

Electrocatalytic gas sensors based on Nasicon and Lisicon

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The principle of operation, construction, and properties of gas sensors based on Nasicon and Lisicon are presented. These types of materials are known to exhibit high ionic conductivities and relatively high chemical stabilities at elevated temperatures. Electrocatalytic sensors have been prepared using ceramic technology. Their working principle is based on electric current acquisition, when a voltage ramp is applied to the sensor. The current–voltage plot has a unique shape, depending on the surrounding gas and its concentration. Measurements conducted in mixtures of nitrogen dioxide, sulphur dioxide, and synthetic air are presented.

Key words: *solid-state electrolyte; gas sensor; Nasicon; Lisicon*

1. Introduction

In recent years, solid-state ion conducting materials, also known as superionic or fast ion conductors, have been intensively developed. These materials exhibit relatively high ionic conductivities at elevated temperatures, resulting from high concentration and mobility of ion charge carriers. Such conductors are characterized by the crystallographic structure, in which mobile ions can be delocalised over a number of free interstices in an immobile sublattice. Solid-state electrolytes exhibit potential for applications in a variety of solid-state electrochemical devices such as sensors, fuel cells, membranes, and pumps [1].

With increasing environmental protection awareness and due to many advantages, such as low cost, small size and the ability of operating on-line or under continuous deleterious conditions, special attention has been paid to solid-state gas sensors [2–4].

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There are several types of solid-state gas sensors, based on a variety of principles and materials [5–7]. Solid state electrochemical sensors have become very popular, in which chemical species reacting at an electronic conductor–ionic conductor interface exchange electric charges, resulting in an electric signal. The output of the electrochemical sensors is directly related to the concentration or partial pressure of gaseous species. Depending on whether the output is an electromotive force or an electrical current, the electrochemical gas sensors can be classified as potentiometric or amperometric. Lack of selectivity, however, is sometimes a shortcoming of such sensors. It seems that an improvement in selectivity can be obtained using electrocatalytic sensors.

Electrocatalytic sensors belong to a new and particularly interesting group of electrochemical gas sensors which employ cyclic voltammetry techniques to solid electrolytes [8–10]. Cyclic voltammetry is a method widely used in liquid electrochemistry for determining concentrations of chemical species. The method is based on the oxidation and reduction of chemical species on electrodes polarised using a linearly varying voltage. Gas concentrations can be determined using information from electrokinetic reactions occurring in a sensor. In the presence of the applied voltage, gases react on the surface of the electrodes, influencing the current flowing through the sensor. This results in a unique voltammetric plot for different types and concentrations of gases. Apart from other features, the current-voltage response of the sensor potentially allows a couple of gases to be detected simultaneously [10].

The most widely used solid-state electrolyte is yttria-stabilized zirconia (YSZ), an oxygen ion conductor. A potentiometric oxygen sensor based on YSZ is used for combustion control in all modern automotive engines. Other very popular solid electrolytes used in sensors are Nasicon and Lisicon, which have mobile sodium and lithium cations, respectively. They are used mostly in potentiometric sensors [11, 12]. In this work, a study of electrocatalytic gas sensors employing Nasicon and Lisicon is presented. The properties of the developed sensors, exposed to mixtures of nitrogen dioxide, sulphur dioxide, and synthetic air are investigated.

2. Experimental

Nasicon powder (with the chemical formula of $\text{Na}_{2.8}\text{Zr}_2\text{Si}_{1.8}\text{P}_{1.2}\text{O}_{12}$) was prepared by the conventional solid-state ball milling method [13]. A mixture of chemically pure NaHCO_3 , ZrO_2 , SiO_2 , and $\text{NH}_4\text{PO}_4 \cdot 3\text{H}_2\text{O}$ was milled several times, and then calcinated at 900 °C and fired at 1200 °C to finalize synthesis. Lisicon (with a chemical formula of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$) powders were prepared by the conventional solid-state reaction [14]. Stoichiometric quantities of Li_2CO_3 , GeO_2 , and ZnO were thoroughly milled and then calcinated for 2 hours at 700 °C in platinum boats. The products were reground and fired again for 1 hour at 1100 °C to complete the reaction. White, fine-grained powders were obtained in both cases.



The structure of the sensor made in this way is shown in Fig. 1. Pellets in the form of discs 12 mm in diameter and 1 mm thick were prepared by isostatic pressing and sintering. Electrodes were made by coating opposite pellet faces with gold paste (ESL 8880) for the Lisicon-based sensor and with platinum paste (ESL 5542) for the Nasicon-based sensor.



Fig. 1. Structure of the sensor

Measurements were conducted in mixtures of high-purity gases: nitrogen dioxide, sulphur dioxide and synthetic air with controlled concentrations. A precision mass flow controller (Tylan) was used to obtain gas mixture compositions. A constant gas flow of 100 sccm was maintained. The measuring stand consisted of a tube furnace, impedance analyser SI 1260, electrochemical interface SI 1287, and a PC computer with suitable software for system control and data acquisition. The measurements were performed in the temperature range 200–500 °C. While a linearly changing voltage of symmetrical triangular shape (ranging from 5 V to –5 V) was applied to the sensor, its current response was recorded. The voltage sweep rate was adjusted from 20 to 50 mV/s. Impedance measurements were conducted in the frequency range 100 mHz–1 MHz, with an excitation amplitude of 20 mV.

3. Results and discussion

The electrical conductivity of the prepared sensors was determined by means of ac admittance spectroscopy. In the measured frequency range, a well-resolved semicircular arc appears in the Nyquist plot. This arc is attributed to the bulk properties of the electrolyte. On the basis of this plot, the resistive component of total impedance was established and used to derive conductivity as a function of temperature. Typical Arrhenius plots for both electrolytes are shown in Figure 2. The conductivity of Nasicon is higher than that reported for Lisicon, which makes Nasicon-based sensors very promising for operation at lower temperatures. Activation energies of 0.19 eV for Nasicon and 0.4 eV for Lisicon were determined.

The performance of Nasicon and Lisicon electrocatalytic sensors exposed to mixtures of nitrogen dioxide of various concentrations and synthetic air was investigated at 300 °C. In the case of the Nasicon sensor, current-voltage plots (Fig. 3) show two relatively steep peaks near ± 2.3 V. In the case of Lisicon (Fig. 4), two sets of rather broad peaks are observed near ± 0.8 V and ± 1.9 V. As shown in Figure 5, for both kinds of sensors an almost linear dependence of the peak current on NO_2 concentration is observed with the slopes about 24 $\mu\text{A/ppm}$ and 35 $\mu\text{A/ppm}$ for the Nasicon and

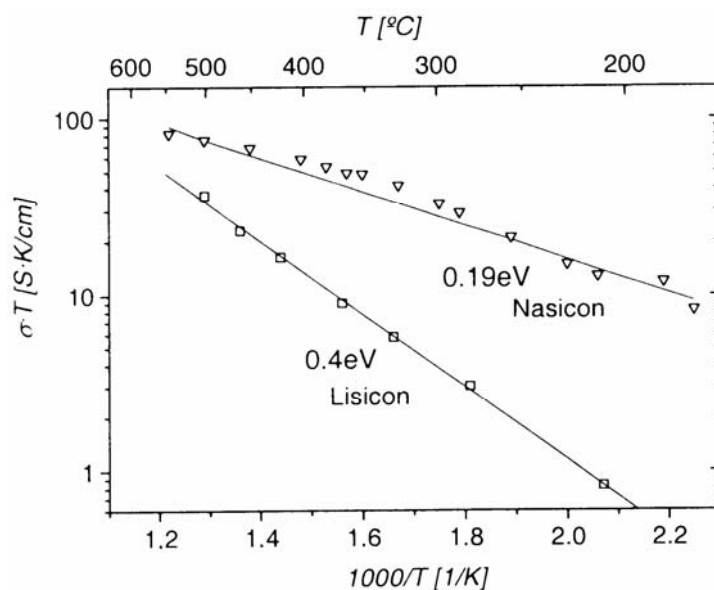


Fig. 2. Arrhenius plots of the sample's electrical conductivity

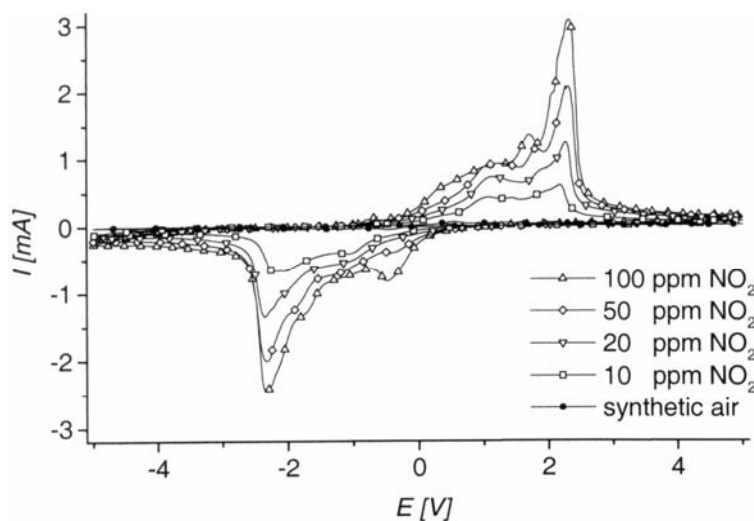


Fig. 3. Nasicon sensor response to different NO_2 concentrations (300 °C, 20 mV/s)

Lisicon sensors, respectively. At higher temperatures, the positions and shapes of both current–voltage plots remain almost the same (Fig. 6). The Nasicon sensor at those temperatures has a much higher nitrogen dioxide sensitivity due to low values of current measured in synthetic air. Lisicon and Nasicon sensors do not respond to NO_2 at temperatures higher than 500 °C and 600 °C, respectively. Therefore, they can be

used for multi-gas detection when their temperature of operation is altered during detection. Both sensors respond similarly to sulphur dioxide (Fig. 7). In this case, however, a higher sensitivity is observed for the Lisicon electrolyte.

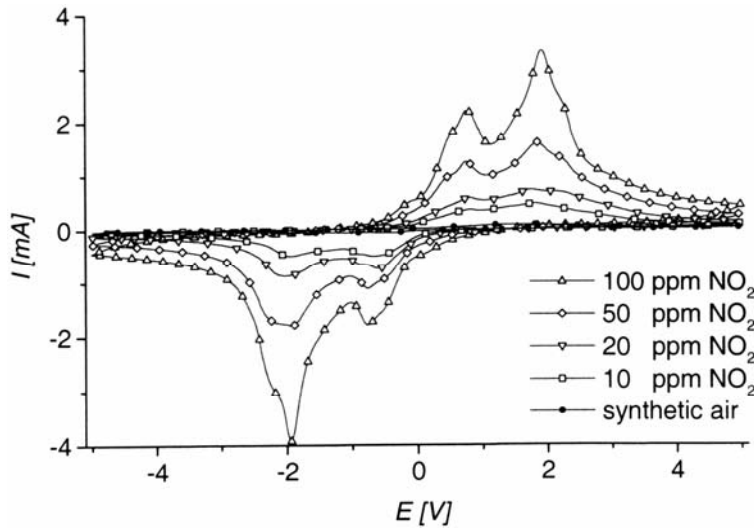


Fig. 4. Lisicon sensor response to different NO_2 concentrations (300 °C, 20 mV/s)

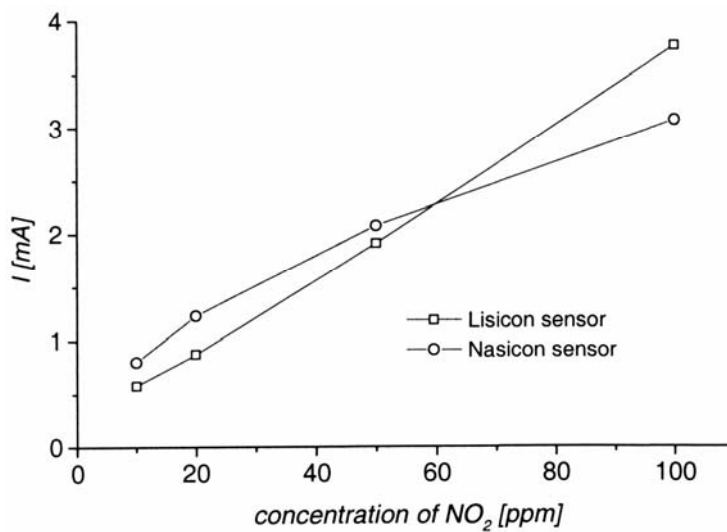


Fig. 5. Maximum current value of the NO_2 peak (300 °C, 20 mV/s)

In the case of a solid electrolyte with mobile Li^+ ions and gases used in the experiment, the following chemical reactions can be responsible for the peaks occurring on the current–voltage plots [15]:



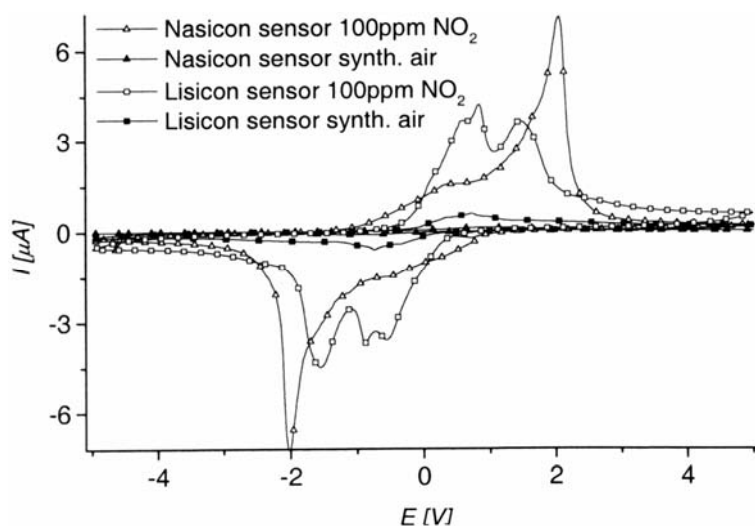
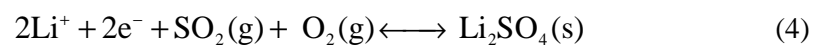
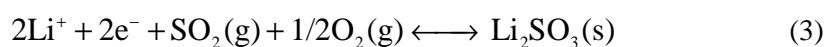
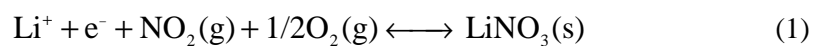


Fig. 6. Sensor response to NO_2 at $400\text{ }^\circ\text{C}$ (50 mV/s)

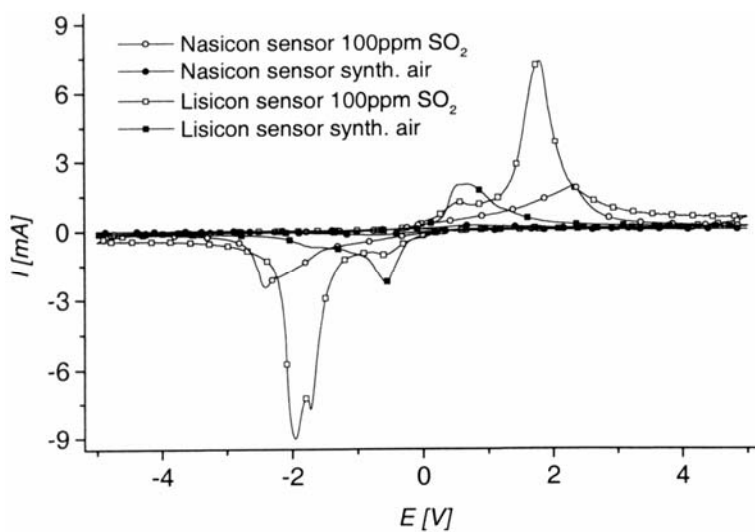
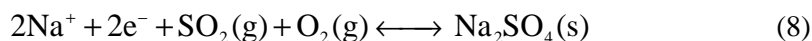
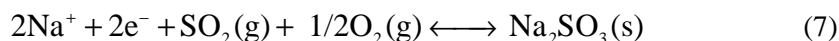
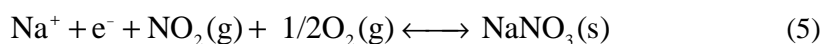


Fig. 7. Sensor response to SO_2 at $500\text{ }^\circ\text{C}$ (50 mV/s)

and the following ones in the case of a solid electrolyte with mobile Na^+ ions [16]:



These reactions are very similar but their kinetics might be different. Therefore, the peaks in the current–voltage plots are different for Nasicon and Lisicon.

It is interesting to note that the peak current of the Lisicon sensor is larger than that for the Nasicon-based sensor, even though the conductivity of Lisicon is lower than that of Nasicon. Moreover, gold was used as an electrode material in the case of the Lisicon-based sensor, which is known to have a lower catalytic activity than platinum (used in the Nasicon-based sensor). Therefore, it can be inferred that the larger peak current in the case of the Lisicon sensor is related to lithium ion reactivity.

4. Conclusions

In this paper, the results of cyclic voltammetry for electrocatalytic gas sensors employing solid electrolytes that conduct lithium or sodium ions are presented. It was shown that both investigated sensors could be used for detecting NO_2 and SO_2 . The current-voltage response depends in a unique way on the type of gas and its concentration exposed to the sensor. Nasicon and Lisicon respond in a similar way, confirming that they have a similar working principle. The number, positions, and heights of the peaks, however, are different due to the occurrence of different chemical reactions at the sensor electrodes. Sensors can be used for multi-gas detection if their temperature of operation is altered.

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