CO₂ sensing performances of potentiometric sensor based on Na₁₊ₓZr₂Si₂PO₁₂ \(0 < x < 3\)

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Potentiometric CO₂ sensors based on NASICON (Na₁₊ₓZr₂Si₂PO₁₂) were fabricated by combining with a Li₂CO₃–BaCO₃ (1:2 in molar ratio) auxiliary phase. The CO₂ sensing properties of NASICON \((x = 0, 1, 2, 2.75)\) sensors were investigated under dry condition at 450 °C. The electromotive force (EMF) values of NASICON sensors were proportional to the logarithm of CO₂ concentrations in the range of 250 to 2500 ppm. When exposed to dry air containing 250 ppm CO₂, the EMF values of each sensor continuously changed toward a negative potential. From a X-Ray Diffraction (XRD) measurement, it was confirmed that new crystal phases such as Li₂ZrO₃, ZrO₂, Na₂Zr(PO₄)₂ and Na₅Zr(PO₄)₃ were formed at the interface between sensing electrode and solid-state electrolyte, because of reaction between Li₂CO₃ and NASICON. The result of XRD measurement suggested that the base-EMF change closely related with the decrease of Li⁺ activity in auxiliary phase and Na₂O activity in NASICON.

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1. Introduction

The potentiometric solid-state electrolyte sensors have become of great attractive as a compact structure and an inexpensive commercial price. The electrochemical cells are fabricated by combining an alkaline metal carbonate (so-called auxiliary phase) with a solid-state electrolyte such as Na-beta-alumina, NASICON \((Na₂Zr₂Si₂PO₄)\), MSZ \((MgO-stabilized zirconia)\), Li₄Ti₅O₁₂ \((Y₂O₃-stabilized zirconia)\) and Na₂O–Al₂O₃–SiO₂. Among these sensors, the NASICON \((Na₁₊ₓZr₂Si₂PO₁₂ \(0 < x < 3\)))-based sensor has become of major interest, because of an excellent selectivity to CO₂ gas, in addition to practical utility in gas sensitivity, response time and commercial price. However, this type sensor includes a serious problem that should be improved to practical use. The problem is that the EMF of the sensor continues to decrease toward negative potential during the operation under a static condition (so-called EMF-drift). It is pointed out that the change of activities on an auxiliary phase\(^{9-11}\) or a reference material causes the EMF-drift.\(^{3,12,13}\) In general, the development of a NASICON-based potentiometric device has been usually carried out by using Na₃Zr₂Si₂PO₁₂ that has the highest ionic conductivity among Na₁₊ₓZr₂Si₂PO₁₂ \(0 < x < 3\). Recently, it was reported that EMF could become fairly stable by using Na₃.75Zr₂Si₂.75P0.5O₁₂ with Na-rich.\(^{14}\)

In the present study, we researched the correlation between the amount of Na in NASICON and the long-term stability. Four kinds of NASICON \((Na₁₊ₓZr₂Si₂PO₁₂ \(x = 0, 1, 2, 2.75\)) -based sensors were fabricated and those CO₂ sensing properties compared each other. Furthermore, the reactivity of NASICONs with Li₂CO₃ auxiliary phase was examined by using an XRD measurement.

2. Theory

In general, solid-state electrolyte sensor detects a target gas concentration from the change of electrochemical equilibrium state between the gas and an auxiliary phase on the sensing electrode.\(^{40}\) An electrochemical cell combined NASICON \((Na₃Zr₂Si₂PO₁₂)\) with alkaline metallic carbonate \((Li₂CO₃\) and \(Li₂CO₃–BaCO₃\) etc.) is expressed as the followings.

Air, Au \| NASICON \((Na₃Zr₂Si₂PO₁₂)\) \| Li₂CO₃–BaCO₃, \nAu, Air \+ CO₂

The CO₂ sensing reaction can be explained as reaction Eq. (2).

\[2Li^+ + CO₂ + 1/2O₂ + 2e⁻ = Li₂CO₃\]  \(2\)

On the other hand, the reference electrode (Au electrode) reaction can be given by

\[2Na^+ + 1/2O₂ + 2e⁻ = Na₂O \quad (\text{in NASICON})\]  \(3\)

By using Nernstian equation, both of the electrode potentials in the reactions \(2\) and \(3\) are expressed as the Eqs. \(4\) and \(5\), respectively.

\[E' = C₁ \text{ (constant)} + \left(\frac{RT}{nF}\right) \ln \frac{[a_{Li^+}]²[PO₄^{3-}]/[a_{Na^+}]}{[a_{Na₂O}]^{1/2}}\]  \(4\)

\[E'' = C₂ \text{ (constant)} + \left(\frac{RT}{nF}\right) \ln \frac{[a_{Na₂O}]^{1/2}/[a_{Na₂O}]}{[a_{Na₂O}]²[PO₄^{3-}]/[a_{Na₂O}]}\]  \(5\)

where \(n\) is the number of electrons associated with the electrode reaction of CO₂, \(P\) the partial pressure, \(R\) the gas constant, \(T\) the absolute temperature, \(F\) Faraday constant, \(C\) constant of standard electrode potential estimated from Gibbs energy and \(a\) the activity of chemical species such as \(Li^⁺\), \(Na⁺\), Li₂CO₃ and Na₂O (in NASICON), respectively. The EMF of the sensor is observed as the difference of an electrode potential between the sensing and the reference electrodes. It is assumed that \(P₂\) is kept constant and \(n\) is equal to 2 as given in reaction \(2\). The observed EMF
E\text{cell} \text{(6)} \text{can be given by the next equation,}
\[
E_{\text{cell}} = C_1 \text{ (constant)} + (RT / 2F) \ln \left[ \frac{a_{\text{CO}_2}^{(1)} / \text{No}_{\text{CO}_2}^{(1)}}{(a_{\text{Na}_2}^{(0)} / \text{Na}_{\text{CO}_2}^{(0)})} \right].
\]

When CO₂ concentration is varied from P'\text{CO}_2 to P''\text{CO}_2, the theoretical EMF change (ΔEMF\text{CO}_2) is written in Eq. (7).
\[
\Delta \text{EMF}_{\text{CO}_2} = (RT / 2F) \cdot \ln \left( P'' \text{CO}_2 / P' \text{CO}_2 \right).
\]

For instance, the ΔEMF value is estimated about 72 mV in the range of 250 ppm–2500 ppm at 450°C.

3. Experimental

3.1 Materials preparation

Four kinds of NASICON powders were prepared by a sol–gel technique using Si(OCH₃)₄, Zr(OCH₃)₄, PO(OCH₃)₃ and Na₂CO₃. These alkoxides were stoichiometrically dissolved in an ethanol solution containing HNO₃ with stirring. This operation was carried out in a dry N₂ atmosphere and the ethanol solution was kept at 80°C. Then, the distilled water was added to the ethanol solution for the hydrolysis. The resulting precipitate was dried at 120°C in air for 24 h. After calcined at 750°C in air for 5 h, the precursor powders were compacted into a disk (9 mm in diameter and 1.2 mm thick). The NASICON disks were inserted into Na₃PO₄ powder to avoid the sublimation of phosphorus and then sintered at 1200°C in air for 5 h. In this paper, NASICON (NaₓZrₓSiₓPOₓO₁₂) with x = 0, 1, 2, 2.75 is called NASICON (x = 0), NASICON (x = 1), NASICON (x = 2) or NASICON (x = 2.75), respectively. An auxiliary phase was synthesized by calcining a mixture of Li₂CO₃ and BaCO₃ powders (1:2 in molar ratio) with Au crucible at 750°C in air for 10 min.

3.2 Sensors fabrication

NASICON (x = 0, 1, 2, 2.75) sensors were fabricated by combining the NASICON disks with an auxiliary phase (Li₂CO₃–BaCO₃), as schematically drawn in Fig. 1. The reference electrode was prepared by using Au paste, followed by calcination at 800°C in air for 2 h. On top of it, the sensing electrode was formed by applying Li₂CO₃–BaCO₃ binary carbonate. Then, the whole assembly was calcined at 750°C in air for 5 min. The reference (Au electrode) potential was decided by Na₂O activity in NASICON and O₂ partial pressure. However, the reference potential might shift with changing humidity and CO₂ concentration, because of the instability of Na₂O. Therefore, in order to suppress the influence of the changes on humidity and CO₂ in atmospheric air, the reference electrode was covered with an inorganic adhesive (TOAGOUSEI, ARON CERAMIC C) as a protective layer. The NASICON (x = 0, 1, 2, 2.75) sensors were fixed on the end of a quartz glass tube (9 mm in diameter) with an inorganic adhesive, as shown in Fig. 1.

3.3 Sensing measurements

Gas sensing properties were measured in a conventional gas-flow apparatus equipped with a heating facility. Sample gases consisting of synthetic air and CO₂ were prepared by diluting a parent CO₂ gas (5000 ppm CO₂ in dry synthetic air) with dry synthetic air. The concentration of CO₂ was varied in the range of 250 to 2500 ppm CO₂. The sample gases were let to flow over the sensing electrode at a rate of 0.1 dm³/min. On the other hand, the reference electrode was always exposed to static atmospheric air. As a sensing signal, the electromotive force (EMF) of the sensor was measured with a digital electrometer.

4. Results and discussion

4.1 Preparation of NASICON

Powder X-Ray Diffraction (XRD) measurements were carried out to analyze the NASICON powders synthesized by sol–gel method. The crystal phases were identified by referring to JCPDS files. Figure 2(a)–(d) show the XRD patterns of NASICON (x = 0, 1, 2.75) after calcination at 1200°C in air for 5 h, respectively. NASICON (x = 0) was composed of Na₂ZrSi₂PO₄O₁₂ (No.36-0350) and ZrO₂ (No.34-1084) phases. In the case of NASICON (x = 1), it was confirmed Na₃Zr₂Si₂PO₄O₁₂ (No.36-0351), Na₃Zr₂Si₂PO₄O₁₂ (No.35-0412) and ZrO₂ phases. In NASICON (x = 2.75), it was confirmed Na₂Zr₂Si₂PO₄O₁₂, Na₃Zr₂Si₂PO₄O₁₂ and ZrO₂ phases. Although the formation of ZrO₂ phase was observed, the NASICON (x = 2) was mainly composed of the Na₂Zr₂Si₂PO₄O₁₂ phase. It is supposed that sublimation of P₂O₅ causes the formation of impurity phase such as ZrO₂ and SiO₂ phase, as written in reactions (8) and (9). The result of XRD measurement was indicated that NASICON powders synthesized were composed of some sorts of crystal phases, as the followings reactions (8)–(11), respectively.

\[
\begin{align*}
14\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 & \rightarrow 5\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_4 + 18\text{ZrO}_2 + 2\text{P}_2\text{O}_5 + 19\text{SiO}_2 + 7\text{O}_2, (8) \\
3\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 & \rightarrow 11\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 + 5\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 + 30\text{ZrO}_2 + 17\text{P}_2\text{O}_5 + 22\text{SiO}_2 + (31/4) \text{O}_2 + 6\text{Na}_2\text{SiO}_3, (9) \\
4\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 & \rightarrow 6\text{Na}_2\text{SiO}_3 + 8\text{ZrO}_2 + 2\text{P}_2\text{O}_5 + 2\text{SiO}_2, (10) \\
2\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 & \rightarrow 2\text{ZrO}_2 + (9/2)\text{O}_2 \rightarrow 10\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 + \text{Na}_2\text{SiO}_3 + 10\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_4 + 8\text{ZrO}_2 + 8\text{Na}_2\text{PO}_4 + 3\text{SiO}_2, (11)
\end{align*}
\]
4.2 CO₂ sensing properties and EMF drift

Four kinds of NASICON ($x = 0, 1, 2, 2.75$) were combined with a Li₂CO₃–BaCO₃ (1:2 in molar ratio) auxiliary phase to investigate their CO₂ sensing properties. The CO₂ sensing properties were measured in the rage of 250 to 2500 ppm CO₂ under dry condition at 450°C. Figure 3 shows the correlation between EMF values and CO₂ concentrations under dry condition at 450°C for NASICON ($x = 0, 2, 2.75$) sensors. On the other hand, base-EMF of the NASICON ($x = 1$) sensor was instable after aging for 250 h, as described later in Fig. 4. Therefore, CO₂ sensing properties of NASICON ($x = 1$) sensor was not evaluated. It is supposed that some reactions might continue to take place at the interface between NASICON and auxiliary phase for long-term. However, we cannot explain exactly the instability of base-EMF for the NASICON ($x = 1$) sensor. As shown in Fig. 3, EMFs were correlated linearly with the logarithm of CO₂ concentrations in the range of 250 to 2500 ppm. When CO₂ concentration was increased, the EMF change ($\Delta$EMF) of each sensor was estimated 64.7 mV, 69.7 mV and 55.8 mV, respectively. The theoretical $\Delta$EMFCO₂ of the potentiometric NASICON-based sensor is expressed by using Nernstian Eq. (7). According to Nernstian equation, the electron number (n) of NASICON ($x = 0, 2, 2.75$) sensors were calculated n = 2.22, 2.06 and 2.63, respectively. This result coincides with electrochemical reaction (2). However, strictly speaking, their electron number did not indicate n = 2.00. It might include the experimental error.

Figure 4 shows the relationship between aging time and EMF values of NASICON sensors at 450°C in dry condition containing 250 ppm CO₂. When exposed to 250 ppm CO₂ for a long time, the EMFs of NASICON sensors decreased with aging time and EMF changes were stablized within 0.2 mV/h about 50 h. From the result of Fig. 4, it was obvious that EMF-drift phenomena of NASICON ($x = 0, 2, 2.75$) sensors were hardly different by using NASICON disks with various Na contents.

4.3 XRD measurements

The EMFs of each sensor went downward during aging treatment, as shown in Fig. 4. According to Nernstian Eq. (6), it was suspected that the decrease of $a_{Li^+}$ in Li₂CO₃ auxiliary or $a_{Na^+}$ in NASICON, or increase of $a_{Na^+}$ in NASICON caused EMF drift phenomena. As previously reported in Refs. 9)–11) NASICON was easily corroded by reaction with an auxiliary phase such as a Li₂CO₃ and a Na₂CO₃. Furthermore, it is well-known that Li⁺ radius (59 pm) is smaller than that of Na⁺ (102 pm). Therefore, the influence of the activities changes on base-EMF can be drawn.

(1) The reaction of Li₂CO₃ with NASICON (Na₃Zr₂Si₂PO₁₂, Na₃.4Zr₂Si₂.4P0.6O₁₂) brings about the decrease of $a_{Li^+}$.

(a) Fig. 3. Correlation between EMF values and CO₂ concentrations under dry condition at 450°C for NASICON ($x = 0, 2, 2.75$) sensors.

(b) Fig. 4. Relationship between aging time and base-EMF values of various NASICON sensors at 450°C in dry air containing 250 ppm CO₂.

(c) Fig. 5. XRD patterns of the mixture that consists of NASICON ($x = 2$) and Li₂CO₃ after exposure to dry air containing 250 ppm CO₂ at 450°C: (a) 0 h, (b) 20 h, (c) 60 h and (d) 120 h.

(d) Fig. 6. XRD patterns of the mixture that consists of NASICON ($x = 2.75$) and Li₂CO₃ after exposure to dry air containing 250 ppm CO₂ at 450°C: (a) 0 h, (b) 20 h, (c) 60 h and (d) 150 h.
The decomposition of NASICON causes the change of $a_{Na^+}$. If Li$^+$ in Li$_2$CO$_3$ diffuses into the Na$^+$ site in NASICON, $a_{Na^+}$ might seem to be increased.

In order to inspect the factor of EMF-drift, the XRD measurement was carried out after exposed to dry air containing 250 ppm CO$_2$ at 450°C for mixture powders of NASICON and Li$_2$CO$_3$. Figures 5 and 6 show XRD patterns of the mixture powders that consist of NASICON ($x = 2$ and 2.75) and Li$_2$CO$_3$, respectively. As shown in these figures, after aging for 20 h, the new crystal phases were confirmed such as a Li$_2$ZrO$_3$ (No. 16-0837) at $2\theta = 22^\circ$, ZrO$_2$ at $2\theta = 35^\circ$, Na$_5$Zr(PO$_4$)$_3$ (No. 37-0384) at $2\theta = 34^\circ$, Na$_5$Zr(Po$_3$)$_3$ (No. 35-0124) at $2\theta = 21^\circ$ and 31°. Since the intensities of peaks corresponded to Li$_2$CO$_3$ (at $2\theta = 21^\circ$) decreased with increasing aging time, it was supposed that these new crystal phases were formed because of reaction between auxiliary phase and solid-state electrolyte. Although Si-containing crystal phases such as Na$_2$SiO$_3$ and SiO$_2$ phases could not be confirmed for the XRD measurements, the reactions of the formation of Li$_2$ZrO$_3$, ZrO$_2$, Na$_2$Zr(PO$_4$)$_2$ and Na$_5$Zr(PO$_4$)$_3$ phases are respectively expressed as the followings (12) – (15). Si-containing phases might be present as an amorphous phase.

(The formation of Na$_2$Zr(PO$_4$)$_3$)

\[
\begin{align*}
&2\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_12 + n\text{Li}_2\text{CO}_3 (0 \leq n \leq 3) \rightarrow \\
&\text{Na}_2\text{Zr}(\text{PO}_4)_2 + 2\text{Na}_2\text{SiO}_3 + 2\text{SiO}_2 + \\
&n\text{CO}_2 + n\text{Li}_2\text{ZrO}_3 + (3 - n)\text{ZrO}_2 \\
&5\text{Na}_2\text{Zr}_2\text{Si}_2\text{P}_0112 + 2\text{mLi}_2\text{CO}_3 (0 \leq m \leq 17) \rightarrow \\
&3\text{Na}_2\text{Zr}(\text{PO}_4)_2 + 14\text{Na}_2\text{SiO}_3 + 10\text{SiO}_2 + \\
&m\text{CO}_2 + m\text{Li}_2\text{ZrO}_3 + (17 - m)\text{ZrO}_2
\end{align*}
\]

(12)

(13)

(14)

(15)

From these results, it was supposed that the base-EMF change closely relates with the decrease of Li$^+$ activity in Li$_2$CO$_3$ auxiliary phase and NaO activity in NASICON. Furthermore, since EMF-drift phenomena of NASICON sensors with various Na contents were hardly different, it was supposed that the change of $a_{Na^+}$ in NASICON was not influenced on the drift phenomena. It is effectively suspected that improvement of the EMF-drift needs to select an auxiliary phase, which has resistance to the reaction with NASICON, or to insert the interfacial layer to reduce the reaction between auxiliary phase and NASICON.

5. Conclusions

In this study, the improvement of EMF-drift was investigated on NASICON (Na$_{1+x}$Zr$_2$Si$_2$PO$_{12}$: $x = 0, 1, 2$ or 2.75) - based potentiometric CO$_2$ sensors combined with a Li$_2$CO$_3$-BaCO$_3$ (1:2 in molar ratio) auxiliary phase. The following conclusions are drawn from the present study.

The EMFs of NASICON ($x = 0, 2, 2.75$) sensors were correlated linearly with the logarithm of CO$_2$ concentrations in the range of 250 to 2500 ppm at 450°C. When exposed to 250 ppm CO$_2$ for a long time, the EMF of NASICON sensors decreased with aging time. Since EMF-drift phenomena of NASICON sensors with various Na contents were hardly different, it was supposed that the change of $a_{Na^+}$ in NASICON was not influenced on the drift phenomena. Subsequently, in order to inspect the factor of EMF-drift, XRD measurement was carried out after exposed to dry air containing 250 ppm CO$_2$ at 450°C for mixture powders of NASICON and Li$_2$CO$_3$. From the result of the XRD measurement, it was supposed that the base-EMF change closely relates with the decrease of Li$^+$ activity in Li$_2$CO$_3$ auxiliary phase and NaO activity in NASICON.

References