Stabilization of NASICON-based CO_2 sensor operative at room temperature by using Li_2CO_3-$BaCO_3$ auxiliary phase

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We have shown that the NASICON ($Na_3Zr_2Si_2PO_{12}$)-based potentiometric device attached with a metal oxide (In_2O_3 or ITO) sensing electrode has exhibited good CO_2 sensing properties at room temperature when a metal carbonate like $NaHCO_3$ is incorporated as an auxiliary phase [1, 2]. However the EMF output of the devices was found to suffer from a disturbance (base line shift) by a change in humidity. The disturbance seems to originate from the instability of the auxiliary phase involved. In this study, we tried to eliminate the disturbance by introducing a mixed carbonate auxiliary phase of Li_2CO_3-$BaCO_3$.

Figure 1 shows a schematic drawing of the CO_2 sensor fabricated. The NASICON powder derived by a sol-gel method was used for fabricating the NASICON disk. Li_2CO_3-$BaCO_3$ (0:1-1:4 in molar ratio) was attached on one side of NASICON disk by mechanical press, followed by calcining at 500 °C for 30 min. On top of it, Indium Tin oxide (ITO) paste was applied with a gold mesh electrode inserted in it and calcined at 500 °C for 30 min in air. The reference gold electrode was attached on the reverse side of the disk by applying gold paste and calcining at 800 °C for 2 h before the Li_2CO_3-$BaCO_3$ auxiliary phase was attached. Gas sensing properties were measured in a conventional gas-flow apparatus equipped with a heating facility.

Figure 2 (a) shows CO_2 sensing properties of the device attached with an auxiliary phase at room temperature under various conditions of humidity (RH). The EMF response was linear to the logarithm of CO_2 concentration, with its slopes indicating n=1.7 - 1.8 where n is the number of reaction electrons involved in the electrochemical reduction per CO_2. With an increase in RH, however, the EMF vs. CO_2 concentration correlations tended to shift up. The shift (disturbance) by a humidity change was observed with this device, although the extent of the shift was far smaller compared with the devices attached with an $NaHCO_3$ or Na_2CO_3 auxiliary phase. This phenomenon may originate from the instability of the auxiliary phase involved. Thus the auxiliary phase was replaced by Li_2CO_3-$BaCO_3$, which has been known to give stable sensing properties for a high temperature type CO_2 sensor. The resulting device was found to exhibit good CO_2 sensing properties stable against humidity changes, as shown in Fig. 2 (b).

References

[1] K. Obata, S. Kumazawa, K. Shimanoe, N. Miura, N. Yamazoe, *Sensors and Actuators B*, **76**, 639(2001).
[2] K. Obata, K. Shimanoe, N. Miura, N. Yamazoe, *Sensors and Actuators B*, submitted.

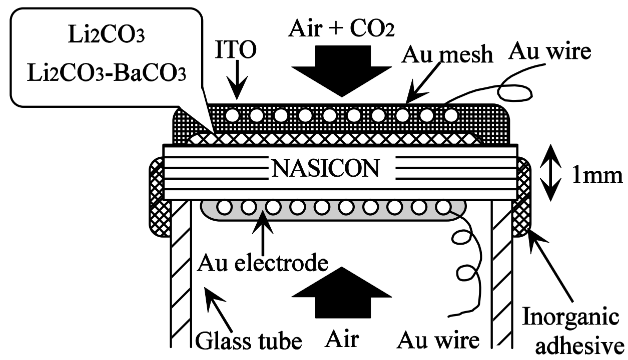

Fig. 1 Schematic drawing of CO_2 sensor.

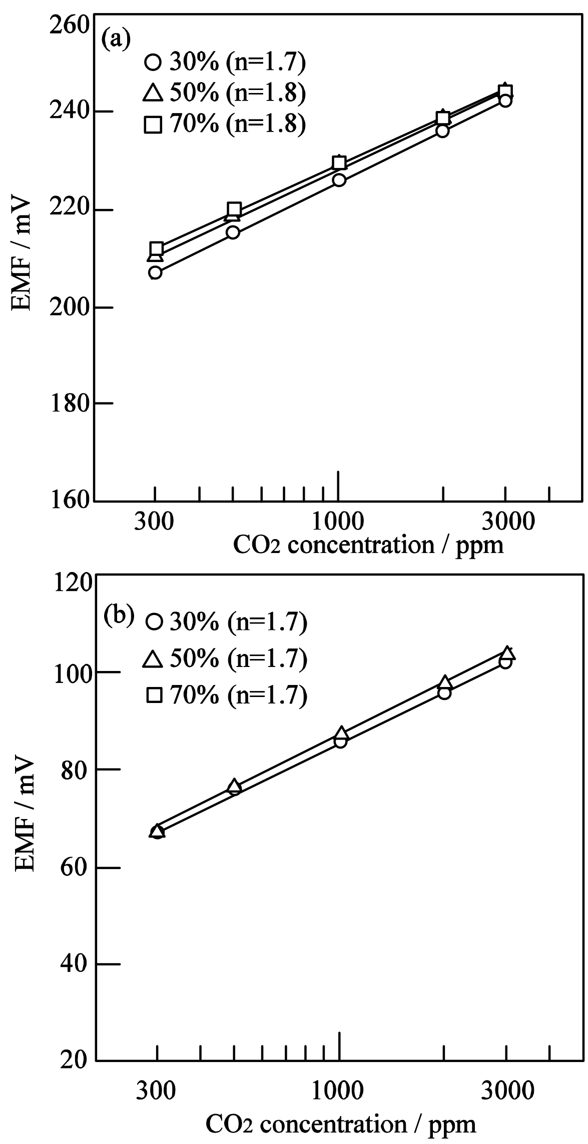

Fig. 2 EMF vs. CO_2 concentration relations for (a) Li_2CO_3 and (b) Li_2CO_3-$BaCO_3$ (1:2 in molar) attached devices at 30 °C.