production.

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