Reactivity of Solid Electrolyte and Auxiliary Phase on Pt, Li_2CO_3/Na_2O-Al_2O_3-4SiO_2//YSZ/Pt Electrochemical CO_2 Gas Sensor

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Introduction

The increasing need of a reliable and continuous monitoring of CO_2 levels in the atmosphere has promoted the development of potentiometric sensors, based on an alkali ion-conducting solid electrolyte because of their good selectivity to CO_2. We have studied to use of Na_2O-Al_2O_3-nSiO_2 glass-ceramics as a dense Na^+-conductor [1,2].

In this study, the stability and reversibility of CO_2 sensing characteristics were examined in a wide range of CO_2 concentration for monolithic type sensor with CO_2,O_2,Pt/Li_2CO_3/Na_2O-Al_2O_3-4SiO_2//YSZ/Pt,CO_2,O_2 structure. Furthermore, the correlation between the sensing characteristics and the stability of Li_2CO_3 was examined.

Experimental

Na_2O-Al_2O_3-4SiO_2 (NA4S) melts were prepared with the mixture of Na_2CO_3, Al_2O_3 and SiO_2 in the prescribed ratio by the calcination at 1300^{o}C in air with box furnace. The sample after cooled was ball-milled, and then mixed with α-terpineol for the screen print. For the monolithic type, NA4S layer with ca. 40 μm in thickness was formed on 8mol% YSZ plate with 0.2 mm in thickness and then heated at 1150^{o}C. After cooled, porous Pt electrodes were formed by screen-prints with Pt paste on both side of the YSZ and NA4S and then heated at 600 ^{o}C. Li_2CO_3 layer was formed as an auxiliary electrode on the NA4S side by painting of the mixture of Li_2CO_3 and methanol. Furthermore, to examine the reactivity of Li_2CO_3 and silica, their mixture with amorphous and/or quartz phase SiO_2 (*a*-SiO_2, *q*-SiO_2) were heat-treated at various temperature from 200 to 800^{o}C.

Results and Discussion

Fig.1 shows the response behavior recorded in dry condition for the freshly prepared sensor. At 460 ^{o}C, the EMF increased gradually in the initial period and then a stable response was observed.

To determine the reason of EMF drift, we investigated reactivity of the components (1) at the interlayer between NA4S and YSZ, (2) between NA4S and CO_2 gas and (3) between NA4S and Li_2CO_3 layer in CO_2.

Cross section analysis was applied for the YSZ-NA4S interconnected layer. The interlayer region was 2-3 μm in thickness. From the compositional analysis across the layers, it was confirmed that the Na in NA4S diffused in YSZ layer and Al, Si, and Zr remained in each region [2].

For the Na_2O-Al_2O_3-nSiO_2 system, nepheline ($NaAlSiO_4$, n=2, hexagonal), carnegieite ($NaAlSiO_4$, n=2, cubic), and albite ($NaAlSi_3O_8$, n=6) are known as crystalline phases. By heating at 1300 ^{o}C or higher, a broad band at around 2θ=23^o was confirmed for XRD patterns with several weak peaks due to Al_2O_3 and $NaAlSiO_4$ (like-carnegieite) [2]. The stability of NA4S, synthesized for nepheline and like-carnegieite phases in syn-air and 100%CO_2 was examined by TGA. The weight changes could not be observed for the NA4S both in syn-air and 100%CO_2.

The reactivity of NA4S and Li_2CO_3 was examined for the mechanically mixed powders. The weight increase was observed when the ambient was changed from syn-air to 100%CO_2, although it was very small (ca. 0.5%). When pure Li_2CO_3 was heated in syn-air, the weight change was almost zero below 550 ^{o}C and it started to decompose above 550 ^{o}C. It seems that NA4S slightly reacts with Li_2CO_3. To confirm the product formed by the heating, the mixed powders were examined with XRD in ambient air. The peak intensity assigned to Li_2CO_3 phase decreased by heating at 400 ^{o}C, and further heating at 500 ^{o}C resulted to the disappearance of the Li_2CO_3 signals. Some small signals due to nepheline and Li_4SiO_4 were detected for the mixture heated at 500 ^{o}C and the intensity of the signals increased by heating at higher temperature. For the mixture, the heat treatment induced the formation of nepheline, Li_4SiO_4 and Li_2SiO_3. In addition, when we investigated for the mixture of the synthesized nepheline and Li_2CO_3, any distinct changes in the XRD patterns could not be observed even after heating at 600 ^{o}C. It is concluded that the glassy SiO_2 in NA4S is reactive with Li_2CO_3.

To examine the reactivity of the mechanically mixed Li_2CO_3 with *a*-SiO_2, TGA was measured in air and CO_2. The mixture of Li_2CO_3 and *a*-SiO_2 (1:1 in mole ratio) heated in ambient air from 300 to 700 ^{o}C was examined by XRD. Heat treatment leads to the decomposition of Li_2CO_3 and the formations of Li_4SiO_4 and Li_2SiO_3 phases. For the powders heated at 700 ^{o}C, most of Li_2CO_3 phase diminished. We confirmed the reaction, $Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3$ by TGA and XRD. The humidification of the ambient resulted in the acceleration of the reaction of Li_2CO_3 and *a*-SiO_2 resulting in the formation of Li_2SiO_3.

References

[1] Y.Sadaoka, Y.Sakai and T.Manabe, *Sensors and Actuators B,* 13-14 (1993) 532-535.
[2] Y.Shimamoto, T.Okamoto, H.Aono, L.Montanaro and Y.Sadaoka, *Sensor and Actuators B,* 99 (2004) 141-148.

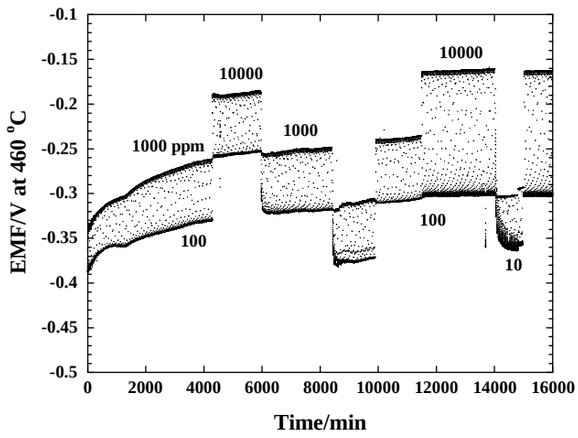

Fig. 1 EMF response of the monolithic type sensor at 460^{o}C. CO_2 gas concentration in ppm is indicated in the figure.