

Potentiometric CO₂ Sensor Using Li⁺ Ion Conducting Li₃PO₄ Thin Film Electrolyte

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Received: 9 June 2005 / Accepted 15 November 2005 / Published: 16 November 2005

Abstract: Li⁺ ion conducting Li₃PO₄ thin film electrolytes with thickness 300nm, 650nm and 1.2μm were deposited on Al₂O₃ substrate at room temperature by thermal evaporation method. Reference and sensing electrodes were printed on Au interfaces by conventional screen printing technique. The overall dimension of the sensor was 3 x 3 mm and of electrodes were 1 x 1.5 mm each. The fabricated solid state potentiometric CO₂ sensors of type: CO₂, O₂, Au, Li₂TiO₃-TiO₂ | Li₃PO₄ | Li₂CO₃, Au, CO₂, O₂ have been investigated for CO₂ sensing properties. The electromotive force (emf) and Δemf/dec values of the sensors are dependent on the thickness of the electrolyte film. 1.2μm thickness deposited sensor has shown good sensing behavior than the sensors with less thickness. The Δemf values of the sensor are linearly increased up to 460°C operating temperature and became stable above 460°C. Between 460-500°C temperatures region the sensor has reached an equilibrium state and the experimentally obtained Δemf values are about 80% of the theoretically calculated values. A Nernst's slope of -61mV/decade has been obtained between 250 to 5000 ppm of CO₂ concentration at 500°C temperature. The sensor is suitable for ease of mass production in view of its miniaturization and cost effectiveness after some further improvement.

Keywords: Thin film, Thick film, Potentiometric CO₂ sensor, Li⁺ ion electrolyte.

Introduction

The alarming increase of industrial pollutants and combustible gas exhausts in the global environment have stimulated the development of selective, reproducible, long life and affordable CO₂ sensors in order to control the green house effects. Moreover, the use of CO₂ sensors in the fields of agriculture, automobile, air conditioning, chemical processing, and concrete industries have been increasing. Electrochemical sensors, which use the effect of the concentration on the equilibrium of the redox reactions occurring at the electrode-electrolyte interface in an electrochemical cell, are considered to be the most promising ones for the low level detection and monitoring of environmental pollutants such as NO_x, SO_x, HC and CO₂. According to Weppner, the potentiometric sensors in which the sensing electrode reaction converts the target gas to the mobile ion or the immobile ion or neither of them of the solid electrolyte are called as type I, II, and III potentiometric sensors [1]. Among the type III sensors, potentiometric CO₂ sensor combining a solid electrolyte with an auxiliary phase of carbonate is eminently suited for practical applications [2]. Li⁺ ion conducting electrolyte [3] and LIPON [4] combined with a Li₂CO₃ auxiliary phase have been tried in view of their promising ability to use even in humid conditions due to the less reactivity with water [5].

A typical potentiometric sensor is made up of three components such as an ionic conductor, a sensing or auxiliary phase and a reference electrode material. Most of the potentiometric sensors are being fabricated by bulk and stack type. Many researchers have been tried to use thick film technology in electrolyte fabrication [6,7]. Some researchers have also tried to make electrolyte, and sensing materials using thin film process [8,9]. However, some of the qualitative factors of these sensors are still need to be improved further.

In this experiment, we have adopted both thin and thick film processes for the development of a miniaturized, long life and cost effective CO₂ sensor from a commercial point of view. The properties of the thin film electrolyte were studied with the variation of thickness, and operating temperature. The thin film electrolyte of Li₃PO₄ for potentiometric sensor may be the first attempt and result.

Experimental

Planar type CO₂ sensors were fabricated by using thick film process for sensing and reference materials and thin film process for solid electrolytes. Li₃PO₄ (Aldrich, 99.9%) thin films of 300 nm, 650 nm and 1.2 μm thickness were deposited on Al₂O₃ substrate by thermal evaporation. During deposition, the applied chamber pressure was 10⁻⁶ Torr and power was 10 A. The as-deposited thin

films were sintered at 700°C for 2 hr in air. Two Au electrodes were attached to the electrolyte thin films each at 2 mm apart and sintered at 700°C for 1 hr to make good contact with the electrolyte. Li_2TiO_3 (Aldrich, 99.99%) and TiO_2 (Aldrich, 99.9%) were mixed with an organic binder and grinded in a three roll mixer. The paste was screen printed of about 10 μm thicknesses on Au electrode as reference material and sintered at 700°C for 1 hr. In the similar way, Li_2CO_3 (Alfa Aesar 99.99%) paste was prepared and screen printed as sensing material and sintered at 600°C for 1 hr. The schematic diagram of the fabricated sensor is shown in Fig.1. The overall dimensions of the fabricated sensor was 3mm x 3mm. Li_3PO_4 electrolyte was deposited over the whole area, though, the dimensions of the screen printed sensing and reference materials were 1mm x 1.5 mm.

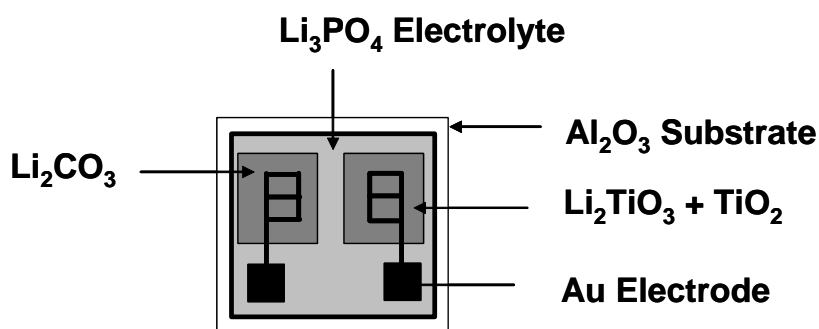
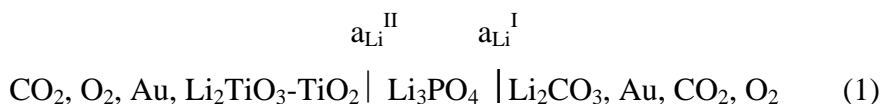


Figure 1. Schematic diagram of the fabricated planar sensor.

The surface morphology and the cross section of the Li_3PO_4 thin films were observed by FE-SEM (Hitachi S-4700). The electromotive force, emf, of the sensor was measured by a two probe HP34401A multimeter of high impedance (above 10G Ω) connected to a computer through HP 34812A Benchlink software for data acquisition.

Results and discussion

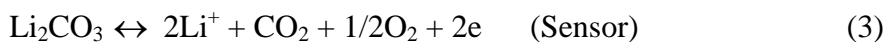
In this work, the studied electrochemical sensor structure was



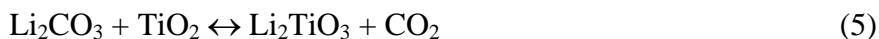
The emf measured for the open circuit gives the Li^+ ion activity ratio between the two interfaces, sensing electrode (a_{Li}^{I}) and the reference electrode ($a_{\text{Li}}^{\text{II}}$), of Li_3PO_4 electrolyte in accordance with eqn (2),

$$\text{Emf} = - (RT/F) \ln (a_{\text{Li}}^{\text{II}} / a_{\text{Li}}^{\text{I}}) \quad (2)$$

where, F is the Farady's constant, R the gas constant and T the absolute temperature. The magnitude of a_{Li^I} and $a_{Li^{II}}$ on the anodic and cathodic sides (measuring and reference electrodes) of the electrode reaction can be determined by equations (3) and (4)



And the overall reaction for the open cell can be expressed as,



Thus, the oxygen partial pressure or chemical potential of the oxygen is same at both the electrodes and cancels in the overall cell reaction causing oxygen independency and hence the sensor depends only on the CO_2 partial pressure.

The SEM micrographs of the surface morphology of Li_3PO_4 electrolyte thin films are shown in Fig.2. The pictures (a), (b), (c) represents the thin films of 300nm, 650nm, and 1.2 μ m thickness sintered at 700°C for 30 m in air respectively. It is observed from the figure, that the grain size of thin films was increased with increasing thickness. In case of 300 nm deposited film (a), the morphology of Li_3PO_4 electrolyte is similar to that of alumina substrate because of less thin film thickness and high roughness of alumina substrate. Whereas, in the 650nm (b) and 1.2 μ m (c) thickness films, a different morphology of Li_3PO_4 electrolyte have been formed on the Al_2O_3 surface and their grain size is increased with thin film thickness. The film deposited of 1.2 μ m thickness and sintered at 700°C has an average grain size of 5 μ m and of uniform shape.

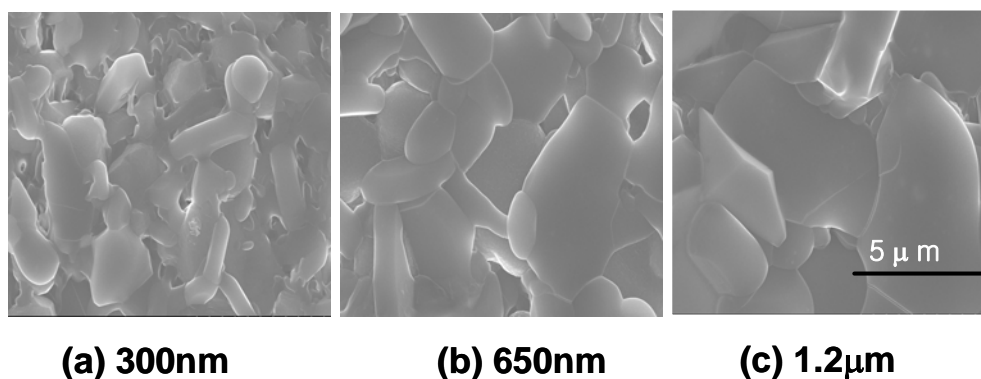


Figure 2. SEM micrographs of the surface morphology of Li_3PO_4 electrolyte thin films with thickness (a) 300nm, (b) 650nm, and (c) 1.2 μ m and sintered at 700°C for 30 m in air.

The dependence of emf as a function of concentration of CO_2 ($\log P_{CO_2}$) for 300nm, 650nm and 1.2 μ m thickness electrolyte devices sintered at 700°C and operated at 500°C temperature are shown in Fig. 3. It can be observed that the emf values were increased with increasing thickness of the electrolyte. The emf value of 300nm deposited electrolyte sensor is low while 650nm and 1.2 μ m

deposited electrolyte sensors is high and similar. The low emf value of 300nm sensor is related to the low connectivity of Li_3PO_4 electrolyte as estimated from Fig. 2(a). This suggests that a minimum thickness of electrolyte is needed to obtain a good emf value.

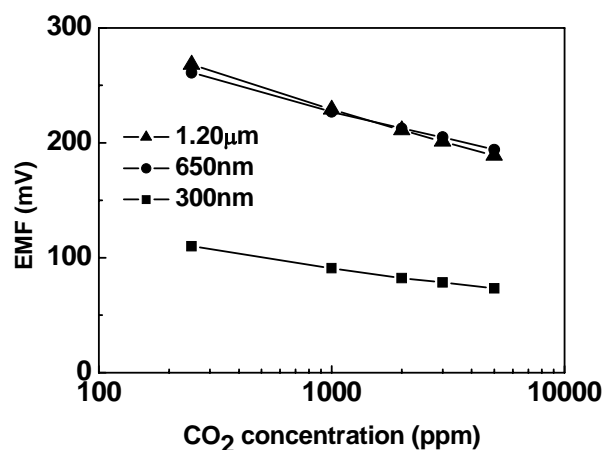


Figure 3. EMF as a function of concentration of CO_2 ($\log P_{\text{CO}_2}$) for 300nm, 650nm and 1.2μm thickness deposited electrolyte sensors sintered at 700°C and operated at 500°C temperature.

The $\Delta\text{emf}/\text{dec}$ values obtained for sensors with various electrolyte thicknesses at different sintering and operating temperatures are shown in Table.1. The emf values were increased with increasing electrolyte thickness and operating temperatures.

Table.1. $\Delta\text{EMF}/\text{dec}$ values for the sensors of various electrolyte thicknesses at different sintering and operating temperatures.

Sintering Temp.		700°C		
		Operating Temp.		
		400°C	450°C	500°C
$\Delta\text{emf}/\text{dec}$ (mV)	300nm	-1.67	-10.9	-28.4
	650nm	-6.33	-18.54	-51.34
	1.2μm	-25.6	-56.69	-61

Fig.4 shows the dependence of $\Delta\text{emf}/\text{dec}$ as a function of operating temperature for the sensor based on Fig. 2(c). It can be seen from the figure, that the Δemf values were increased up to 460°C operating temperature, and reached a plateau between 460-500°C temperatures. The theoretically

calculated Δemf values were showed in the figure as a continuous line. The theoretical value of -76.6 mV/dec was calculated from the equation $-2.3(RT/nF)$, where n equals to 2 representing number of reaction electrons participating in the cell reaction at 500°C operating temperature, R the universal gas constant, T the absolute temperature and F the faraday constant. Between 460 - 500°C operating temperatures, the experimental values approached about 80% of theoretical value. However, the Δemf values below 460°C operating temperature are very low and much deviated from the theoretical values. This can be attributed to the effect of low kinetic energies produced between each electrode and the electrolyte and reaching a non-equilibrium state [4].

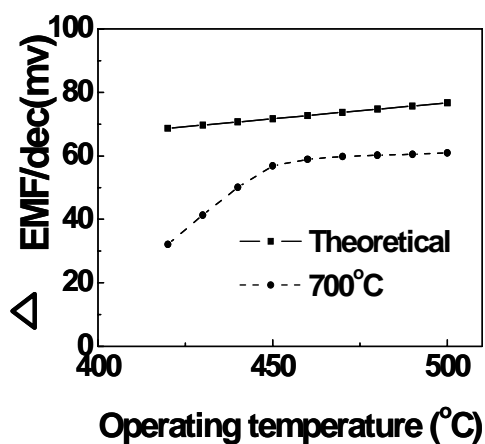


Figure 4. Dependence of $\Delta EMF/dec$ as a function of operating temperature ($^\circ\text{C}$).

It is found that in this temperature region the response and recovery of the sensor is good for all the investigated CO_2 partial pressures.

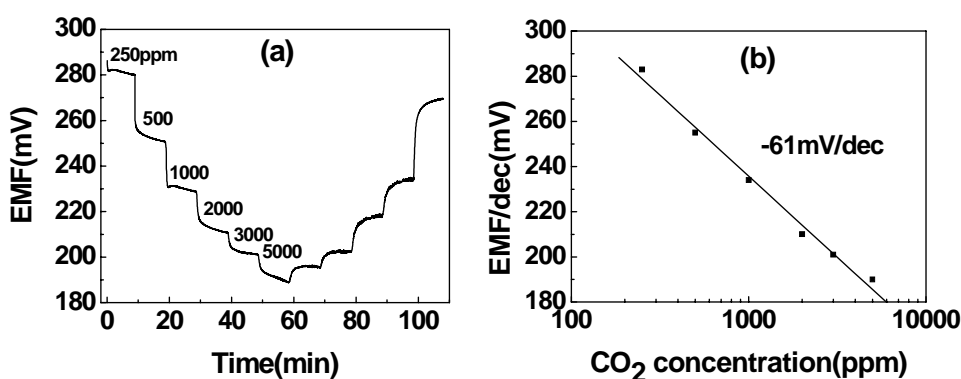


Figure 5. (a) Sensitivity and recovery and (b) $\Delta EMF/dec$ measurements of the $1.2 \mu\text{m}$ thickness electrolyte sensor at 500°C operating temperature.

Fig.5 (a) shows the sensitivity and recovery characteristics of the $1.2 \mu\text{m}$ thickness electrolyte sensor sintered at 700°C for different CO_2 concentrations at 500°C operating temperature. The sensor

exhibits good response but some irreversible recovery. Fig. 5 (b) shows the $\Delta\text{emf}/\text{dec}$ as a function of CO_2 concentration. A Nernst's slope of $-61\text{mV}/\text{decade}$ has been obtained between 250 to 5000 ppm of CO_2 concentration at 500°C temperature. It was observed for three months a satisfactory performance of the proposed sensor. However, sensing characteristic of the sensor can be improved further if the thickness and microstructure are optimized by the deposition process and sintering temperatures. The investigations will be reported elsewhere as soon as possible.

Conclusions

Li_3PO_4 thin films with thickness 300nm, 650nm and $1.2\mu\text{m}$ were deposited on Al_2O_3 substrate as Li^+ ion conducting electrolytes. Planar type CO_2 potentiometric sensors were fabricated using Li_2CO_3 as an auxiliary phase and a mixed phase of Li_2TiO_3 and TiO_2 as the reference electrode. The sensor with $1.2\mu\text{m}$ thickness electrolyte and sintered at 700°C has shown good response and recovery characteristics with an $\Delta\text{emf}/\text{dec}$ value of $-61\text{mV}/\text{dec}$. It is observed that below 460°C operating temperature the Δemf values are deviated from the theoretical values and above 460°C operating temperatures they are approaching 80% of the theoretically calculated values all over the CO_2 concentrations. The emf of the sensor was increased with increasing electrolyte thin film thickness. We suggest a possibility to make a miniaturized potentiometric CO_2 sensor using Li^+ ion conducting Li_3PO_4 thin film electrolyte.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2004-005-D00008).

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