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NASICON devices attached with Li_2CO_3-$BaCO_3$ auxiliary phase for CO_2 sensing under ambient conditions

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NASICON ($Na_3Zr_2Si_2PO_{12}$)—based electrochemical devices, constructed in a gas-separation type or planar type, were attached with a Li_2CO_3-$BaCO_3$ (1:2 in molar ratio) auxiliary phase to investigate their CO_2 sensing properties under ambient conditions. The devices were found to be far more resistant to the disturbance by a change in relative humidity (RH) than those using Na_2CO_3 or $NaHCO_3$ auxiliary phase. The EMF was correlated linearly with the logarithm of CO_2 concentration in the range of 0.03–50% CO_2 at 30°C, and the linear correlation shifted up or down only slightly with a change in RH between 30 and 90%. For a change in operating temperature, the CO_2 sensing capability was kept almost the same at 45°C, while it was deteriorated significantly at 60 and 75°C, especially in the lower RH range. Applicability of a cobalt oxide bronze ($Na_{0.6}CoO_2$) as a solid reference electrode for the planar type device was also investigated. The devices using the bronze reference electrode exhibited the CO_2 sensing capability as good as those using the Au reference electrode did. In addition, the bronze electrode was found to much improve the reproducibility of the EMF to a fixed concentration of CO_2 among devices.

1. Introduction

There has been an increasing demand for the measurement and/or control of CO_2 for conditioning indoor spaces and green houses as well as for monitoring respiration-related bio-functions. Among the solid-state CO_2 sensors so far reported [1–7], those NASICON ($Na_3Zr_2Si_2PO_{12}$, Na^+ conductor)-based potentiometric devices which are attached with a Li_2CO_3-$BaCO_3$ (or $CaCO_3$) binary carbonate auxiliary phase and gold electrodes appear to be most promising for CO_2 sensing at elevated temperature (400°C and above) [7]. On the other hand, the possibility of potentiometric CO_2 sensing at room temperature was first reported by Bredikhin *et al.* [8], who fabricated a NASICON device attached with a SnO_2 sensing electrode. Similar devices were also reported by other researchers [9–12]. The CO_2 sensor operative at room or ambient temperature is attractive in practice from a standpoint of saving the electric power consumption and downsizing the device. From this recognition, we started investigations on the CO_2 sensor of this type.

We have focused attention to the kinds of metal oxides useful for the sensing electrode, the auxiliary phase involved and the relevance of the CO_2 sensing capability with the coexistent water vapor. As for the sensing electrode materials, several semiconducting oxides other than SnO_2, such as In_2O_3, ZnO and Co_3O_4, have also been found to give the CO_2 sensing capability at room temperature. It seems that electrical conductivity is the most important property of the sensing electrode oxides, since indium-tin oxide (ITO) appears to be the most promising among the tested oxides [13]. The devices fabricated in the initial works were unattached with any auxiliary phases, which should be indispensable for the CO_2 sensor of this type. It was found, however, that $NaHCO_3$ and/or Na_2CO_3 were formed

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spontaneously as auxiliary phases from Na_3PO_4 impurity of NASICON in a humid atmosphere containing CO_2 [13, 14]. If NASICON was synthesized through a sol-gel method, the Na_3PO_4 impurity was reduced in content so that the spontaneous formation of metal carbonates became more difficult. Even in this case, however, the CO_2 sensing capability could be attained easily when $NHCO_3$ or Na_2CO_3 was introduced externally [15]. The presence of water vapor was shown to be also indispensable for the CO_2 sensing capability [13, 14]. Unfortunately, however, the Nernst's correlation between EMF and CO_2 concentration for these devices shifted up or down rather extensively with a change in relative humidity (RH). We found that such dependence on RH could be reduced effectively by introducing Li_2CO_3 in place of $NaHCO_3$ or Na_2CO_3. In particular, a binary carbonate auxiliary phase of Li_2CO_3-$BaCO_3$ (1:2 in molar ratio) was most effective, making the CO_2 sensing performance almost independent of RH over the range of 30–70% RH [16].

This paper aims at reporting in more detail the CO_2 sensing properties of NASICON devices attached with Li_2CO_3-$BaCO_3$ (1:2) auxiliary phase under various conditions in RH and operating temperature. It is also concerned with the applicability of a cobalt oxide bronze ($Na_{0.6}CoO_2$) as a solid reference electrode for a planar type device.

2. Experimental

NASICON ($Na_3Zr_2Si_2PO_{12}$) as an Na^+-ionic conductor was prepared by a sol-gel method [17]. The powder of it was compacted into a disk and sintered at 1200°C for 5 h in air. The disk was then polished with a sand paper into the geometry of 9 mm in diameter and 1.2 mm in thickness. By using the NASICON disks thus obtained, two types of devices were constructed as schematically drawn in Fig. 1. Gas-separation type (a) was fabricated to test the basic sensing properties to CO_2, while planar type (b) was to explore practical CO_2 sensors. The carbonate mainly used was Li_2CO_3-$BaCO_3$ (1:2 in molar ratio). To prepare it, the mixture of Li_2CO_3 and $BaCO_3$ was calcined at 750°C for 10 min and the resulting partially molten system was cooled and pulverized in an agate mortar. ITO (10 at.% Sn-doped In_2O_3) was prepared from an aqueous mixed solution of $InCl_3$ and $SnCl_4$ through hydrolysis and calcination in a conventional way. The calcination was carried out at 1200°C for 2 h in air to obtain coarse particles of ITO (grain size 0.5–1 μm). Na_XCoO_2 ($X = 0.6$) was obtained by calcining a mixture of Co_3O_4 and Na_2O (2:3 in molar ratio) at 500°C for 12 h in air. To be applied on the NASICON surface, these powder samples were converted into a paste by mixing with about the same mass of an α-terpineol-ethyl cellulose (5 wt%) dispersant.

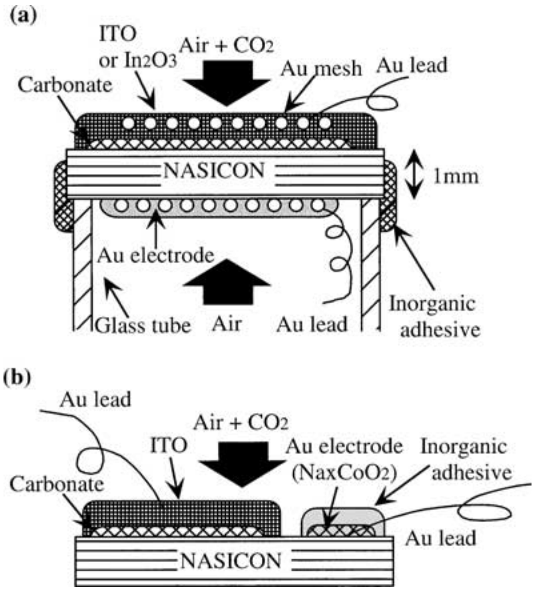

Figure 1 Schematic drawing of NASICON-based devices: (a) Gas-separation type and (b) planar type.

For the gas-separation type devices, the NASICON disk was fixed on the end of a quartz glass tube (9 mm in diameter) with an inorganic adhesive. The Au reference electrode was attached in advance on the inside surface of the disk by applying a gold paste together with a gold lead, followed by calcination at 800°C for 2 h in air. On the outer surface of the disk, the carbonate paste and the ITO paste (with an inbedded gold mesh) were applied about 100 μm thick each in succession, and the whole assembly was calcined at 500°C for 30 min in air.

The planar devices were also fabricated in the same order, i.e., the deposition of Au or Na_XCoO_2 reference electrode, followed by that of Li_2CO_3-$BaCO_3$ auxiliary phase and ITO sensing electrode. The calcination conditions were also the same as those used for the gas-separation type devices. Finally, the reference electrode was covered with a protective layer (about 300 μm thick) of inorganic adhesive (Aron Ceramic C, TOAGOSEI. cc Japan) and kept at room temperature overnight for drying.

Gas sensing properties were measured in a conventional gas-flow apparatus equipped with a heating facility. Sample gases consisting of air, CO_2 and water vapor were prepared by diluting a parent CO_2 gas (pure CO_2 or 1 vol% CO_2 in dry synthetic air) with wet and/or dry synthetic air. The wet air was prepared by allowing dry synthetic air to bubble through water kept at 25°C. The concentration of CO_2 in the sample gas was varied in the range of 0.03% (300 ppm)–50% CO_2, while relative humidity (RH) was set in the range of 10–90% at 25°C. The sample gas was let to flow at a rate of 100 cm^3 min^{-1} over the device kept at an operation temperature between 30 and 75°C. For the gas-separation type devices, the reference electrode (Au) was always exposed to dry synthetic air. The EMF was measured on an electrometer (ADVANTEST TR8652).

3. Results and discussion

3.1. Humidity dependence of EMF as related with auxiliary phase materials

The CO_2 sensors operative at room temperature have usually been attached with $NaHCO_3$ and/or Na_2CO_3 auxiliary phase spontaneously formed or intentionally introduced. A problem about these devices is that the EMF to a fixed concentration of CO_2 depends sensitively on the relative humidity (RH) of the surrounding atmosphere. As mentioned earlier, this dependence

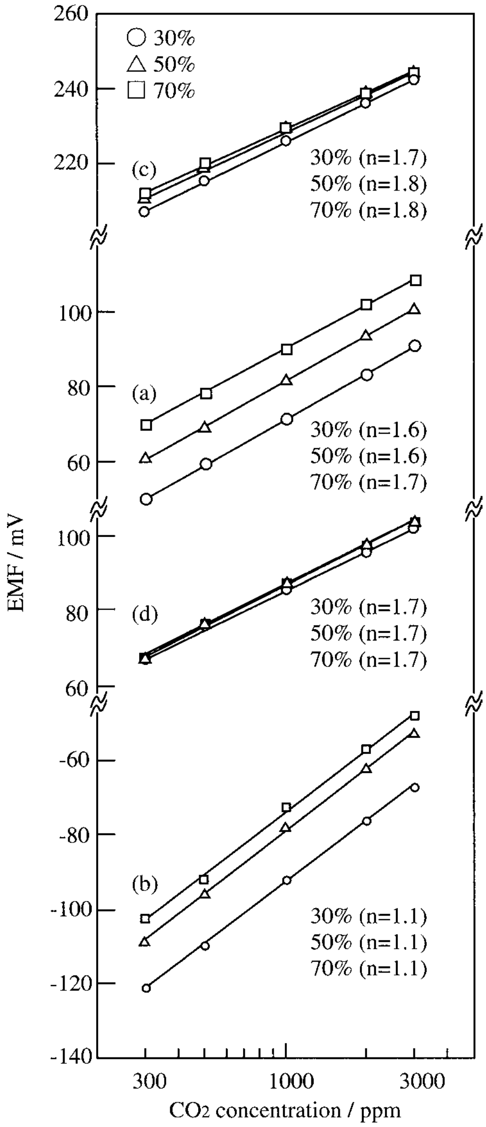

Figure 2 CO_2 sensing properties at 30, 50 and 70% RH for devices using various auxiliary phase materials at 30°C (gas-separation type devices): (a) Na_2CO_3, (b) $NaHCO_3$, (c) Li_2CO_3 and (d) Li_2CO_3-$BaCO_3$ (1:2).

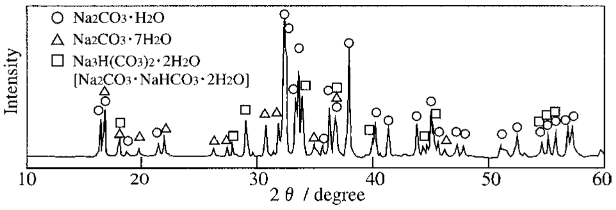

Figure 3 XRD pattern of Na_2CO_3 powder after exposure to air containing 3000 ppm CO_2 and 70% RH at 30°C for a week.

on humidity could be reduced remarkably by introducing Li_2CO_3-based auxiliary phase. For instance, Fig. 2 shows the EMF vs. CO_2 concentration correlations at 30, 50 and 70% RH for four kinds of gas-separation type devices attached with Na_2CO_3 (a), $NaHCO_3$ (b), Li_2CO_3 (c) or Li_2CO_3-$BaCO_3$ (1:2) (d). For each device, the EMF was linearly correlated with the logarithm of CO_2 concentration. The correlation shifted up or down rather extensively depending on RH for the devices attached with Na_2CO_3 and $NaHCO_3$, while the shift was much smaller for those attached with Li_2CO_3 and Li_2CO_3-$BaCO_3$. Especially, the last device was the most stable, with the EMF shift being smaller than 2 mV over a change in RH between 30 and 70%. In addition, the number of electrons associated with the electrode reaction of CO_2 (n) was $n = 1.6$–1.7 or 1.1 with Na_2CO_3 or $NaHCO_3$, respectively, while n was 1.7–1.8 for the other carbonates.

The large EMF shifts in the former two devices are likely to be attributed to the instability of Na_2CO_3 or $NaHCO_3$. It is known that Na_2CO_3 combines with the water of crystallization to form hydrates, $Na_2CO_3 \cdot mH_2O$ ($m = 1$, 7 or 10), depending on RH. In addition, Na_2CO_3 can be partially converted into $NaHCO_3$ to form a complex salt, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, in the presence of humidity and CO_2. When unhydrous Na_2CO_3 was kept in the humid air (70% RH) containing 3000 ppm CO_2 at 30°C for a week, for example, it was converted into a mixture of $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot 7H_2O$ and $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, as revealed from the XRD pattern in Fig. 3. The partial formation of $NaHCO_3$ seems to be consistent with the decrease in n (1.4–1.6) from the nominally expected one ($n = 2$) for the Na_2CO_3 auxiliary phase, i.e., $2Na^+ + CO_2 + 1/2O_2 + 2e^- = Na_2CO_3$. It is remarked that $NaHCO_3$ is also unstable under humid conditions, being partially converted into the hydrated phases of Na_2CO_3. Consistently, the $NaHCO_3$-attached device usually shows $n = 1.1$–1.2, while is slightly lager than nominally expected ($n = 1$) from $2Na^+ + CO_2 + 1/2H_2O + 1/4O_2 + e^- = NaHCO_3$. Unlike these carbonates, Li_2CO_3 does not form hydrates or bicarbonate. This stability of Li_2CO_3 appears to contribute to stabilizing the EMF to a change in RH. The dependent on RH could be further reduced by the use of Li_2CO_3-$BaCO_3$ (1:2), as shown.

Fig. 4 shows the EMF response transients of one of the planar devices attached with Li_2CO_3-$BaCO_3$ (1:2) to the CO_2 concentration stepwise in the range of 300–3000 ppm at 30°C under three RH conditions. The transients are fairly sharp, and the EMF response to each

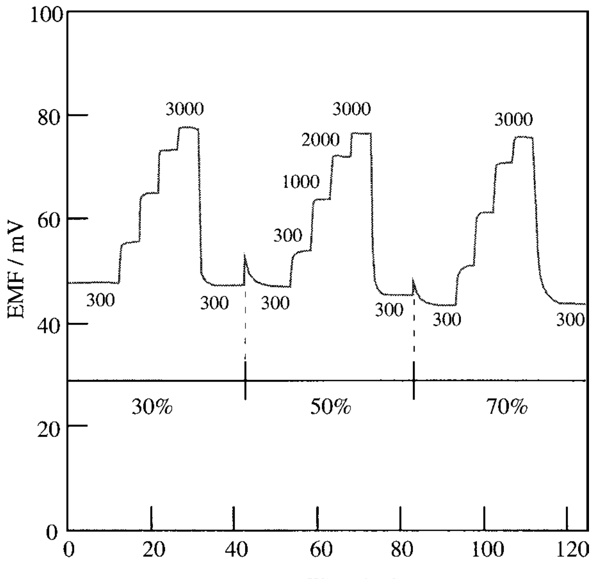

Figure 4 EMF response transients to stepwise changing concentrations of CO_2 under various humidity conditions at 30°C (planar device).

concentration of CO_2 remains almost unchanged regardless of a variation in RH between 30 and 70%. In this way, the stability of the EMF against a humidity change could be improved greatly by introducing Li_2CO_3-$BaCO_3$ (1:2) as an auxiliary phase. The following sections are devoted to the CO_2 sensing properties of the planar devices attached with this particular auxiliary phase.

3.2. CO_2 sensing properties under various conditions

The planar devices attached with Li_2CO_3-$BaCO_3$ (1:2) auxiliary phase and Au reference electrode were tested for CO_2 sensing properties under various conditions. The first test was carried out for the adoptability to a wider range of CO_2 concentration. Fig. 5 shows the EMF response to CO_2 in the range of 0.03% (300 ppm)–50% at 30°C under humidity conditions of 50, 70 and 90% RH. The data fit Nernst's equation well with n equal to 2 under each RH condition. The Nernst correlations under the three RH conditions were fairly close to each other, with mutual deviations remaining within ±3 mV in EMF to a fixed concentration of CO_2. This means that the device can be used for approximate monitoring of CO_2 under three humid conditions, although the RH dependence should be calibrated for more precise monitoring.

The second test was carried for CO_2 sensing capability at more elevated temperatures. Fig. 6 shows the EMF vs. CO_2 concentration correlations under 30, 50 and 70% RH at 30, 45, 60 or 75°C. The CO_2 sensing capability at 45°C (b) was almost the same as that at 30°C (a), though n tended to be somewhat larger than 2, especially under the lower RH conditions. This tendency became conspicuous at 60°C where $n = 2.3$–2.5, indicating a considerable deterioration of the CO_2 sensing capability (c). The deterioration became serious at 75°C where $n = 2.7$–5.9. It has been reported [14–16] that the CO_2 sensing capability is achieved only in the presence of physisorbed water at the CO_2 sensing interface. The decrease of the amount of physisorbed water is supposedly responsible for the deterioration of the CO_2 sensing capability at the higher operating temperatures.

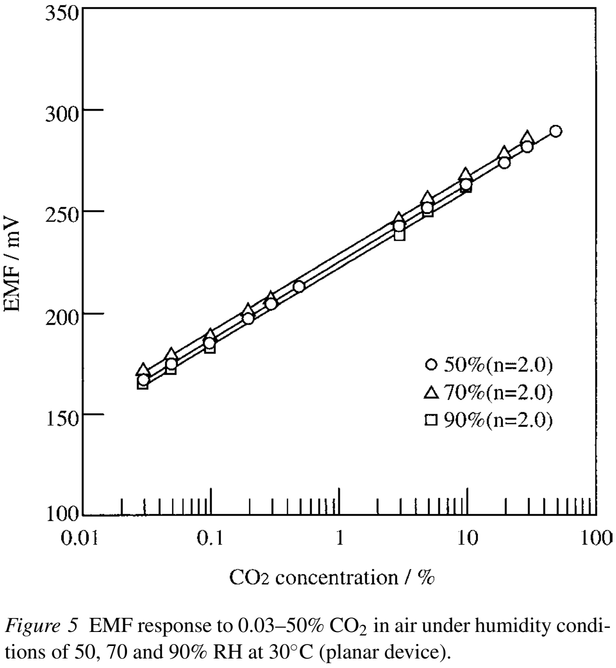

Figure 5 EMF response to 0.03–50% CO_2 in air under humidity conditions of 50, 70 and 90% RH at 30°C (planar device).

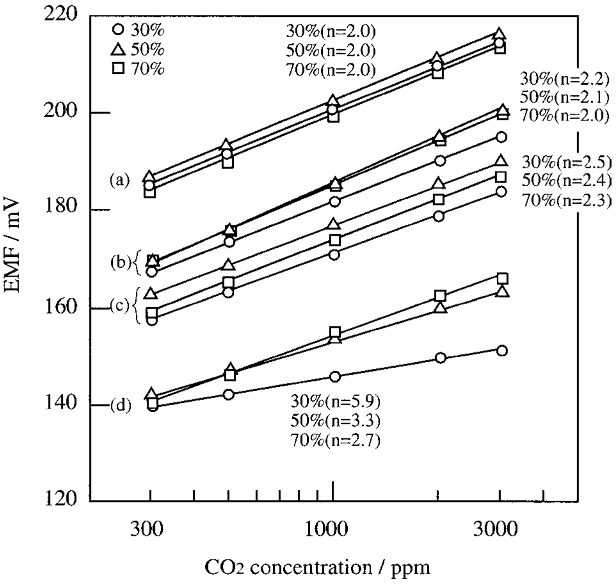

Figure 6 CO_2 sensing properties at various temperatures under humidity conditions of 30, 50 and 70% RH (planar device): (a) 30°C, (b) 45°C, (c) 60°C and (d) 75°C.

3.3. Na_XCoO_2 reference electrode

The planer devices tested above were attached with gold reference electrode covered with protective layer of inorganic adhesive. The gold electrode has been supposed participate in the electrochemical reaction, $2Na^+ + 1/2O_2 + 2e^- = Na_2O$ (in NASICON). Its potential is thus determined by the partial pressure of O_2 (thus air-reference electrode), beside the other factors. This means that the protective layer covering it should not be gas-tight to the diffusion of oxygen. On the other hand, the surface of the NASICON is vulnerable to chemical attacks by CO_2 and moisture, eventually leading to the formation of Na_2CO_3 and/or $NaHCO_3$, as stated earlier. If such surface changes take place at the gold/NASICON interface, the gold electrode no longer works as a stable reference. This means that the protective layer should be gas-tight to CO_2. It is not always easy to fabricate such a protective layer which is permeable to O_2 but not permeable to CO_2. The gold electrode covered with the protective layer, fabricated in the present study, was stable for a short term (weeks), but an apprehension remained about the stability for long-term. This apprehension can be eliminated if a solid reference electrode is available.

Solid reference electrodes for solid electrolyte devices have so far been provided with mixed metal oxides such as Na_XCoO_2 [8, 9], $LiCoO_2$ [18] or $Na_2Ti_6O_{13}$ [19]. The first oxide, often called cobalt oxide bronze, is actually composed of a group of suboxides varying in X. In the present study, Na_XCoO_2 ($X = 0.6$) was tested as a solid reference electrode. Fig. 7 shows the EMF response to CO_2 in the range of 300–3000 ppm

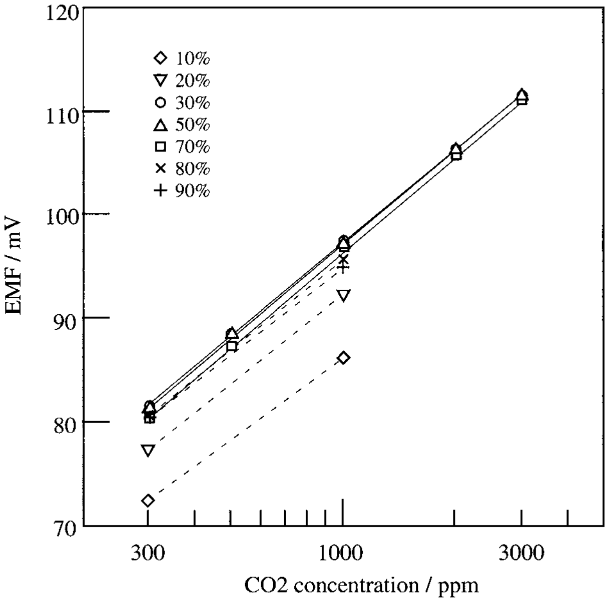

Figure 7 CO_2 sensing properties of the device attached with Na_XCoO_2 reference electrode under various humidity conditions at 30°C (planar device).

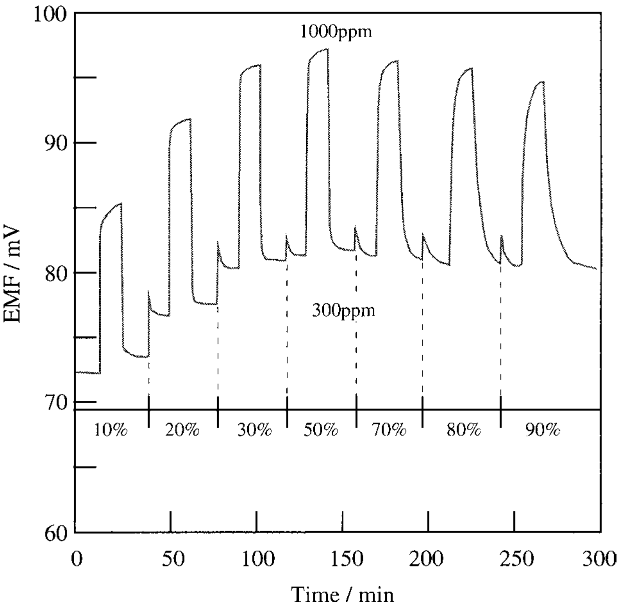

Figure 8 EMF response transients of the device using Na_XCoO_2 reference electrode to switching between 300 and 1000 ppm CO_2 under humidity conditions steping-up from 10 to 90% RH at 30°C (planar device).

under various RH conditions at 30°C for a planar device using Na_XCoO_2 reference electrode. The correlations between EMF and CO_2 concentration were close to each other over the RH range of 30–90%, while the correlations shifted down conspicuously as RH decreased to 20 or 10%. The dependence of the EMF on RH is shown more clearly in Fig. 8, where the CO_2 concentration was switched between 300 and 1000 ppm under RH conditions stepwise increasing from 10 to 90%. The EMF to 300 ppm CO_2 (base EMF) as well as that to 1000 ppm CO_2 are seen to go up rather steeply with increasing RH up to 30%, above which the EMF values becomes stabilized remarkably. Even in the latter region, however, the EMF is not stabilized completely, going through a modest maximum at 50% RH. Apparently two kinds of humidity effects can be recognized, i.e., the EMF increases rather sensitively with increasing RH in the lower RH region (<30%), while it decreases gradually in the higher RH region (>50%). The mechanisms of these humidity effects are yet to be elucidated. However, these humidity effects are associated with the CO_2 sensing electrode, not with Na_XCoO_2 reference electrode.

A merit of using Na_XCoO_2 reference electrode was recognized in the reproducibility of the EMF among the fabricated devices. For example, the EMF to 300 ppm CO_2 (base EMF) was 75, 82 and 108 mV among three devices using Na_XCoO_2 reference electrode, whereas it scattered between 62 and 186 mV among those using Au reference electrode. As stated before, the potential of Au reference electrode is affected by the surface contamination of NASICON. It seems that the surface contamination induced during the fabrication of the NASICON devices can be an origin of the large scattering of the base EMF among the devices. In contrast, the potential of Na_XCoO_2 reference electrode is determined by the electrochemical property of Na_XCoO_2, independent of the chemical state of NASICON surface. This appears to give the reduced scattering of the base EMF.

4. Conclusions

NASICON devices attached with Li_2CO_3-$BaCO_3$ (1:2 in molar ratio) auxiliary phase, ITO sensing electrode and Au or Na_XCoO_2 ($X = 0.6$) reference electrode were investigated for CO_2 sensing properties under ambient conditions. The following conclusions can be drawn from the present study.

1. The selection of auxiliary phase materials is important for stabilizing the EMF response to CO_2 from drifting with a change in relative humidity (RH). The most stable device given by Li_2CO_3-$BaCO_3$ auxiliary phase hardly suffers from serious disturbances over the RH range of 30–90% at 30°C.
2. The same device shows fairly excellent sensing properties to 0.03–50% CO_2 at 30°C. The CO_2 sensing capability remains almost the same at 45°C, but is deteriorated at 60 and 75°C.
3. Na_XCoO_2 ($X = 0.6$) can be used as a solid reference electrode of planar type devices. Use of Na_XCoO_2 is effective in reducing the scattering of the EMF response to CO_2 among devices, as compared with the case of Au reference electrode.

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