

Kinetic Studies of Nasicon Based Sensors with Cyclic Voltammetry

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Usually one kind of gas is measured by conventional solid state electrochemical gas sensors. We report here results on a simple electrochemical sensor which makes possible the simultaneous detection of several different gases. Kinetic studies of thick film Nasicon sensors with platinum electrodes exposed to sulfur dioxide and nitrogen dioxide are presented.

1. Introduction

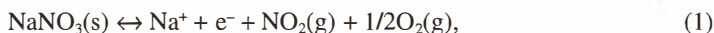
Among sensors employing solid-state electrolytes, the most common devices are based on potentiometric and amperometric principles in which the measured response is a voltage or a current, respectively. This allows measurement of one gaseous species by an individual single electrochemical sensor.⁽¹⁾ In addition, although these sensors are quite specific compared to devices based on other principles, there exist cross-sensitivities under certain circumstances. This means that the presence of other gases may influence the performance of the sensor.^(2,3) In view of these difficulties, a new type of sensor based on the kinetics of chemical reactions has been proposed and is now under development to detect different gases simultaneously.^(4,5) The basic principle is the dynamic measurement in current response when variations of the voltage are applied to a solid ionic conductor.

The response provides a unique pattern for different gases, and in this way it may be possible to detect several gases using a single electrochemical cell. Similar technologies are now being employed by other groups.⁽⁶⁾ The data extraction technique is based on neural networks in this case, however.

In this paper, a simple Nasicon sensor with platinum electrodes is presented and its response to sulfur dioxide and nitrogen dioxide using cyclic voltammetry is described.

2. Fundamental Aspects

The sensor consists of a Nasicon electrolyte sandwiched between two metal electrodes. The sensing phenomenon is based on the growth and decomposition of the gas-sensitive layer and the reactivity of this layer with the surrounding gas. When a voltage ramp is applied to the sensor, the formation of the gas-sensitive layer occurs at the side of the negative polarity of the voltage. At the other electrode, which is positive, decomposition of the existing gas-sensitive layer proceeds correspondingly. When the voltage is reversed, the formation and decomposition occur at the opposite electrodes. The overall chemical reaction is the formation and decomposition of the sodium nitrate layer in the case of nitrogen dioxide in an environment which contains oxygen:



where 'g' and 's' indicate the gas and the solid phase, respectively. The current passed through the sensor is the sum of the currents carried by the formation and decomposition of the NaNO_3 layer at the two electrodes. Different gas-sensitive layers have different kinetics of formation and decomposition. This may give us an opportunity for the simultaneous determination of different gases.

Figure 1 illustrates the sensing mechanism of the sensor. The figure shows the more realistic situation when, in addition to NaNO_3 , NaNO_2 , Na_2O_2 and Na_2O layers are formed and decomposed simultaneously.

3. Experimental Description

We have employed solid sodium ion conductors in this work. Both gold and platinum electrodes were used. The response was more reproducible with platinum electrodes.⁽⁷⁾ According to our previous experience, the sandwich-type configuration of the electrodes was also adopted for this study.

The sensors were prepared by thick film technology using sodium ion conducting Nasicon ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, $x = 1.8$) as a solid state electrolyte. The Nasicon paste consists of Nasicon powder prepared by the conventional solid-state ball milling method⁽⁸⁾ and the organic vehicle of terpeneol, ethyl cellulose and butylcarbinol.

First, planar platinum electrodes were printed onto an alumina substrate, as shown in Fig. 2. Then, the Nasicon paste was printed on top of these electrodes. Finally, the comb-type pattern of platinum electrodes was printed onto the Nasicon layer. The Nasicon film is porous and its thickness is about 80 μm . A platinum heater is printed on the back of the

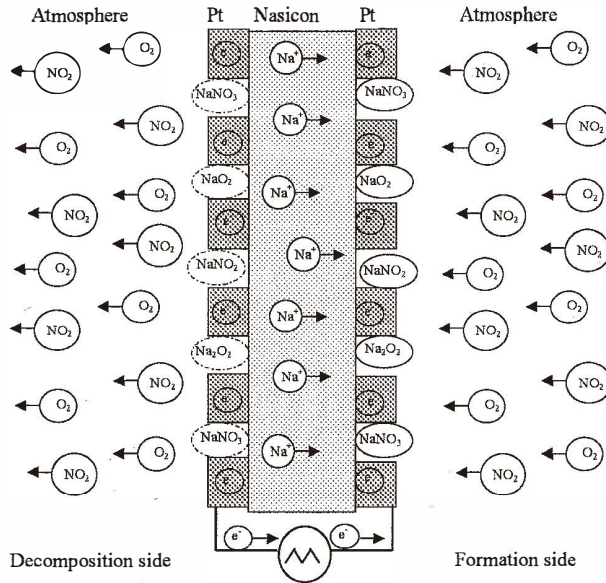


Fig. 1. Schematic representation of the sensing mechanism.

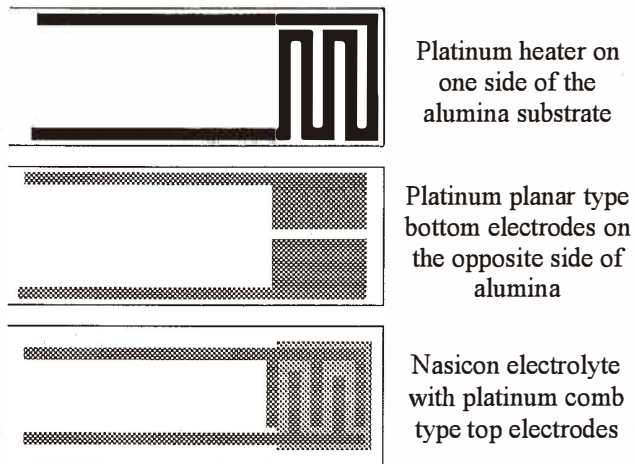


Fig. 2. Structure of the sensor.

substrate. Details of the sensor technology can be found in a previous paper.⁽⁹⁾

A semi-automatic system for sensor monitoring consists of the sensor element, a temperature controller, the potentiostat SOLARTRON SI1287, TYLAN mass flow controllers and reference gases. The measurements were performed using mixtures of dry synthetic air, sulfur dioxide and nitrogen dioxide. The voltage was applied between the top and the bottom electrodes and the current response of the sensor was measured. The sign of the voltage refers to the bottom electrode. The current peak observed at an applied positive voltage is called a "positive" peak. Results are shown for a scan rate of 10 mV/s in the cyclic voltammetric measurements, unless otherwise stated.

4. Results

Figure 3 represents the current-voltage plots of the sensor exposed to 100 ppm nitrogen dioxide at different temperatures. The peak height increases with increasing temperature up to about 230°C. Further increase in the temperature to 264°C lowers the height of the peak drastically. The position of the peak is thereby shifted from 2.25 V at 127°C to 0.75 V at 264°C.

Figure 4 shows the results of the current-voltage curves of the sensor when only synthetic air was used and also when synthetic air with 100 ppm NO₂ was applied. In contrast to lower temperatures, at more than 264°C the current during the voltage sweep is lower in the presence of 100 ppm NO₂ in synthetic air than in synthetic air alone. The voltammogram reveals two positive and two negative peaks at voltages of about 0.5 and 1.7 V.

Figure 5 shows the voltammogram of the sensor exposed to a mixture of nitrogen dioxide and synthetic air at 230°C. The positive and negative peaks appear nearly at the same absolute value of the voltage, i.e., about 1.5 V. The height of the peaks depends

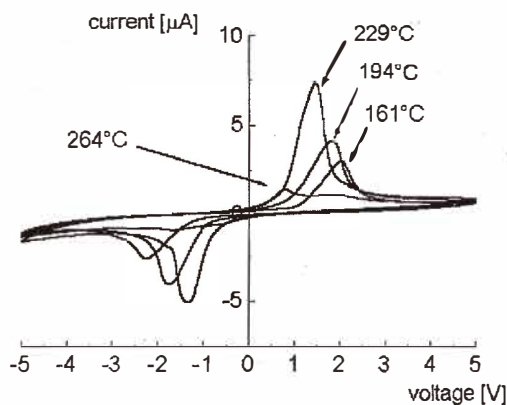


Fig. 3. Temperature dependence of the current - voltage relationship of the sensor exposed to 100 ppm NO₂.

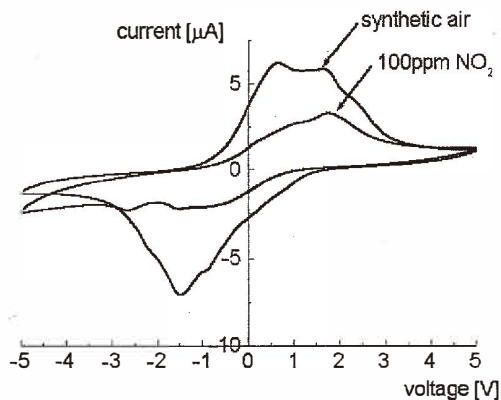


Fig. 4. Response of the sensor to synthetic air and synthetic air +100 ppm NO_2 at 298°C.

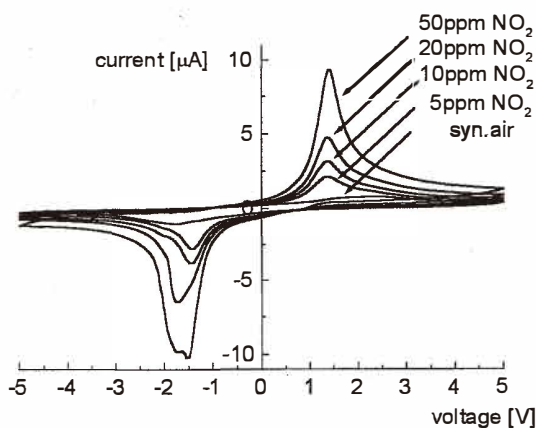


Fig. 5. Response of the sensor to different concentrations of nitrogen dioxide in synthetic air at 230°C.

monotonically on the nitrogen dioxide concentration (Fig. 6).

If the sensor is exposed to sulfur dioxide, a sodium sulfate layer forms and decomposes. The question arises whether the positions of the peaks related to the decomposition and formation of sodium nitrate and sodium sulfate are sufficiently different in the current-voltage plot so that the sensor may be used for the simultaneous detection of nitrogen dioxide and sulfur dioxide.

Figure 7 shows the response of the sensor exposed to 100 ppm NO_2 , 100 ppm SO_2 and the absence of these gases in synthetic air at 230°C. The positions of the positive peaks

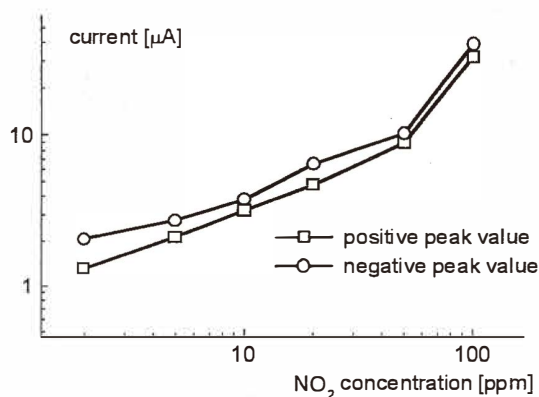


Fig. 6. Height of the peak as a function of the nitrogen dioxide concentration at 230°C.

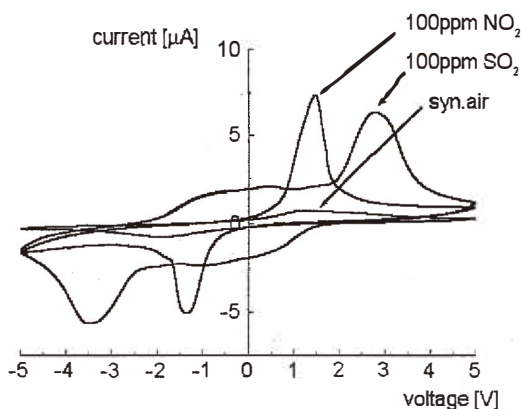


Fig. 7. Response of the sensor exposed to 100 ppm NO₂, 100 ppm SO₂ and in synthetic air alone at 230°C.

related to decomposition and formation of the sodium nitrate and sodium sulfate layers occur at 1.5 and 3V, respectively. The separation of the negative peaks is even larger, i.e., from about -1.3 to -3.5V.

The response of the sensor exposed to a mixture of both NO₂ and SO₂ in synthetic air at 230°C is shown in Fig. 8. This reveals one major peak at about 2.5 V; however, with a small peak indicated by a shoulder at about -1 and 1.5 V for negative and positive, respectively.

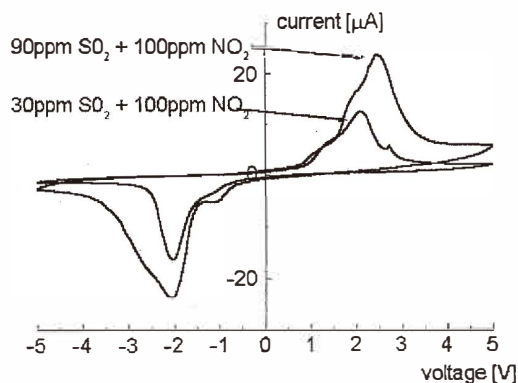


Fig. 8. Response of the sensor to a mixture of nitrogen dioxide and sulfur dioxide in synthetic air at 230°C.

5. Discussion

The increase in the current with the increase in temperature up to 230°C (Fig. 3) is caused by enhanced electrochemical reactions. The strong decrease in the current above 230°C cannot be explained by the thermal decomposition of the sodium nitrate layer, since that only occurs at 307°C.⁽¹⁰⁾ However, a thermodynamically less stable layer of NaNO₂ and a eutectic mixture with NaNO₃ might have been formed and decomposed. The melting point of such a mixture of NaNO₃ and NaNO₂ may be as low as 226°C and may be higher depending on the molar ratio.⁽¹¹⁾ In addition, there may be a small error in the sensor temperature measurement caused by an incorrect determination of the sensor temperature. This was calculated using the a calibration obtained from experiments based on the melting points of some selected salts deposited on the alumina substrate. In our case the calibration was performed without the Nasicon electrolyte. However, the error caused by this difference should not be bigger than a few degrees Celsius.

Comparing the peak position with the equilibrium voltage expected from the Gibbs energies of formation of NaNO₃ and NaNO₂ (Fig. 9), it might be possible to determine which reaction, formation of NaNO₃ or NaNO₂, does occur. The equilibrium voltage was calculated using thermodynamic data⁽¹²⁾ assuming that the counter electrode is not being charged. This is, however, not the case, and a larger slope is expected which is in agreement with the experimental results. The results indicate that the activity of the second electrode is simultaneously changing in view of the high porosity of the electrolyte.

The peaks visible in the response of the sensor exposed to pure synthetic air (Fig. 4) are probably related to the formation and decomposition of a sodium oxide and/or a sodium peroxide layer. The current of the sensor exposed to 100 ppm NO₂ in synthetic air should be at least as large as the one observed for pure synthetic air. This result needs further clarification.

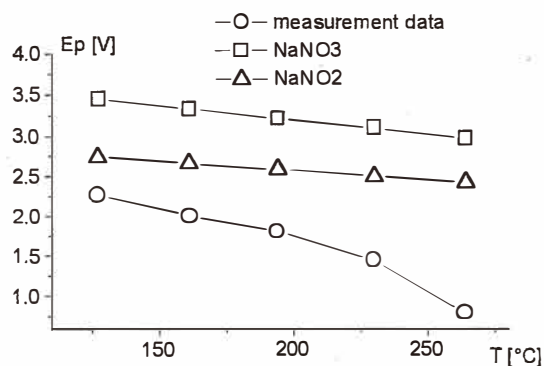


Fig.9. Equilibrium voltage values from the Gibbs energies of NaNO_3 and NaNO_2 and measured data as a function of temperature.

It is possible to relate the nitrogen dioxide concentration (Fig. 5) to the charge passed through the electrolyte for the formation and decomposition of the layers (Fig. 10). This charge is calculated from the area underneath the peak. It must be emphasized that the electrodes are not expected to behave in the same way. The top one is completely open to the atmosphere, whereas the gas must diffuse through the Nasicon layer to reach the bottom electrode. The Nasicon electrolyte is porous due to the thick film technology used and it may act like a diffusion barrier. However, this is not evident from the plots. With diffusion taking part in the reaction it is expected that the peak flattens out. Since that does not occur, the effect may be explained by a faster diffusion process than the kinetics of the electrode process.

Assuming that the areas of the electrodes are about 1 cm^2 and the charge related to the formation and decomposition at 50 ppm NO_2 is about 1 mC (see Fig. 10), it is possible to evaluate the change of thickness of the sodium nitrate layer to be ten monolayers.

At 230°C , the positive and negative peaks related to 100 ppm of nitrogen dioxide and 100 ppm of sulfur dioxide are well separated (Fig. 7). However, the response of the sensor to a mixture of SO_2 and NO_2 (Fig. 8) reveals only a minor separation. The position of the major peak is in the middle between the peaks of SO_2 and NO_2 alone and is shifted to lower values of voltage with decreasing SO_2 concentration. This information may be used for the simultaneous detection of SO_2 and NO_2 . It is an indication that it may be possible to detect concentrations of different gases at the same time with the same galvanic cell. Our research is focused on developing improved cell operation parameters for a more clear separation of the influences of the two gases.

6. Conclusion

The Nasicon sensor with platinum electrodes exposed to sulfur dioxide and nitrogen dioxide reveals characteristic peaks in the current-voltage curves. At a temperature of 230°C the peaks are well separated. Although the response of the sensor exposed to a

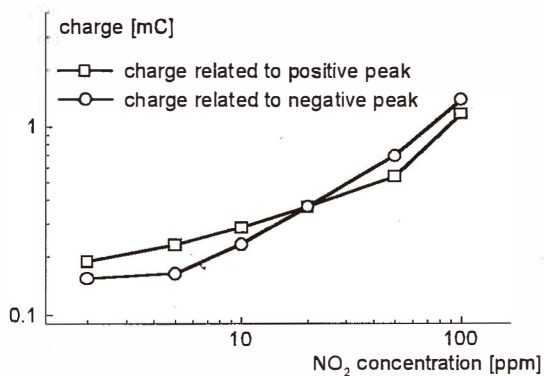


Fig. 10. Charge related to the formation and decomposition of the peaks (Fig. 5) as a function of NO₂ concentration at 230°C.

mixture of these gases reveals basically only one peak, it may be possible to detect both gases by applying pattern recognition techniques. It should be underlined that cyclic voltammetry is not the only technique for the simultaneous detection and distinction of several different gases. Another possible measurement technique may be the application of specific values of voltage excitations to a sensor and the measurement of charges related to each voltage. The specific values of voltage excitations may be selected on the basis of the knowledge obtained from cyclic voltammetry experiments.

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