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Lisicon solid electrolyte electrocatalytic gas sensor

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Abstract

In this paper fabrication and examination of electrocatalytic gas sensor based on Lisicon ($Li_{14}ZnGe_4O_{16}$) solid electrolyte is described. Electrocatalytic sensors form a relatively new group of gas sensors, which employ kinetics of a controlled chemical reaction. Its working principle is based on electric current acquisition, while voltage ramp is applied to the sensor. Measurements of the sensor in mixtures of nitrogen dioxide, sulfur dioxide and synthetic air are presented. Current–voltage response depends in a unique way on the type of gas and its concentration exposed to the sensor.

Keywords: Electrical properties; Impedance; Sensors; Lisicon

1. Introduction

A concentration of gases is a key parameter measured in many industrial or domestic activities. In the last decade the specific demand for gas detection and monitoring has emerged particularly as the awareness of the need to protect the environment has grown.[1] Solid state gas sensors, based on a variety of principles and materials, are the best candidates to the development of commercial gas sensors for a wide range of applications. There is a large variety of different solid state gas sensors.[2–7] Among them very popular become solid state electrochemical sensors, which include potentiometric and amperometric sensors.

Electrocatalytic sensors belong to a new and particularly interesting group of electrochemical gas sensors, which employ chemically controlled kinetic reactions.[8–15] The principle of operation is based on the concept of applying cyclic voltammetry for gas concentration determination, using information from electrokinetic reaction occurring in a sensor. In the presence of applied voltage gases react on the surface of the electrodes influencing current flowing through the sensor. Unique voltammperometric plots are created for different types and concentrations of gases. Apart from other features, current–voltage response of the sensor potentially allows detection of a few gases simultaneously.[11,13]

The principle of operation of electrocatalytic sensors requires presence of solid electrolyte and metal electrodes. It has been demonstrated the successful application of Nasicon solid electrolyte with sodium ions[12] as well as yttria-stabilized zirconia (YSZ),[10] tungsten-stabilized bismuth oxide (WBO)[14] and samarium doped ceria[15] with oxygen ions in the development of the electrocatalytic sensors. In this paper the study on kinetic reactions of the Lisicon solid electrolyte with lithium ions is presented. Lisicon has been used as a solid electrolyte for potentiometric sensors,[16] however, this is the first report of its application for electrocatalytic sensor.

2. Experimental

Lisicon (chemical formula $Li_{14}Zn(GeO_4)_4$) powders were prepared by the conventional solid state reaction applying the method described by Hong.[17] Stoichiometric quantities of the substrates (Li_2CO_3, GeO_2 and ZnO) were thoroughly milled and then calcinated for 2 h at 700 °C in platinum boats. The products were regrind and fired again for 1 h at 1100 °C to

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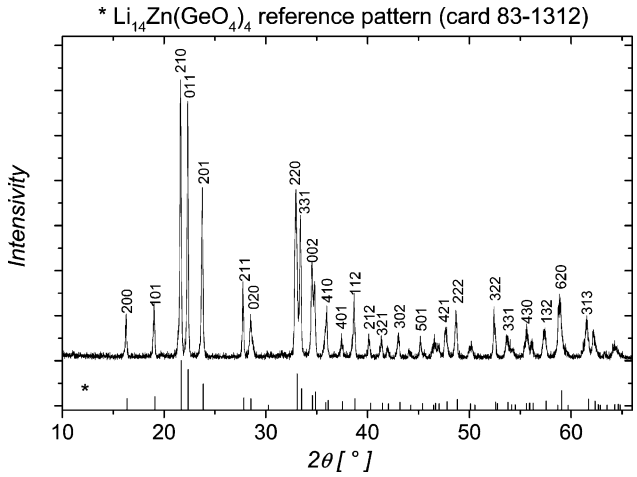

Fig. 1. X-ray diffraction pattern of a Lisicon powder.

complete the reaction. White, fine-grained powder was obtained. X-ray diffraction (XRD) analysis measurements were carried out using Philips X'Pert diffractometer system. Results (Fig. 1) show a very good agreement in peak positions and intensity with previously reported.[17]

Pellets in the form of discs of 12-mm diameter and with a thickness of 1 mm were prepared by isostatic pressing and sintering at 1100 °C. Electrodes were made by coating the opposite pellet faces with the gold paste (ESL 8880) and applying platinum wires and finally fired at 900 °C. The sensor structure made in this way is shown in Fig. 2.

Measurements were conducted in mixtures of high purity gases: nitrogen dioxide, sulfur dioxide and synthetic air of controlled concentrations. The precision mass flow controllers (Tylan) were used for obtaining gas mixture composition. Constant gas flow of 100 sccm was maintained. The measuring stand included a tube furnace, impedance analyzer SI 1260, electrochemical interface SI 1287 and a PC computer with suitable software for system control and data acquisition. Measurements were performed in the temperature range from 150 to 600 °C. While linearly changing voltage of symmetrical triangular shape (range 5 to −5 V) was applied to the sensor its current response was recorded. The voltage sweep rate was adjusted from 10 to 100 mV/s. Impedance measurements were conducted in the frequency range from 100 mHz to 1 MHz with the excitation amplitude of 50 mV.

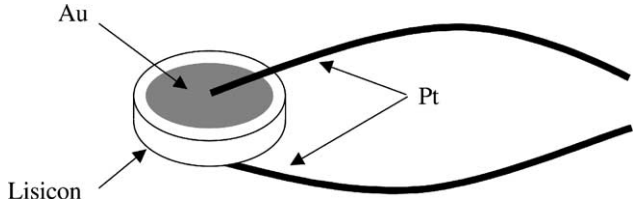

Fig. 2. Structure of the sensor.

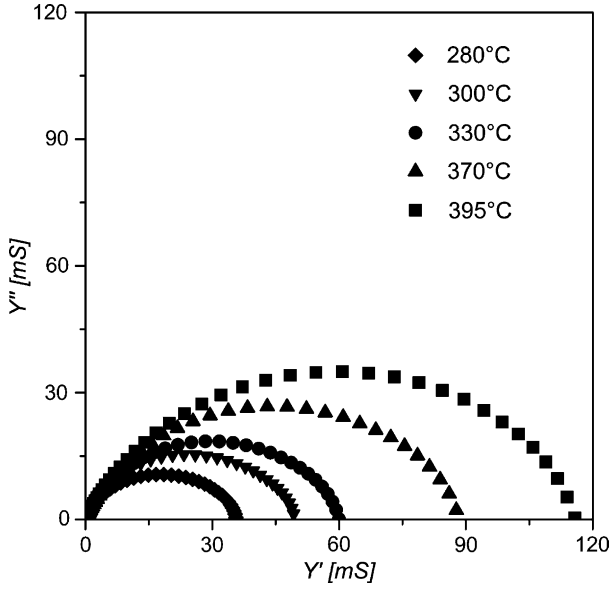

Fig. 3. Admittance plot for Lisicon sensor.

3. Results and discussion

The electrical conductivity of Lisicon was determined by means of the ac admittance spectroscopy. The Nyquist plots of admittance spectra are shown in Fig. 3. In the measured frequencies range well-resolved semicircular arc appears. This arc is attributed to the bulk properties of electrolyte. On basis of this plot the resistive component of total impedance was established[18] and used to derive the values of conductivity as the function of temperature. A typical Arrhenius plot for Lisicon electrolyte is illustrated in Fig. 4. The conductivity of prepared Lisicon is similar to reported previously.[17] The activation energy of 0.4 eV was resolved.

The sensing phenomenon of electrocatalytic sensor is based on formation and decomposition of gas sensitive layer

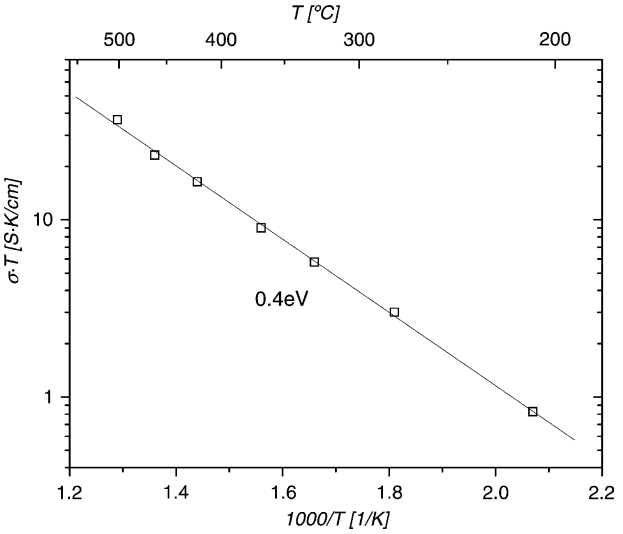

Fig. 4. Arrhenius plot of the electrical conductivity of the Lisicon electrolyte.

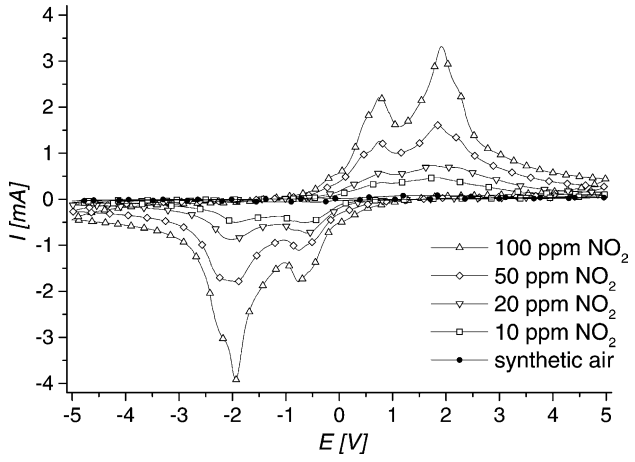

Fig. 5. Response of the sensor to different concentration of NO_2 (300 °C, 20 mV/s).

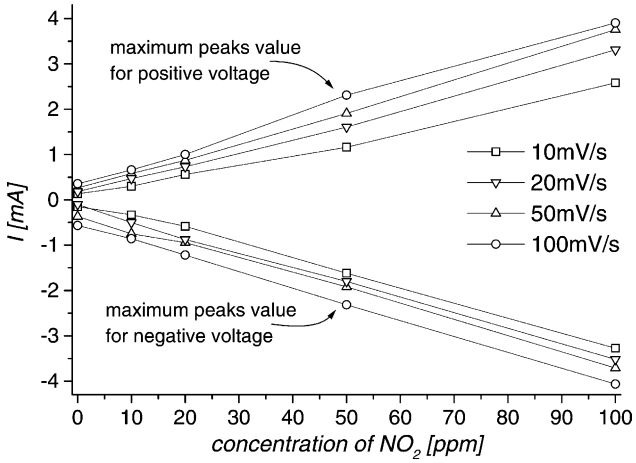

Fig. 6. Maximum current value of NO_2 peak (300 °C) as a function of concentration for different sweep rates.

and the reactivity of this layer with surrounding gas.[19] When a voltage ramp is applied to the sensor, the formation of the gas sensitive layer occurs at the negative electrode. At the other electrode, decomposition of the existing gas sensitive layer proceeds correspondingly. When the voltage is reversed, the formation and decomposition occur at the opposite electrodes. 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 those processes:

$$4Li^+ + 4e^- + O_2(g) \Leftrightarrow 2Li_2O(s) \quad (1)$$

$$2Li^+ + 2e^- + O_2(g) \Leftrightarrow Li_2O_2(s) \quad (2)$$

$$2Li^+ + 2e^- + CO_2(g) + \tfrac{1}{2}O_2(g) \Leftrightarrow Li_2CO_3(s) \quad (3)$$

$$Li^+ + e^- + NO_2(g) + \tfrac{1}{2}O_2(g) \Leftrightarrow LiNO_3(s) \quad (4)$$

$$2Li^+ + 2e^- + SO_2(g) + \tfrac{1}{2}O_2(g) \Leftrightarrow Li_2SO_3(s) \quad (5)$$

The current flowing through the sensor is the combination of the currents connected with different reactions occurring at the electrodes and current related with the charging of the double layer capacitance. Different gas sensitive layers have different kinetics of formation and decomposition. This may give an opportunity for simultaneous determination of different gases. Speed of chemical reaction is the fastest for the specific voltage, which is characteristic for given chemical reaction. This results in a rise of current. When applied voltage pasts the specific voltage, the speed of reaction decreases due to kinetic reasons like decreasing number of triple point boundary, limited diffusion of lithium ions in the sensitive layer, etc. As a result the peaks may be observed in the current–voltage response of the sensor.

Sensor current–voltage plot measured in synthetic air at 300 °C shows two relatively plane peaks—one for positive voltage near 0.7 V and other for negative near −0.7 V. While sensor is exposed to different concentration of nitrogen dioxide additional peaks appear near ±2 V on the current–voltage plot (Fig. 5). As shown in Fig. 6, a linear dependence of the

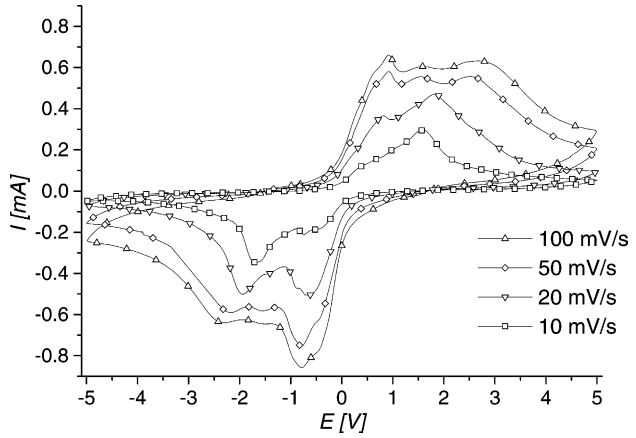

Fig. 7. Current–voltage plot for different voltage sweep rates (10 ppm NO_2, 300 °C).

maximum current of peak on NO_2 concentration is observed. The slopes of the curves of about 32 μA/ppm, which are almost sweep rate independent, are observed for both peaks. In Fig. 7 influence of the voltage sweep rate on shape of voltammograms is presented. At low scan rates, when non-faradaic current related to double layer capacitance is not significant, peaks are steeper and it is easier to distinguish both peaks. However, low scan rates increase time of measurements.

At higher temperatures, the sensor shows sulfur dioxide sensitivity, while nitrogen dioxide sensitivity is significantly decreased. The current–voltage plots of the sensor exposed to sulfur dioxide at 525 °C are presented in Fig. 8. The presence of sulfur dioxide causes appearance of peaks on current voltage plot. In 10 ppm of SO_2, two additional peaks appear at ±1.75 V. The peaks observed in synthetic air (near ±0.7 V) tend to disappear with higher sulfur dioxide concentration, and for 100 ppm only one pair of very steep current peaks is observed.

Based on the presented results it can be concluded that Lisicon solid electrolyte can be used in the development of electrocatalytic sensor. The sensor at 300 and 525 °C shows

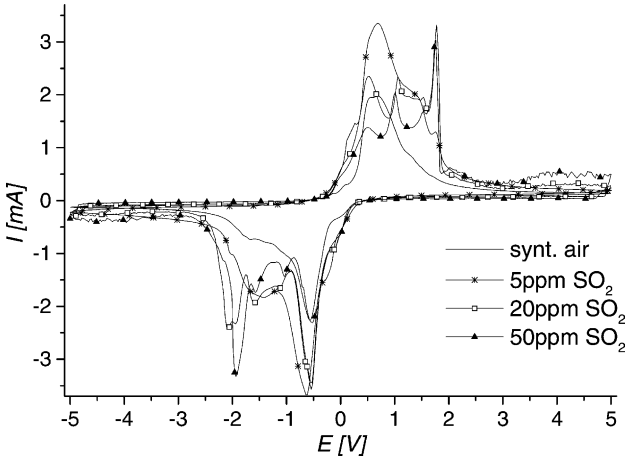

Fig. 8. Response of the sensor to different concentration of SO_2 (525 °C, 50 mV/s).

sensitivity to nitrogen dioxide and sulfur dioxide, respectively. However, constant exposure of the sensor to toxic gases for extended amount of time causes decrease of its performance. This aging effect can be explained by high stability of formed sensitive layer. The sensitive layer, which cannot be fully decomposed, influences further sensor operation. Development of highly catalytic sensor electrodes may help solving this problem.

4. Conclusions

In this paper construction of the electrocatalytic gas sensor based on Lisicon solid electrolyte and gold electrodes has been evaluated. Sensor was used for determining nitrogen dioxide and sulfur dioxide presence in air. The current–voltage plot of the sensor at 300 and at 525 °C shows peaks resulted from NO_2 and SO_2 presence, respectively. Maximum of the current peak can be used as the measure of gas concentration.

Acknowledgements

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