

Response/Recovery Behaviors of Solid Electrolyte CO₂ Gas Sensors Depending on Reference Materials

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Abstract

Effects on response and recovery behaviors depending on reference materials such as lithium cobalt oxide (LiCoO₂) and lithium manganese oxide (LiMn₂O₄) as well as lithium titanate (Li₂TiO₃) were investigated by fabricating the sensor composed of those reference materials and a sensing material Li₂CO₃ on a solid electrolyte Li₃PO₄. Selection of the reference materials was adopted from cathode materials in lithium ion battery field because of the similar working mechanism. The results showed that LiMn₂O₄ and LiCoO₂ as the reference materials were effective in enhancing Δ EMFs/decade value and recovery time of the sensors compared to Li₂TiO₃, which might come from the facile lithiation of the reference materials, LiMn₂O₄ and LiCoO₂, resulting from their unique crystal structures.

Key words: Solid electrolyte, CO₂ gas sensor, reference material, response time

Background and Motivations

There have been international interests on CO₂ gas sensing due to global warming and corresponding climate changes [1]. Accurate and robust sensing of CO₂ gas is requested in order to solve the international problem on CO₂ gas. There are several types of CO₂ sensors such as an optical, a semi-conductor and an electrochemical type that are governed by different working mechanisms. The optical type CO₂ gas sensors utilize absorption at infrared wavelength by CO₂ and quantitate the concentration of CO₂ gas. However, the optical type CO₂ sensors are expensive and difficult to minimize due to complex mirror design, an IR light source and a precision detector. In case of the semi-conductor type, the resistance changes of the sensor on CO₂ gas can be converted into concentrations of CO₂ [2]. However, the mechanism of resistance change is still ambiguous and needs to be carefully investigated.

Wireless sensor networks have been considered as one of the methods that are effective in monitoring environments at wide range area in real time [3]. Therefore, the authors have been trying developing micro CO₂ sensor consuming low power less than 100mW for effective monitoring of CO₂ concentration using WSNs. We considered electrochemical type CO₂ sensor using solid electrolytes as a candidate because the whole manufacturing

process of the CO₂ sensor can be applied in MEMS micro heater fabrication resulting in cutting power consumption of the sensors [4-6].

To realize a low power-consuming CO₂ sensor that can be installed into wireless sensor node, we need not only to adopt micro sensor based on MEMS heater but also to develop the sensor showing quick response/recovery behavior which is helpful for decreasing duty time of the sensor nodes. Here, we report our efforts to achieve fast response and recovery of the solid electrolyte CO₂ gas sensors by selecting the reference materials from the cathodes materials in lithium ion battery field.

Experimental Details

Li₃PO₄ (1μm) was deposited on alumina substrates on back side of heater through thermal evaporation followed by heat treatment at 700~800°C in a tube furnace [7]. A pair of Au electrodes for the reference and the sensing material was screen-printed with space of 1 mm between electrodes to make a coplanar configuration and fired at 700~800°C. Li₂TiO₃, LiCoO₂, and LiMn₂O₄ were used as the reference materials of the solid electrolyte CO₂ sensors and screen-printed on one of a pair of Au electrodes. Lithium carbonate (Li₂CO₃) was used as the sensing material and screen-printed on the other electrode. Those screen-printed materials were 5~10 μm thick after heat treatments. All components of the sensors

were characterized by scanning electron microscopy, EDX and X-ray diffraction (XRD).

Responses of the sensors to CO₂ gas were monitored by measuring electromotive forces (EMFs) at 500°C under various CO₂ concentrations using modified tube furnace with mass flow controllers (MFCs). During measurements, air as a balance gas was used at a 2000 cc/min flow rate, and CO₂ gas of 10% concentration was used as an analyte. Desired analyte concentrations from 500 parts per million (ppm) to 5000 ppm were prepared by mixing the balance gas and the 10% CO₂ gas through mass flow controllers (MFCs). Responses of the sensors were investigated at 500, 1000, 5000 ppm concentration respectively for 2 min in sequential manner by monitoring electromotive force (EMF), and recovery behaviors of the sensors were investigated by decreasing gas concentration from 5000 ppm to 500 ppm.

Discussion

Solid electrolyte CO₂ gas sensors are composed of the sensing materials, the reference materials and the solid electrolytes. There are a number of researches investigating effects of the sensing and the reference materials on CO₂ gas responses [8, 9]. However, the reference materials have been just considered as a basis for a potential generated by a reaction of the sensing material and CO₂ gas, which have required inertness against CO₂ gas of the reference material. That has been considered as the only important factor for the reference materials. Given that the sensing responses of solid electrolyte CO₂ gas sensors come from lithium ions movements from the sensing material to the reference material, the electromotive force would be affected by the reference material property such as lithium ions uptake/release performances. Therefore, the authors selected lithium cobalt oxide (LiCoO₂) and lithium manganese oxide (LiMn₂O₄) as well as lithium titanate (Li₂TiO₃) as the reference material. Li₂TiO₃ has been used for the reference material of the solid electrolyte CO₂ gas sensor [7]. LiCoO₂ and LiMn₂O₄ have been used for the cathode material in the lithium ion battery field due to facile intercalation and de-intercalation of lithium ions in lithium ion battery [10]. Considering working mechanism of the CO₂ gas sensors, diffusion of lithium ions through the solid electrolyte occurs in one direction from the sensing electrode to the reference electrode. Therefore, intercalations or lithiations of the reference materials were expected to affect behaviors of response and recovery of the sensors.

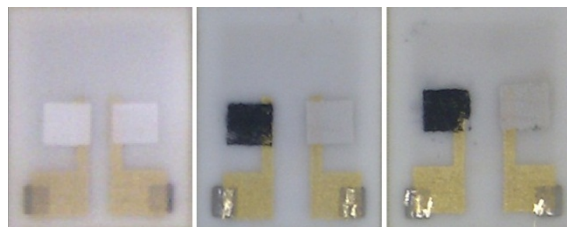


Fig. 1. Photo of the fabricated CO₂ sensors with (a) Li₂TiO₃, (b) LiCoO₂ and (c) LiMn₂O₄ as reference materials

The sensors were fabricated using Li₃PO₄ as the solid electrolyte and Li₂CO₃ as the sensing material (Fig. 1). Li₂TiO₃, LiCoO₂ and LiMn₂O₄ were used as the reference material in order to investigate the effects of the reference materials to the CO₂ gas sensor properties. The sensor composed of Li₂TiO₃ (reference material)/Li₃PO₄ (solid electrolyte)/Li₂CO₃ (sensing material) was fabricated as a reference sensor [7].

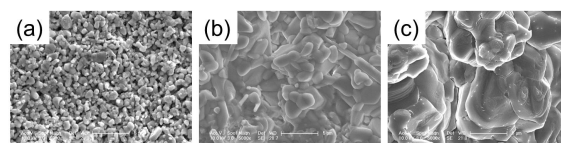


Fig. 2. SEM images of (a) Li₂TiO₃, (b) Li₃PO₄ and (c) Li₂CO₃ at 5K magnification

The materials used for fabrication of CO₂ were observed with SEM (Fig. 2). Li₂TiO₃ was the spherical morphology with several hundreds of micrometers in diameter. And Li₃PO₄ as the solid electrolyte and Li₂CO₃ were found to have several micrometers size.

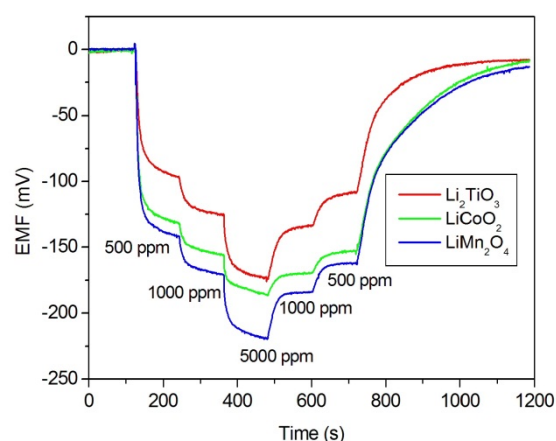


Fig. 3. Responses of the sensors depending on reference materials.

The sensors composed of the same solid electrolytes and the sensing materials except the reference materials were investigated by measuring EMFs with exposures of various CO₂ concentrations at 500°C as working temperature (Fig. 3). The concentrations of CO₂ gas for investigation of the sensor responses were 500, 1000, 5000 ppm. The

sensors were exposed to CO₂ gas for 2 min by increasing CO₂ concentrations in order to observe response behaviors of the CO₂ sensors. Then, the concentrations of CO₂ gas were decreased from 5000 ppm to 500 ppm in order to investigate the recovery behaviors of the sensors. Δ EMFs/decade from the gas response measurements corresponding to slopes of EMF versus CO₂ concentration graphs were shown in Fig. 4 and were summarized in Fig. 5.

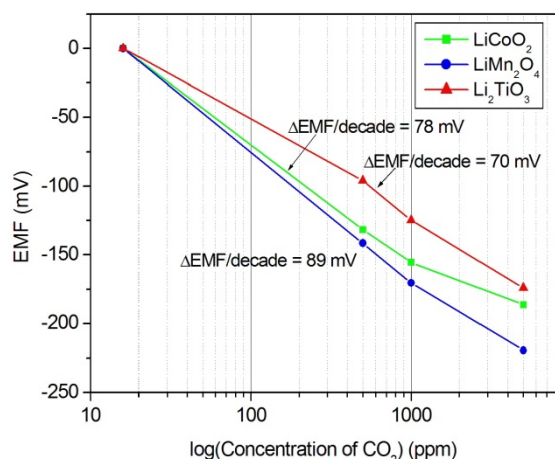


Fig. 4. Electromotive forces of the gas sensors on different CO₂ gas concentrations.

The sensors composed of LiMn₂O₄ and LiCoO₂ as the reference material showed 89 mV and 78 mV as Δ EMF/decade, respectively. On the other hand, the reference sensor containing Li₂TiO₃ showed 70 mV as Δ EMF/decade. LiMn₂O₄ as the reference materials was the most effective in terms of Δ EMF/decade. A distorted rock-salt structure of LiCoO₂ and spinel structure of LiMn₂O₄ have been known to facilitate lithiation and de-lithiation of the cathode electrode in the lithium ion battery [10]. The Authors think that lithium ion capacities of the reference materials such as LiCoO₂ and LiMn₂O₄ would take an effect on the enhancement of Δ EMF/decade.

Furthermore, the sensor response and recovery behaviors were investigated by defining response and recovery time as period from 10 to 90% response and recovery based on maximum response and recovery as 100% (Fig. 5). The cathode materials we adopted from the lithium ion battery showed better recovery time compared to that of the common reference material, Li₂TiO₃.

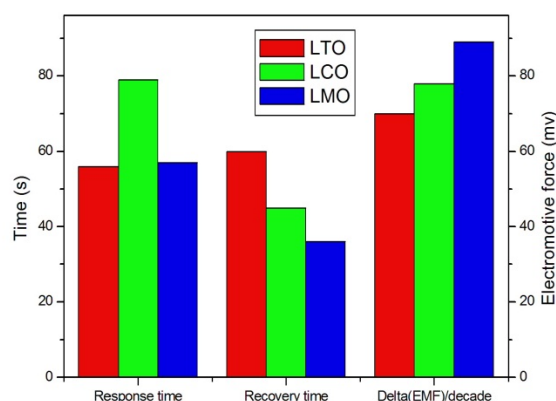


Fig. 5. Response time, recovery time and Δ EMF/decade of the sensors depending on reference materials.

As shown in Fig. 5, LiMn₂O₄ and LiCoO₂ as the reference material were effective in terms of recovery time as well as Δ EMFs/decade of the sensors. Recovery time of the reference sensor using Li₂TiO₃ was 60s, but recovery time of the sensor using LiMn₂O₄ and LiCoO₂ were 36s and 45s. However, the response times of the sensors from the cathode materials of the lithium ion battery were not faster than that of the sensor from Li₂TiO₃ or even slower. Correlations with response/recovery time and the reference materials are still ambiguous. Electrochemical characterizations such as impedance spectroscopy or elemental analysis between interfaces are in progress.

Summary

The effects of the reference materials to the solid electrolyte CO₂ sensor properties were investigated. LiMn₂O₄ and LiCoO₂ as the reference materials that were adopted from lithium ion battery showed improvements of Δ EMFs /decade and recovery time of the corresponding sensors. These improvements would be useful for cutting operation time and reliability of the sensors.

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