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Application of Nasicon and YSZ for the construction of CO_2 and SO_x potentiometric gas sensors

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Solid-state potentiometric CO_2 and SO_x sensors were fabricated using Nasicon ($Na_3Zr_2Si_2PO_{12}$) or YSZ (ZrO_2 + 8 mole % of Y_2O_3) solid electrolytes, with fused carbonates or sulphates as sensing electrodes and $Na_2Ti_6O_{13}$–$Na_2Ti_3O_7$ two-phase systems or porous platinum as reference electrodes. A comparison of the performance and long-term stability of the prepared sensors was made. More stable behaviour of CO_2 sensors was observed for cells prepared from Nasicon while SO_x sensors with YSZ used as the solid electrolyte displayed a better performance. The sensing mechanism and long-term stability of the investigated cells was discussed in terms of the possible reactivity of solid electrolytes with the electrode materials and the formation and modification of “ionic-bridges” at the solid electrolyte–electrode interface.

Key words: *potentiometric gas sensor; CO_2; SO_x; Nasicon; YSZ; carbonate; sulphate*

1. Introduction

A typical potentiometric gas sensor consists of a solid electrolyte (YSZ, Nasicon, Na^+ β-alumina) as well as sensing and reference electrodes attached to both sides of the solid electrolyte. The simplicity of construction, low cost in large-scale production, compatibility with classical electronic devices, short response time, good selectivity, and known dependence of the measured signal on gas content (Nernstian behaviour) are the main advantages of such devices. The main difficulty in applying such sensors is signal instability during long-term use. Numerous efforts have been undertaken to develop systems exhibiting the most stable behaviour. Also, many papers have concerned theoretical aspects of the working mechanism of investigated cells. Various solid electrolytes and sensing and reference electrodes have been proposed and tested to a large extent [1–5].

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The aim of this work was to compare the performance and working mechanisms of potentiometric gas sensors prepared using either a Na^+ ion conductor (Nasicon) or O^{2-} ion conductor (ZrO_2:Y_2O_3) as the solid electrolyte. A comparison was made for sensors designed for detecting CO_2 and SO_x.

2. Materials and measurements

Powders of YSZ (ZrO_2 + 8 mole % of Y_2O_3, Tosoh Corp., Japan) and $Na_3Zr_2Si_2PO_{12}$ (Nasicon) prepared by the co-precipitation method [6] were used. Powders were formed in a pellet die (75 MPa), isostatically pressed (250 MPa), and sintered at 1673 K (5 h) in the case of ZrO_2 and at 1500 K (24 h) in case of Nasicon.

Li_2CO_3–$BaCO_3$ and Li_2SO_4–$CaSO_4$ (2:3 molar ratio) were used to form electrodes sensitive to CO_2 and SO_x, respectively. Porous platinum or $Na_2Ti_6O_{13}$–$Na_2Ti_3O_7$ mixtures were used in the construction of reference electrodes. $Na_2Ti_6O_{13}$–$Na_2Ti_3O_7$ materials were prepared by the solid-state reaction of TiO_2 (anatase, Cookson technology) with sodium carbonate (Sigma-Aldrich). Details are given elsewhere [7, 8].

The electromotive force (EMF) of the prepared cells was measured as a function of temperature (300–650 °C), CO_2 (10–1500 Pa) or SO_2 (0.1–10 Pa) partial pressures, and time. Details concerning the experimental setup are given elsewhere [7, 8].

Additionally, XRD (X-ray diffraction), DTA & TG (differential thermal analysis and thermogravimetry), SEM (scanning electron microscopy), EIS (electrochemical impedance spectroscopy), and MS (mass spectrometry) were used to assist the interpretation of the results.

3. Results and discussion

3.1. Sensing characteristics

The CO_2 sensor has the following electrochemical cell structure:

$$CO_2,\ O_2^{(1)},\ Me \mid Li_2CO_3\text{-}BaCO_3 \mid SE \mid B(Na),\ Pt,\ O_2^{(2)}$$

where SE is a solid electrolyte ($Na_3Zr_2Si_2PO_{12}$ or YSZ), B(Na) denotes a $Na_2Ti_6O_{13}$–$Na_2Ti_3O_7$ mixture (applied when Nasicon was used as SE), Me = Ag, Au, or Pt, and superscripts (1) and (2) denote sensing and reference electrodes, respectively.

SO_x sensors were prepared similarly as the CO_2 sensors. The following electrochemical cells were prepared:

$$SO_x,\ O_2^{(1)},\ Me \mid Li_2SO_4\text{-}CaSO_4 \mid SE \mid B(Na),\ Pt,\ O_2^{(2)}$$

Figure 1 shows example dynamics at 748 K for a CO_2 sensor with Nasicon used as the solid electrolyte. Abrupt changes in carbon dioxide partial pressure (solid line, right axis) cause changes in the electromotive force (EMF). In the case of SO_x sensors with a silver electrode (Me = Ag), no acceptable sensor characteristics were obtained. The observed EMF changes with changes in SO_x partial pressure were not reversible, probably due to silver corrosion by SO_x. The replacement of Ag by Au was also unsuccessful, and typical sensor characteristic were still not observed. Only the use of Pt at the sensing electrode led to stable sensor characteristics.

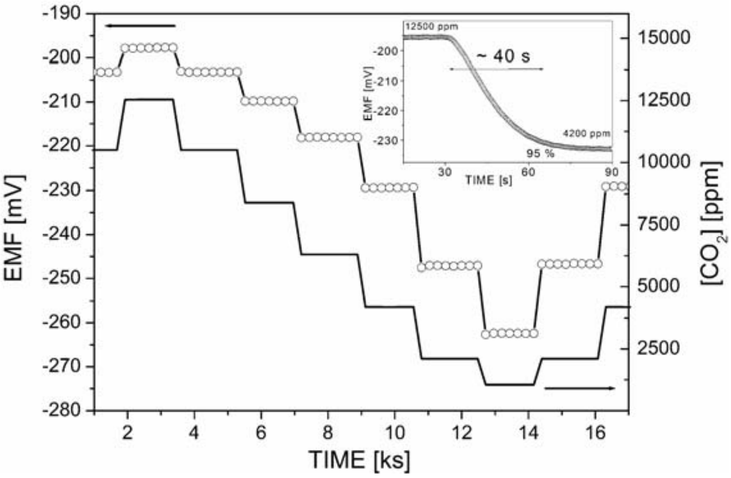

Fig. 1. Response of the carbon dioxide sensor with Nasicon as a solid electrolyte at $T = 748$ K. Stepwise changes in CO_2 partial pressure are shown as solid lines (right axis). The determination of the response time is shown in the inset

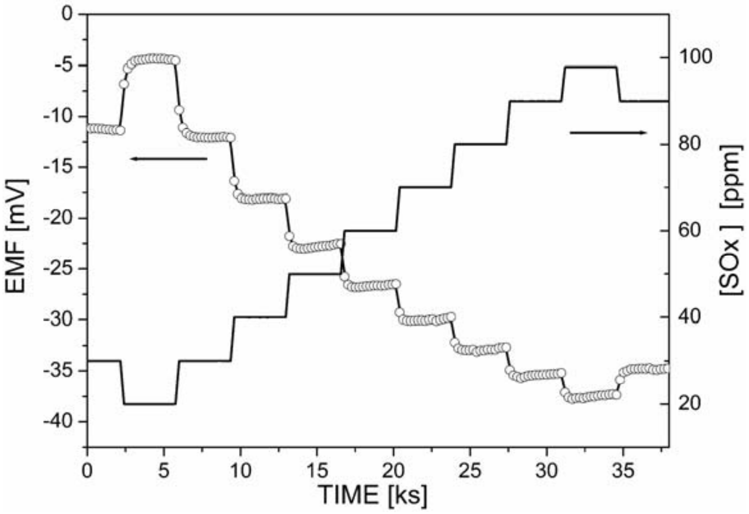

Fig. 2. Response of the sulphur oxide sensor with YSZ as the solid electrolyte at $T = 873$ K. Stepwise changes in SO_2 partial pressure are shown as solid lines (right axis)

Figure 2 shows the SO_x sensor dynamics measured at $T = 873$ K for the sensor prepared using YSZ as the solid electrolyte. As can be seen, the measured electromotive force follows the changes in SO_x partial pressure (solid line, right axis). The constructed prototype sensor exhibited a reversible signal in short time experiments. The response and recovery times of the CO_2 sensors ranged from 30 s to 60 s, depending on the gas flow rate (20–100 cm^3/min.), as shown in the inset of Figure 1. The response time of SO_x sensors was several minutes.

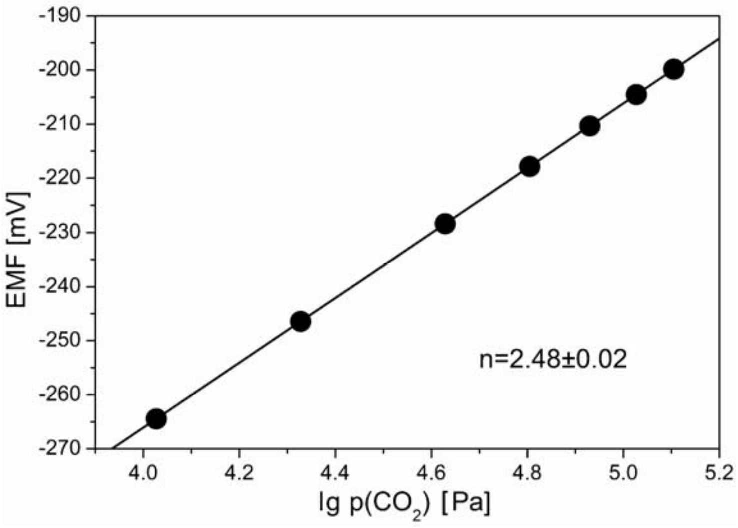

Fig. 3. Measured electromotive force EMF as a function of the logarithm of carbon dioxide partial pressure shown for the data from Fig. 1

The obtained results were fitted using the Nernst equation, as shown in Figure 3. The determined parameter n (corresponding to the number of electrons in the electrode reaction) was found to be between 2.2 and 2.8. The observed discrepancy of the parameter n from the theoretical value ($n = 2$) may be explained by the mixed conductivity of either sensing carbonates or electrolyte phases [7, 9]. In the case of SO_x sensors, the explanation of the observed non-integer n values must include the SO_2/SO_3 gas equilibrium [3]. Mass spectroscopy measurements confirmed that the Pt connection acts as a catalyst in the oxidation of SO_2 to SO_3 at the temperatures above 673 K. Above $T = 723$ K, a partial reduction of SO_3 to SO_2 may occur, thus affecting the measured EMF signal. The obtained results agreed well with thermodynamic predictions for a system of $SO_2 + O_2$.

3.2. Sensor long-term stability

CO_2 sensors with Nasicon as the solid electrolyte exhibited a stable behaviour over long time (above 6 months). Excellent long-term stability in this case may be attributed to the formation of a liquid phase at the sensing electrode/solid electrolyte interface and well-defined ion transport [8]. On the other hand, a long-term drift of the sensing signal was observed for CO_2 sensors with stabilised zirconia as the solid electrolyte. Thermodynamic considerations as well as DTA, XRD, and SEM [8] analyses indicate that the observed instability may result from an irreversible chemical reaction between carbonate and stabilised ZrO_2 phases. EIS measurements showed that the uncontrolled reaction above $T = 723$ K between carbonate and YSZ leads to a continuous, substantial decrease of the electrical conductivity of the cell, as shown in Figure 4.

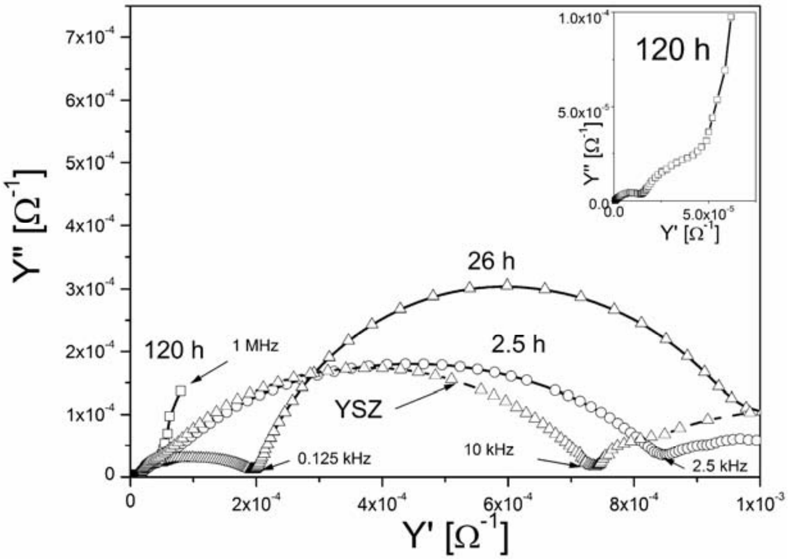

Fig. 4. Admittance diagrams for the $Li_2CO_3 + BaCO_3$|Au|YSZ|Pt cell after heating at 773 K for 2.5 h, 26 h and 120 h. The admittance diagram for a Pt|YSZ|Pt cell is shown for comparison

A drift of the electromotive force was also observed in the case of both SO_x sensors (Nasicon and YSZ based) during long-term experiments (carried out for several weeks). The observed drift cannot be explained by uncontrolled chemical reactions in the solid state alone, as is the case of YSZ-based CO_2 sensors. The thermodynamic analysis excluded the possibility of a reaction between the sulphate phase and the solid electrolyte. The lack of local equilibrium at the electrode/solid electrolyte interface may be the reason for the unstable behaviour of SO_x sensors.

4. Conclusions

Experimental results concerning potentiometric CO_2 and SO_x sensors have been described in this work. Most of the sensors exhibited a reproducible signal during short-time experiments (below 24 h). The measured electromotive force (EMF) of the cells was found to be linear with the logarithms of CO_2 and SO_x concentration in the measured ranges of concentration (100–15000 ppm of CO_2 and 1–100 ppm of SO_x). These sensors exhibited quasi-Nernstian behaviour, with the n parameter having a non-integral value higher than the theoretical one ($n = 2$). The operating temperature range was 300–500 ºC and 500–650 ºC for CO_2 and SO_x sensors, respectively. The response time was found to be below 60 s and several minutes for CO_2 and SO_x, respectively. The most stable behaviour was observed in the case of the Nasicon-based CO_2 sensor working in the presence of a liquid phase at the electrode–solid electrolyte interface. In case of SO_x sensors, the lack of local equilibrium at the electrode/solid electrolyte interface may be responsible for unstable behaviour.

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