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Effects of Porous Structure of the Auxiliary Electrode on the CO₂ Sensing Properties of a NASICON-based Sensor

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Abstract

Structural effects of the auxiliary electrode layer on the CO₂ sensing properties of NASICON (Na₃Zr₂Si₂PO₁₂) solid electrolyte sensors have been investigated. The sensor with a macroporous Li₂CO₃-BaCO₃-based auxiliary layer showed faster CO₂ response and recovery and a smaller EMF drift against a humidity change than those observed for the sensor equipped with a dense auxiliary layer. The CO₂ response of the present sensors was slightly larger than the theoretical one. This suggests the existence of some impurities capable of reacting with CO₂ in the auxiliary layer prepared in the present study.

Keywords: CO₂; Gas sensor; NASICON; macropores

Introduction

The use of CO₂ sensors is requested in various fields such as maintenance of living atmospheres and agricultural, biological and automobile industries. Electrochemical solid-electrolyte gas sensors with metal carbonates as an auxiliary electrode are very promising among various types of CO₂ sensors proposed¹. However, they have some problems such as large cross-sensitivity to water vapor. Meanwhile, we have so far succeeded to develop high-potential gas sensors with well-developed sub-micron size macropores in the sensing layer². If the adsorption of water molecules onto electrodes makes potential changes, such interferences from water vapor may be reduced by structural control of the auxiliary layer. Therefore, introduction of macropores into the auxiliary layer of a NASICON-based CO₂ sensor was attempted in this study.

Experimental

A pair of Au electrodes was deposited on a NASICON substrate by ion sputtering or screen-printing. One of the electrode was covered with a polymethylmethacrylate (PMMA, 1.5 μm in diameter) template film was covered on one Au electrode by dip-coating of a PMMA aqueous suspension containing a dispersant (P123: (EO)₂₀(PO)₇₀(EO)₂₀, M_w: 5800). Subsequently, the template film was soaked in a 1.5 mol dm⁻³ acetate (CH₃COOLi : Ba(CH₃COO)₂ = 1 : 1 in molar ratio) aqueous solution, pulled up and then dried in vacuum. Heat treatment of the resulting composite film in air at 500°C to decompose and to eliminate PMMA left behind a macroporous carbonate (Li₂CO₃ : BaCO₃ = 1 : 2 in molar ratio) auxiliary layer on the Au. The sensor with such a macroporous auxiliary layer will be referred to as an mp-Sensor. On the other hand, a sensor with a dense auxiliary layer (d-Sensor) was also prepared by the similar process without the PMMA template film. Sensing properties of

these sensors were measured at 400°C by switching between 500 and 5000 ppm CO₂ balanced with air containing 0% or 70% RH calculated at 20°C. In addition, an EMF drift against a humidity change between 0% and 70% RH was also investigated.

Results and Discussions

Figure 1 shows SEM images of carbonate auxiliary layers of mp-Sensor and d-Sensor. It is obvious that decomposition of PMMA left behind porous structure of the carbonate auxiliary layer of mp-Sensor, while the carbonate auxiliary layer of d-Sensor was very dense. The thickness of auxiliary layers of both mp-Sensor and d-Sensor was about 6 μm.

Figure 2 shows response transients of mp-Sensor and d-Sensor. Response and recovery times of mp-Sensor were much faster than those of d-Sensor, since CO₂ molecules could easily diffuse into the porous auxiliary layer, leading to quick adsorption and desorption of CO₂ from the electrodes. In addition, an EMF drift to a humidity change between 0% and 70% RH observed for mp-Sensor was smaller than that observed for d-Sensor. Generally, it is reported that H₂O molecules influence on the potentials of electrodes³⁾. The Au surface below the macroporous auxiliary layer of mp-Sensor was exposed directly to H₂O in comparison with that below the dense auxiliary layer of d-Sensor. Therefore, mp-Sensor showed a small EMF drift against a humidity change as shown in Fig. 2, since the amount of H₂O molecules adsorbed on the Au surface below the macroporous auxiliary layer was expected to be close to that of the uncovered Au counter electrode, in comparison with the case of the dense auxiliary layer.

On the other hand, a conventional sensor fabricated with commercially available carbonates as an auxiliary layer gave the theoretical number of reaction electrons, $n = 2$ (estimated from generally electrode reaction: $2\text{Li}^+ + \text{CO}_2 + 1/2\text{O}_2 + 2e^- \rightleftharpoons \text{Li}_2\text{CO}_3$), while those of mp-Sensor and d-Sensor were about 1.7 and hence the present sensors showed higher CO₂ response. This suggests the existence of some impurities capable of reacting with CO₂ in the auxiliary layer prepared in the present study.

Further improvement of CO₂ response properties is under investigation by both structural and compositional control of the auxiliary layer.

References

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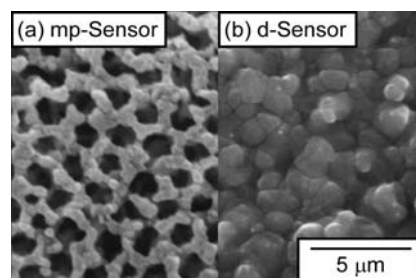


Fig. 1 SEM images of (a) a macroporous auxiliary layer of mp-Sensor and (b) a dense carbonate layer of d-Sensor.

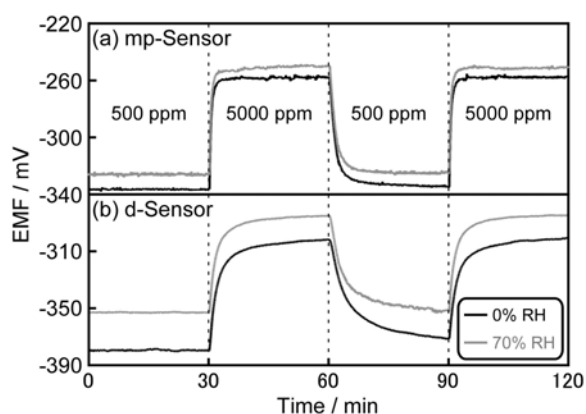


Fig. 2 Response transients of (a) mp-Sensor and (b) d-Sensor to CO₂ gas under 0 and 70% RH at 400°C.