Title: The effect of mixed conduction of lithium electrolyte to electrochemical CO_2 gas sensor
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Electrochemical CO_2 gas sensors of so called type III structure have been studied for various combinations of electrolytes and reference materials in the literature. For the type III CO_2 gas sensor, sodium-ion-conducting electrolytes such as, Na-β-alumina, and NASICON are used in combination with a Na_2CO_3 auxiliary phase or a mixture with Ba_2CO_3 [1]. Sodium ion conductor and sodium carbonate, however, are found to be too reactive with water that deteriorates the sensor performance. The water solubility of Li_2CO_3 is significantly lower than that of other alkali metal carbonate. Therefore, lithium-ion-conducting electrolyte, LIPON combined with a lithium carbonate auxiliary phase was studied in our study [2].

Potentiomtric cell, Au / Li_2TiO_3-TiO_2 / Li_3PO_4 + 5m/o SiO_2 / Li_2CO_3 / Au, was fabricated and investigated for monitoring CO_2 gas. These lithium based sensors show satisfactory performance with fast response time, appreciable sensitivity, and excellent selectivity. It was also tested in an automobile exhaust and the results are shown in figure 1. However, this sensor shows less sensitivity than the theoretical Nernstian slope. In addition, the cell output depends on the oxygen pressure in the ambient, especially in low CO_2 atmospheres even though the solid reference electrode is adopted to fix the activity of lithium oxide. Based on literature, it is possible that mixed electronic and ionic conduction of lithium electrolyte could be a reason for the above behavior [3].

The mixed conducting behavior of the electrolyte as a function of temperature (400°C ~ 600°C) for the electrolyte was calculated from observed EMF for various concentrations of CO_2 with constant oxygen concentration of 10%. Based on this analysis, the sensor follows nearly Nernstian behavior for high CO_2 concentration when ionic conduction is dominant. The conduction behavior of the lithium ion electrolyte with different electrodes (Li_2CO_3/ Li_3PO_4 + 5m/o SiO_2 electrolyte /Li_2CO_3, Li_2TiO_3+TiO_2/ Li_3PO_4 + 5m/o SiO_2 electrolyte /Li_2TiO_3+TiO_2) were characterized by using EIS (Electrochemical Impedance Spectroscopy). As can be seen from figures, the electrolyte resistance of the cell with Li_2CO_3 electrode is much lower than that with Li_2TiO_3+TiO_2 electrode. This seems to indicate that higher lithium activity in Li_2CO_3 makes the electrolyte more mixed conducting.

Reference
1) Norio Miura, Sheng Yao, Youichi Shimizu, and Noborou Yamazoe, Carbon dioxide sensor using sodium ion conductor and binary carbonate auxiliary electrode, J. Electrochem. Soc. 139 (1992) 1384-1388
2) C. Lee, S. A. Akbar and C. O. Park, Potentiometric CO_2 gas sensor with lithium phosphorous oxynitride electrolyte, Sensors and Actuators B80 (2001) pp. 234-242
3) H. Näfe, How to check the validity of Nernst's law in a potentiometric solid electrolyte galvanic cell, Solid State Ionics 113-115 (1998) pp. 205-217

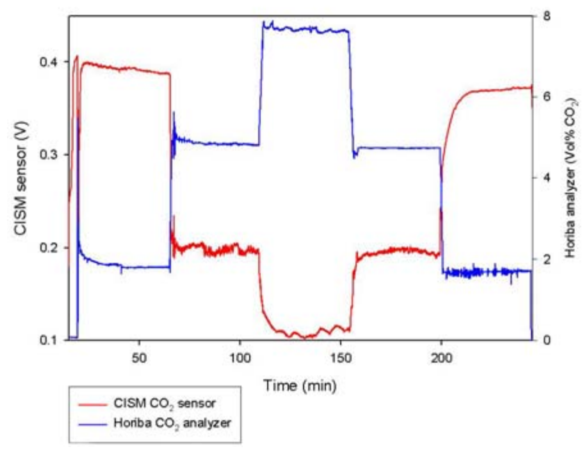

Figure 1: Sensor test in the automobile exhaust.

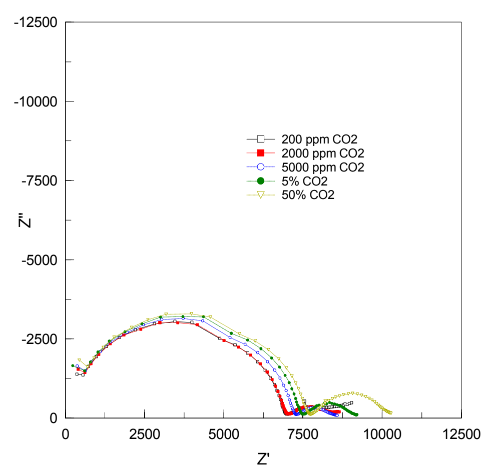

Figure 2: EIS spectra of the Li_3PO_4 electrolyte with the Li_2CO_3 electrode.

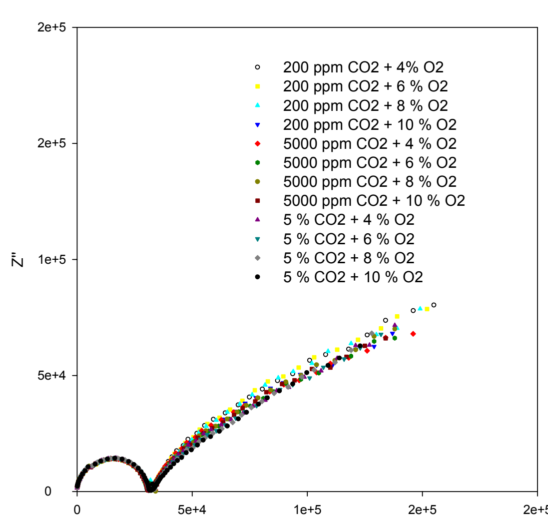

Figure 3: EIS spectra of the Li_3PO_4 electrolyte with the Li_2TiO_3+TiO_2 electrode.