Investigation of counter electrode material for NASICON based potentiometric CO$_2$ sensor

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NASICON (Na$^+$ conductor, Na$_2$Zr$_2$Si$_2$PO$_7$)-based potentiometric CO$_2$ sensor has usually been attached with Au counter electrode, on which the electrode reaction, 2Na$^+$ + (1/2)O$_2$ + 2e$^-$ $\rightarrow$ Na$_2$O (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$_2$O 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 °C). Once it keeps 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 Na$_x$CoO$_2$ (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 Na$_x$CoO$_2$ itself (solid-reference). The Na$_x$CoO$_2$ electrode, covered with a layer of glass composite to protect it from CO$_2$ and H$_2$O, turned out to be quite stable. However, Li$_x$-based reference materials can in principle be better suited to the electrochemical devices using Li$_2$CO$_3$-based sensing electrodes. In this study, we investigated the possibility of Li$_x$CoO$_2$ (x = 0.4, Li$^+$ reservoir) [3] as a counter electrode material at high temperature.

Li$_x$CoO$_2$ (x = 0.4) was prepared as follows. Li$_x$CO$_3$ and Co$_3$O$_4$ powders were mixed and calcined at 700 °C 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$_2$O: B$_2$O$_3$: Al$_2$O$_3$ = 44: 20: 31: 5, in molar ratio) through melt at 800°C. The sensing electrode with auxiliary phase (Li$_{2}$CO$_3$: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 TGDTA. Li$_{0.4}$CoO$_2$ was stable in the whole temperature range tested (50 – 673 °C), while Na$_{0.6}$CoO$_2$ began a gradual weight loss from 450 °C, 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 °C as tested in the device shown in Fig. 1. The potential of the glass-coated Li$_{0.4}$CoO$_2$ 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 Li$_{0.4}$CoO$_2$ 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.

REFERENCES

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![Schematic drawing of three-electrode device with Au reference electrode](image-url)

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

![Behavior of potentials of three-electrode device on changing CO$_2$ concentration stepwise at 450 °C under dry condition](image-url)

**Fig. 2.** Behavior of potentials of three-electrode device on changing CO$_2$ concentration stepwise at 450 °C under dry condition.