High temperature potentiometric carbon dioxide sensor with minimal interference to humidity

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ABSTRACT

We report on the development of a potentiometric sensor with Li_3PO_4 electrolyte and $BaCO_3$-coated Li_2CO_3 sensing electrode for measuring CO_2 over a wide range of concentrations (500 ppm to 20%) at 500 °C with minimal interference to humidity. The active element in the sensing electrode for CO_2 detection is Li_2CO_3. However, sensors with just Li_2CO_3 electrodes showed interference from humidity, which was eliminated by use of the $BaCO_3$ layer. Infrared spectroscopy as well as electrode preparations involving heating above the eutectic temperature of $BaCO_3$–Li_2CO_3 suggests that the $BaCO_3$ layer wets the Li_2CO_3 electrode surface, making it more hydrophobic and thereby reducing the interference from humidity.

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1. Introduction

Carbon dioxide sensors are important for monitoring air-quality, measuring metabolic activity of animals, controlling combustion [1–4], and could also have considerable potential as environmental sensors if CO_2 sequestration involves the deposition into geological structures. While there are commercial sensors for air-quality monitoring, there is a vital need for reliable, miniaturizable sensors for high temperature combustion-related applications. Potentiometric-type sensors that consist of a Na^+ or Li^+ electrolyte and alkali metal carbonate sensing electrodes are promising because they show satisfactory EMF signals over a wide range of gas concentrations and temperatures [5,6].

Potentiometric sensors based on Na^+ conductors such as NASICON [5] with Na_2CO_3 sensing electrodes are reported to respond in a Nernstian fashion to CO_2 concentrations with response times of several minutes at 500–700 °C. The major problem with these sensors is that they suffer from significant interference to humidity.

Attempts to improve sensor performance by the modification of the sensing electrode material have been reported [7–9]. With a binary carbonate (Li_2CO_3–$BaCO_3$) electrode, a faster response was observed as compared to a single-phase Na_2CO_3 electrode [7]. It was also reported that sensors with sensing electrodes of mixtures of alkali and alkaline earth carbonates exhibited better stability

against humidity. However, these studies did not report on long-term stability of these sensors under humid conditions and at high temperatures. Moreover, the exact role of the binary mixture as electrode (Li^+, Ba^+) with a Na^+ conducting electrolyte is unclear.

In this study, we focus on a Li^+-conducting electrolyte, Li_3PO_4 with a Li_2CO_3 electrode. The humidity interference associated with the Li_2CO_3 electrode is eliminated by coating with $BaCO_3$, which also leads to more optimal response and recovery times. The structure of the coated carbonate electrode as well as the CO_2 detection mechanism of this sensor is examined.

2. Experimental

2.1. Fabrication of sensor elements

A schematic structure of the fabricated sensor is shown in Fig. 1. Lithium phosphate (Li_3PO_4, Alfa Aesar, 99.5%) with 5 mol% SiO_2 to enhance the sinterability was used as an electrolyte. The powder mixture was ball-milled in ethanol for 8 h and dried at 120 °C. The dried mixture was compacted into a disk at 1.5 kpsi and sintered at 800 °C for 8 h with a heating and cooling rate of 3 °C/min. A Lindbergh furnace (Model 51732-B) was utilized for the heat treatment. On both sides of Li_3PO_4 electrolyte disk of 1.2 cm in diameter and 0.8 mm thickness, gold paste (Heraeus Gold ink) was painted with a diameter of 4 mm. It was cured at 700 °C for 1 h at a heating/cooling rate of 3 °C/min.

Lithium titanate (Li_2TiO_3, Lithium Corporation of America Inc., 99%) mixed with 5 mol% titania (TiO_2, Alpha Aesar, 99.9%) was

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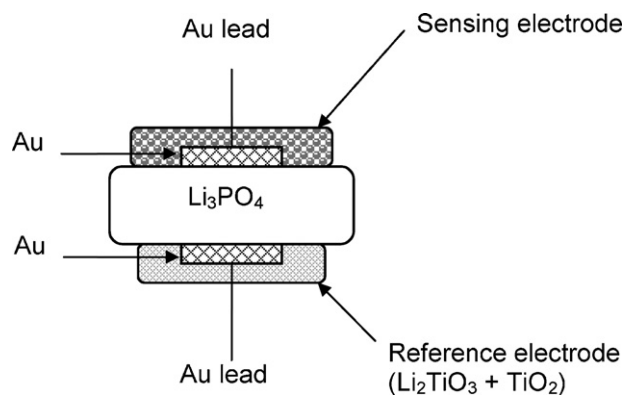
Fig. 1. Schematic structure of the sensor with different metal carbonates as the sensing electrode.

used as the reference electrode. The powder mixture was ball-milled in ethanol. It was mixed with α-terpineol organic binder (Fisher Chemicals) and painted on the surface of the Li_3PO_4 electrolyte. It was cured following the same heat treatment profile of the gold paste curing. In order to compare the sensing behaviors, the sensing electrode was fabricated with three different materials: single-phase lithium carbonate; physical mixture of lithium carbonate and barium carbonate with a molar ratio 1:1; and lithium carbonate with a coating of barium carbonate.

For the sensor with Li_2CO_3 electrode, lithium carbonate (Li_2CO_3, Alpha Aesar, 99%) was ball-milled in ethanol and painted on the surface of the Li_3PO_4 electrolyte followed by curing at 600 °C for 1 h at a heating and cooing rate of 3 °C/min. For the sensors with lithium carbonate and barium carbonate, these two carbonates ($BaCO_3$, J.T. Baker Chemical CO., 99%) were mixed in 1:1 molar ratio, ball-milled in ethanol and deposited on the electrolyte. The sensor was annealed at 500 °C for 3 h at a heating and cooling rate of 3 °C/min. For the sensor with $BaCO_3$-coated Li_2CO_3, the electrode was prepared as follows: barium nitrate ($Ba(NO_3)_2$, Johnson Matthey, 99.999%) was used as a $BaCO_3$ precursor. A 0.02 M $Ba(NO_3)_2$ aqueous solution was prepared in deionized water using magnetic stirring. Then 2 wt% Li_2CO_3 powder was added into the $Ba(NO_3)_2$ solution, and water was removed by heating in a rotary evaporator. The dried powder was heat treated at 580 °C for 3 h under a CO_2 atmosphere. The molar ratio of Li_2CO_3:$BaCO_3$ was changed from 1:1 to 7:1.

In another set of experiments, the sensors with $BaCO_3$-coated Li_2CO_3 sensing electrodes were fabricated and heat treated at 650 °C (eutectic temperature ~609(±4) °C [10]) for 2 h under a CO_2 atmosphere.

2.2. Measurement of sensing characteristics

For sensing tests, the sensor was located in the central uniform temperature zone of a Lindberg horizontal tube furnace. Three gases (air, N_2 and CO_2) were mixed for the sensing tests. Sample gases were prepared from CO_2 diluted in nitrogen by mixing it with air. The CO_2 gas concentration from 500 to 3000 ppm was controlled by mixing gas from a cylinder of 1% CO_2 concentration with N_2. 100% pure CO_2 cylinder was used for CO_2 concentration from 5% to 20% (background concentration of oxygen was 21% with the rest being nitrogen). Humid gas was prepared by bubbling the gas mixture through water at room temperature. In these tests, the relative humidity was 80% (measured by a commercial humidity sensor HMT330, Vaisala) and the test temperature was 500 °C, with gas flow rates of 210 ml/min. The EMF values of the sensor were measured by a two-probe technique with a model HP 34401A voltmeter.

2.3. Microstructure and XRD analysis

The phase analysis of Li_2CO_3 and $BaCO_3$-coated Li_2CO_3 was done using a Scintag PAD-V diffractometer with Cu K_α radiation at 45 kV and 20 mA in the 2θ range from 10° to 70°. JCPDS standard data were compared to the XRD spectra for phase identification. The IR spectra were collected using a PerkinElmer Spectrum 400 Instrument.

3. Results

Fig. 1 shows the schematic of the sensor used in this study. The primary focus was to alter the sensing electrode to minimize humidity response, with the humid condition created by bubbling the test gas through water at ambient temperature.

3.1. Sensing electrodes prepared by physically mixing Li_2CO_3 and $BaCO_3$ and heated to 500 °C

The first electrode modification was to use a mixture of Li_2CO_3 and $BaCO_3$ as compared to Li_2CO_3 alone. Fig. 2 compares the responses of two sensors with the two electrodes (Li_2CO_3 and a physical mixture of Li_2CO_3–$BaCO_3$) measured at a temperature of 500 °C under dry and humid CO_2 gas. Both the sensors responded to dry CO_2 gas, but in the case of the Li_2CO_3 electrode, there was considerable interference to humidity, including slower response and recovery times. Upon the addition of $BaCO_3$ by physical mixing,
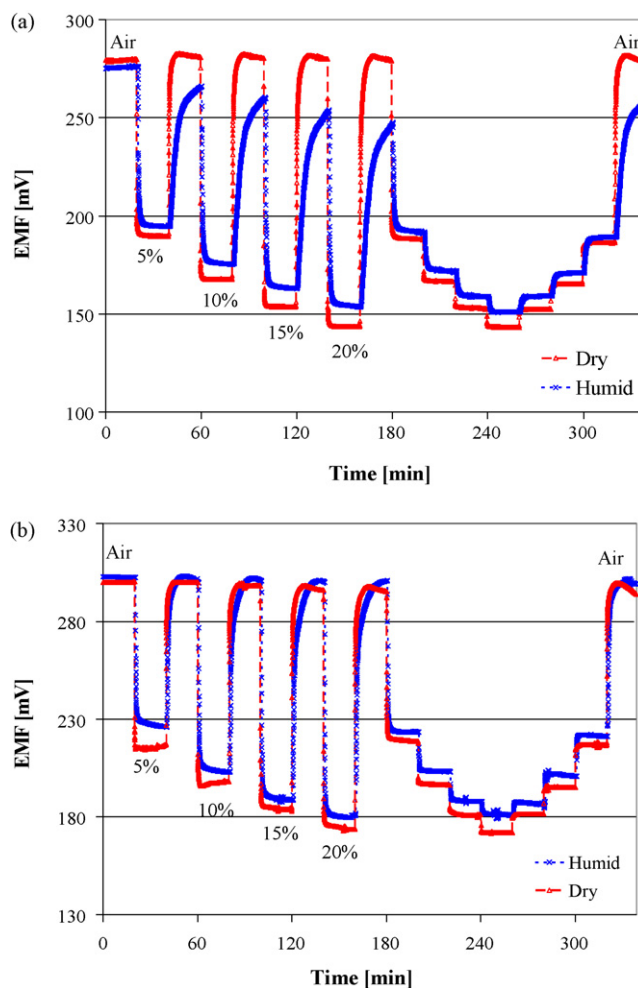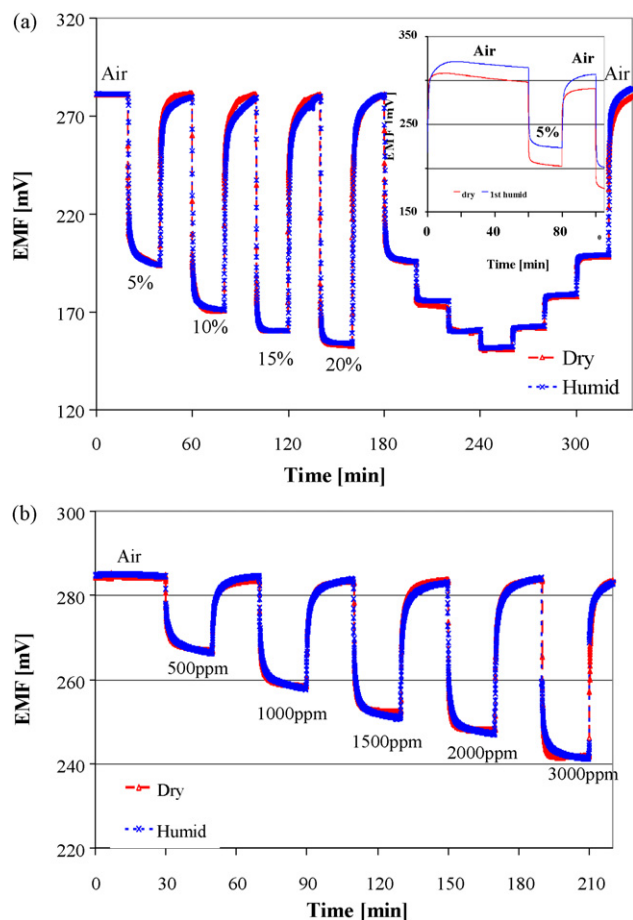

Fig. 2. Response transients of the sensor with (a) pure Li_2CO_3 and (b) physical mixture of $BaCO_3$–Li_2CO_3 as sensing electrodes in dry and humid CO_2 (background gas 21% O_2, rest N_2) at 500 °C.

Fig. 3. Response transient of the sensor with $BaCO_3$ coated on Li_2CO_3 at CO_2 concentration (a) from 5% to 20% and (b) from 500 to 3000 ppm in dry and humid CO_2 at 500 °C (background gas 21% O_2, rest N_2). The inset in (a) shows baseline shift in the 1st humid test.

the interference with humidity improved somewhat as shown in Fig. 2b.

3.2. Sensing electrodes prepared by coating $BaCO_3$ on Li_2CO_3 and heated to 500 °C

For the second set of electrodes, we coated a solution of $Ba(NO_3)_2$ on the Li_2CO_3 via impregnation, followed by heat treatment under a CO_2 atmosphere to form a coating of $BaCO_3$ on the Li_2CO_3 particles. Fig. 3 shows the sensing behavior in the presence of 500–3000 ppm, as well as 5–20% CO_2 in dry and humid conditions. The sensor showed almost identical response to CO_2 under both dry and humid conditions, with differences of peak signals of less than 2%. The response time of the sensor was 14 s under dry condition, and 54 s under humid condition (response time is defined as time taken to reach 90% of the final signal). However, the sensor needed some preconditioning to obtain similar responses to humid and dry conditions, as evident from the data shown in the inset. The baselines of the as-prepared sensor shifted to higher potentials upon initial introduction of humidity, but after being in a humid environment for 3–9 h, the signal recovered to the baseline observed in the dry sample. This type of initial EMF stabilization has been discussed by other researchers in electrochemical CO_2 sensors [11]. All data discussed below are with sensors that have been conditioned in humidity at 500 °C for at least 3 h.

Fig. 4 shows the change of the Nernstian slope of sensors prepared with different molar ratios of Li_2CO_3 and $BaCO_3$ and tested
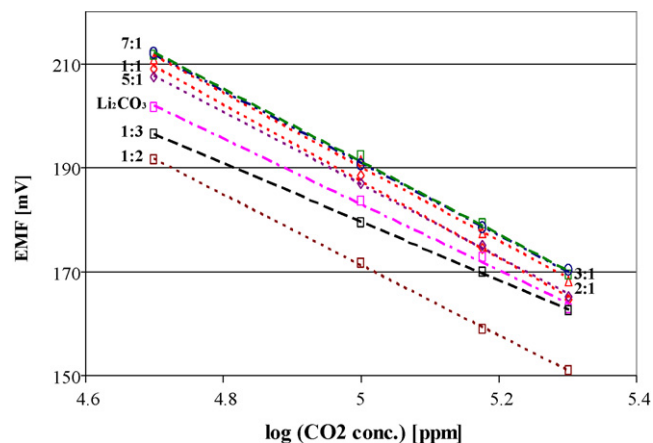
**Fig. 4.** Changes of Nernstian slope of sensors with $BaCO_3$ coated on Li_2CO_3 sensing electrodes with different molar ratios of Li_2CO_3 to $BaCO_3$ under humid conditions (□Li:Ba = 1:3, □Li:Ba = 1:2, ◇Li:Ba = 1:1, △Li:Ba = 2:1, □Li:Ba = 3:1, ◇Li:Ba = 5:1, ○ Li:Ba = 7:1, and □ pure Li_2CO_3).

under humid conditions. As more $BaCO_3$ was added, the Nernstian slope increased to a maximum value of 73.6 mV/decade (theoretical value is 76.6 mV/decade) at a molar ratio of 1:1.

Fig. 5 shows X-ray diffraction patterns of $BaCO_3$-coated Li_2CO_3 powder for 1:1 molar ratio. The XRD patterns for pure $BaCO_3$ and Li_2CO_3 are also shown for comparison. All the peaks observed are identified as either $BaCO_3$ or Li_2CO_3 phase, except for the decrease in intensity in the $BaCO_3$ peak at 23.7°, possibly due to texturing. These results suggest that lithium and barium carbonates do not form substitutional solid solution, an observation expected considering the differences in crystal structures (Li_2CO_3-monoclinic, $BaCO_3$-orthorhombic), ionic radii (Li^+ 0.59 Å, Ba^{2+} 1.36 Å) and valences of both ions [12,13].

Fig. 6 compares the infrared spectra of Li_2CO_3 and $BaCO_3$-coated Li_2CO_3 after exposure to humidity at 500 °C. Addition of $BaCO_3$ led to the loss of the O–H bending and stretching modes associated with water at 1640 and 3400 cm^{-1}, that is found on the Li_2CO_3 sample.

In order to probe the reproducibility of $BaCO_3$-coated Li_2CO_3 electrodes, seven sensors were fabricated using the same procedure. Fig. 7(a) plots the EMF values as a function of CO_2 concentration under humid conditions. The maximum slope was 73.6 mV/decade and the minimum was 70.4 mV/decade, with a standard deviation of 1.3%. In order to check the long-term stability under humid conditions, sensing behaviors were investigated at 500 °C for 60 days, with measurements taken every 2–3 days.
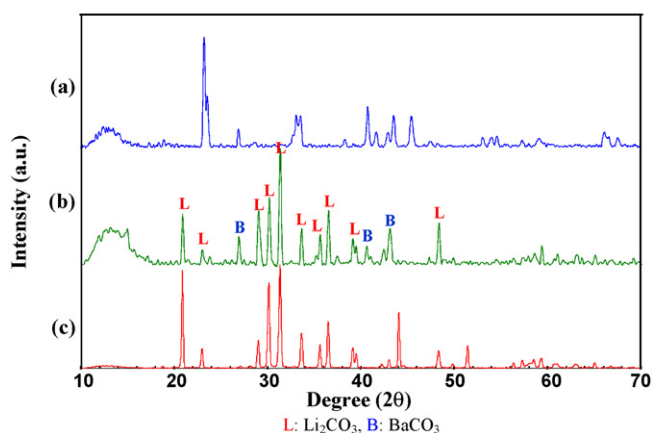
Fig. 5. X-ray diffraction patterns for (a) pure $BaCO_3$ (B), (b) $BaCO_3$ coated on Li_2CO_3 and (c) pure Li_2CO_3 (L).
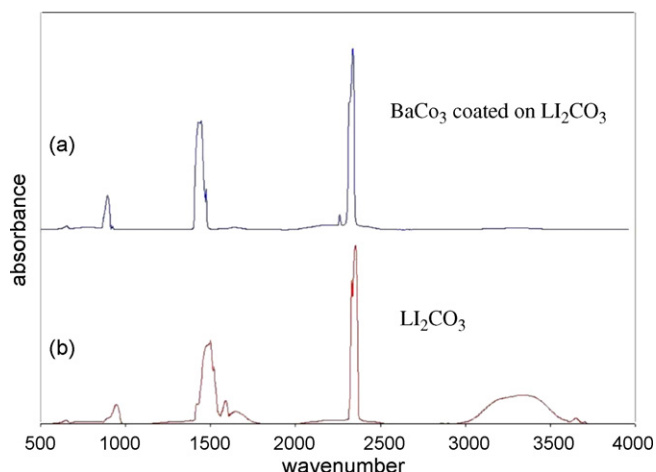
Fig. 6. Infrared spectroscopy of $BaCO_3$ coated on Li_2CO_3 and pure Li_2CO_3 after exposure to humidity at 500 °C for 3 h.

Fig. 7(b) shows that the EMF values at 5% and 10% CO_2 were stable during this test period.

3.3. Sensing electrodes prepared by coating $BaCO_3$ on Li_2CO_3 and heated to 650 °C

A set of sensors were prepared by heating the $BaCO_3$-coated Li_2CO_3 sample to 650 °C, well beyond the eutectic point ($\sim$609($\pm$4) °C) [10], and then sensing electrodes were fabricated, and sensors tested with dry and humid CO_2 gas at 500 °C. The best
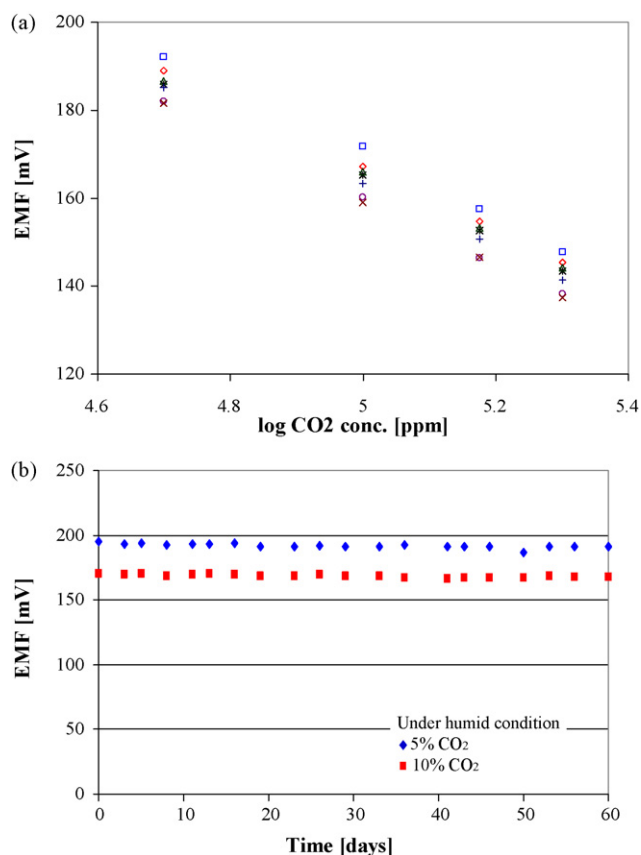
Fig. 7. (a) Reproducibility test of different seven sensors with $BaCO_3$ coated on Li_2CO_3 sensing electrodes and (b) long-term test for 60 days in humid condition at 5% and 10% CO_2 at 500 °C.
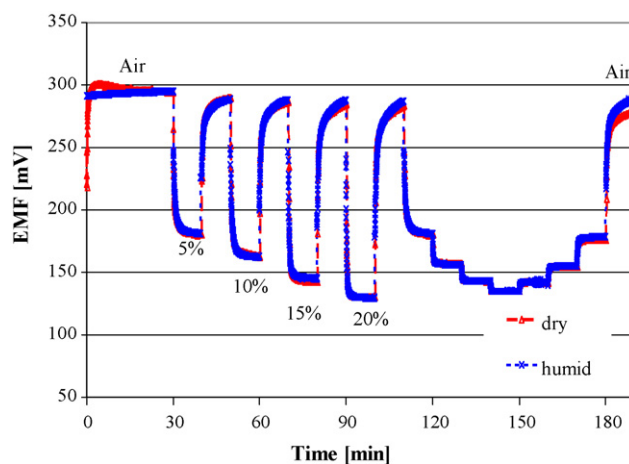
Fig. 8. Response transient of the sensor with $BaCO_3$ coated on Li_2CO_3 sensing electrodes heated beyond the eutectic temperature in dry and humid CO_2 at 500 °C (background gas 21% O_2, rest N_2). The molar ratio of Li_2CO_3 and $BaCO_3$ is 7:1.

results were obtained with a Li_2CO_3 to $BaCO_3$ ratio of 7:1, and these data are shown in Fig. 8, exhibiting elimination of humidity interference, with this sensing electrode.
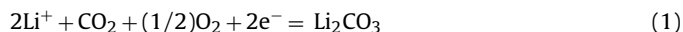
4. Discussion

4.1. CO_2 sensing mechanism

The current sensors are composed of the following solid-state electrochemical cell:

Air, CO_2, Au | $BaCO_3$-coated Li_2CO_3 | Li_3PO_4 | Li_2TiO_3 + TiO_2 | Au, CO_2, Air.

Since Li^+ conductor is used as the electrolyte, the sensing electrode reaction involving Li^+ can be expressed as [6,8]:

$$2Li^+ + CO_2 + (1/2)O_2 + 2e^- = Li_2CO_3 \tag{1}$$

The reference electrode reaction is written as

$$Li_2TiO_3 = 2Li^+ + (1/2)O_2 + 2e^- + TiO_2 \tag{2}$$
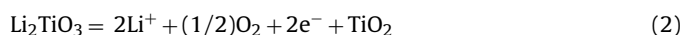
The EMF that is measured between the two electrodes can be expressed as

$$E = -\frac{1}{F}(\mu_{Li^+}^{Re} - \mu_{Li^+}^{Se}) = \frac{RT}{F} \ln \frac{a_{Li^+}^{Re}}{a_{Li^+}^{Se}} = \frac{\Delta G_{(1)}^o - \Delta G_{(2)}^o}{2F} - \frac{RT}{2F} \ln P_{CO_2} \tag{3}$$

where μ is the chemical potential, a_{Li^+} is the Li^+ activity, Re and Se correspond to reference and sensing electrodes and ΔG^o is the free energy change for reactions (1) and (2). For the reference electrode, the lithium ion activity is constant, because reaction (2) is independent of CO_2 partial pressure. The theoretical slope at 500 °C is expected to be 76.6 mV/decade, according to Eq. (3). With the addition of $BaCO_3$, the slope increased and reached an optimal value of 73.6 mV/decade at a ratio of $BaCO_3$-to-Li_2CO_3 of 1:1, not exactly the theoretical value, and could be dependent on the exact temperature of the device in the oven.

4.2. The role of $BaCO_3$ coating

The interference of humidity to sensors with Li_2CO_3 electrode could arise from the solubility of Li_2CO_3 in water (1.3 g/l at 20 °C), which can result in the formation of compounds such as LiOH, $LiHCO_3$ and $Li_2CO_3 \cdot H_2O$ in the presence of water vapor. Sensors prepared with $BaCO_3$-coated Li_2CO_3 electrode removes the

humidity interference, which suggests that the $BaCO_3$ layer is hindering adsorption of water vapor and thus minimizing reaction with Li_2CO_3. Sensing electrodes composed of binary carbonate system such as Li_2CO_3 and $BaCO_3$ have been investigated by earlier researchers [8,13]. Other binary systems such as $CaCO_3$–Li_2CO_3 and $SrCO_3$–Na_2CO_3 were also found to show similar stability in the presence of water vapor because $CaCO_3$ and $SrCO_3$ have no solubility in water [7,14]. We propose that because of the insolubility of $BaCO_3$ in water [15], $BaCO_3$-coated Li_2CO_3 exhibits a hydrophobic surface. The infrared data in Fig. 6 supports this hypothesis, with the loss of bending and stretching modes associated with water at 1640 and $3400\,cm^{-1}$, upon $BaCO_3$ coating.

We also propose that in order to minimize the effect of humidity, the sensing needs to occur at the triple phase boundaries (TPBs) between Li_2CO_3, $BaCO_3$ and CO_2 gas, based on our observation that as the $BaCO_3$ content is increased, the variation in EMF values between the dry and humid condition progressively diminished. The importance of TPBs in minimizing humidity interference has also been illustrated in $BaCO_3$–Na_2CO_3 system by employing physical mixtures [9]. Our observation using physical mixtures of Li_2CO_3 and $BaCO_3$ is that while the humidity effect is reduced, it is not entirely eliminated, as shown in Fig. 2. Thus, the wet barium nitrate impregnation procedure we employed in this study for making $BaCO_3$ provides a more efficient way of optimizing the number of TPBs.

The results shown in Fig. 8 obtained with electrodes prepared by heating the $BaCO_3$-coated Li_2CO_3 sample to $650\,°C$, well beyond the eutectic point of $\sim609(\pm4)°C$ supports the TPB hypothesis. Li_2CO_3 and $BaCO_3$ are reported to form the eutectic at about 55 mol% of Li_2CO_3 [10]. Thus at Li_2CO_3 to $BaCO_3$ ratios of $\gg1$, formation of the eutectic liquid will promote uniform wetting of the Li_2CO_3 surface by $BaCO_3$, resulting in well dispersed TPBs. Thus, elimination of humidity interference was obtained with a Li_2CO_3 to $BaCO_3$ ratio of 7:1, as compared to a 1:1 ratio for electrodes prepared by heating to $580\,°C$, below the eutectic temperature.

5. Conclusions

A potentiometric CO_2 gas sensor with lithium phosphate electrolyte was fabricated with a sensing electrode of $BaCO_3$-coated Li_2CO_3 and it showed good performance toward CO_2 sensing at $500\,°C$ under dry as well as humid conditions. In addition, the sensor showed good reproducibility and long-term stability under humid conditions. To form the $BaCO_3$ layer on Li_2CO_3, a wet chemical process was used. This strategy of coating of $BaCO_3$ was a better approach than physical mixing. We propose that interference to humidity is minimized if sensing occurs at the triple point boundaries of $BaCO_3$, Li_2CO_3 and CO_2. Heating the $BaCO_3$ coated on Li_2CO_3 material to temperatures above the eutectic point led to better wetting of the surface and improved distribution of triple point boundaries at lower $BaCO_3$ to Li_2CO_3 ratios, with good sensing behavior and minimal humidity interference.

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