Investigation of counter electrode material for NASICON based potentiometric CO_2 sensor

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NASICON (Na^+ conductor, $Na_3Zr_2Si_2PO_{12}$)-based potentiometric CO_2 sensor has usually been attached with Au counter electrode, on which the electrode reaction, $2Na^+ + (1/2)\ O_2 + 2e^- \leftrightarrow Na_2O$ (NASICON), takes place. The counter electrode potential thus depends not only on the partial pressure of O_2 (PO_2) but also on the activity of Na_2O of NASICON in the vicinity of the electrode: The potential changes with a chemical change in the NASICON surface even when PO_2 is fixed. This induces a problem about the stability or reproducibility of the EMF response to CO_2, because the NASICON surface is vulnerable to attack by moisture and CO_2 at room temperature [1]. The device EMF is stable at high operating temperature (450 ^oC). Once kept at room temperature under humid conditions, however, it takes a fairly long warming-up time to recover the original EMF, depending on the degree of the contamination of surface, or it may be totally impossible to recover if contamination is too much. In order to overcome this problem, it is necessary to make the counter electrode independent of the surface state of NASICON. For this purpose, we recently reported that $NaxCoO_2$ (x = 1 or 0.6, Na^+ reservoir), first reported by Weppner et. al [2] worked fairly well to stabilize the counter electrode, because the electrode potential is determined by the property of $NaxCoO_2$ itself (solid-reference). The $NaxCoO_2$ electrode, covered with a layer of glass composite to protect it from CO_2 and H_2O, turned out to be quite stable. However, Li-based reference materials can in principle be better suited to the electrochemical devices using Li_2CO_3-based sensing electrodes. In this study, we investigated the possibility of $LixCoO_2$ (x = 0.4, Li^+ reservoir) [3] as a counter electrode material at high temperature.

$LixCoO_2$ (x = 0.4) was prepared as follows. Li_2CO_3 and Co_3O_4 powders were mixed and calcined at 700 ^oC for 5 h in air. The resulting powder was identified to be a single phase of $Li_{0.4}CoO_2$ from a X-ray diffraction pattern. The sensor device with three electrodes used in this study is shown in Fig. 1. $Li_{0.4}CoO_2$ powder was applied on NASICON disk and covered with a layer of glass composite (SiO_2: Na_2O: B_2O_2: Al_2O_3 = 44: 20: 31: 5, in molar ratio) through melting at 800^oC. The sensing electrode with auxiliary phase (Li_2CO_3-$BaCO_3$) and an Au reference electrode were attached in the same way as done in the previous report [4].

At first, we compared $Na_{0.6}CoO_2$ and $Li_{0.4}CoO_2$ for thermal stability by using TG/DTA. $Li_{0.4}CoO_2$ was stable in the whole temperature range tested (50 – 673 ^oC), while $Na_{0.6}CoO_2$ began a gradual weight loss from 450 ^oC, indicating that $Li_{0.4}CoO_2$ is more stable. Figure 2 shows the properties of $Li_{0.4}CoO_2$ counter electrode at 450 ^oC as tested in the device shown in Fig. 1. The potential of the glass-coated $LixCoO_2$ electrode vs. the Au reference electrode was totally independent of changes in CO_2 concentration under dry condition. As a result, the potential difference (EMF response) between the sensing electrode and the $LixCoO_2$ electrode responded sharply to concentration steps of CO_2. The number of reaction electrons was found to coincide with a theoretical value (2). The glass-coated $Li_{0.4}CoO_2$ counter electrode was thus proven to work well under steady operating conditions, more detailed sensing properties and warm-up characteristics are now under investigation.

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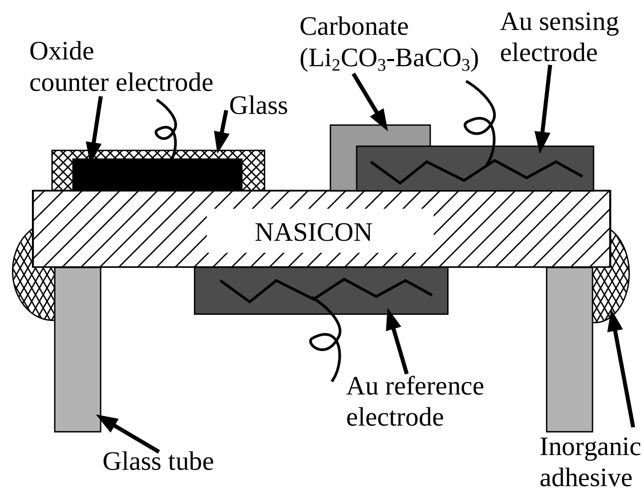

Fig. 1. Schematic drawing of three-electrode device attached with Au reference electrode.

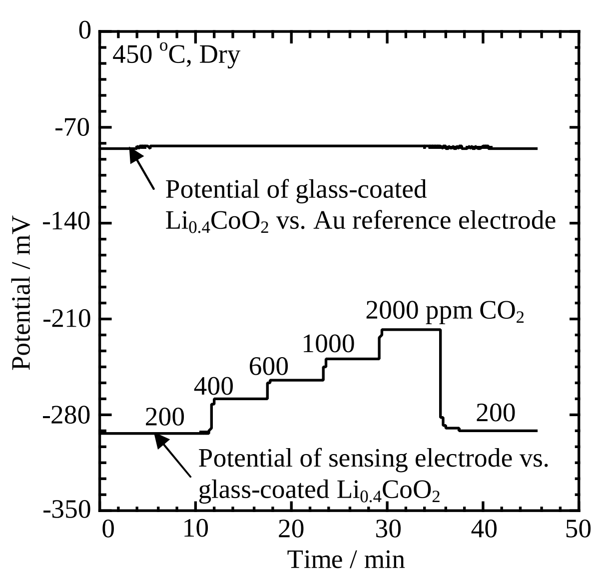

Fig. 2. Behavior of potentials of three-electrode device on changing in CO_2 concentration stepwise at 450 ^oC under dry condition.