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Staircase voltammetry application to electrocatalytic gas sensor

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Abstract

Principle of operation of electrocatalytic gas sensors is based on the excitation of a sensor with a periodic potential signal, while current response is recorded. Usually such sensors employ cyclic voltammetry, where linearly changing voltage excitation of symmetrical triangular shape, typically in range of ±5 V, is used. In this work we present results of electrocatalytic sensors employing staircase cyclic voltammetry technique. Presented results concern sensors based on Nasicon with platinum electrodes. It is demonstrated that such sensor can be used for measuring NO_2 concentration in mixtures with synthetic air.

Keywords: voltammetry; gas sensor; Nasicon;

1. Introduction

Cyclic voltammetry (CV) is a method widely used in liquid electrochemistry for determination of chemical species concentration. The method is based on oxidation and reduction of chemical species on electrodes polarised using linearly changeable voltage. Electrochemical reactions produce peaks on current-voltage plots, which is dependent on the concentration of chemical species. In the case of the electrocatalytic gas sensors, instead of liquid solution the solid state electrolyte is used as ion conducting medium. As in the case of liquids the electric current is measured, while voltage excitation of certain shape is applied to the sensor. Current-voltage (I-V) response shape depends in on the gas type and its concentration. Usually current peaks are observed in the current-voltage sensor response plot. Such a response contains significantly more information comparing with other sensors. Sometimes position of the

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peak can be related to the type of gas, while the peak height can be related to the concentration of this gas. This feature can be used for improvement of selectivity or multigas sensing [1].

During voltammetric experiment, the electric current flowing through the sensors electrodes has two components: the capacitive current and the faradic current. Only the latter corresponds to the useful information from reduction or oxidation of a chemical species. The capacitive current acts non-specific background interference [2]. In CV the current at a working electrode is measured, while the potential is swept linearly in time. Application of staircase cyclic voltammetry (STCV), where the potential sweep is a series of stair steps, may increase sensor sensitivity. In STCV the current is measured at the end of each potential change, so that the contribution to the current signal from the capacitive charging current is reduced. As a result, electrocatalytic sensors properties can be enhanced.

In this work, performance of electrocatalytic sensors employing STCV technique is compared with properties of 'standard' electrocatalytic sensor, which uses CV. Presented results concern sensors based on Nasicon. It is demonstrated that such sensor can be used in NO_2 concentration determination in synthetic air.

2. Experimental

NASICON (chemical formula $Na_{2.8}Zr_2Si_{1.8}P_{1.2}O_{12}$) powder was prepared by the conventional solid-state ball milling method. Pellets in the form of discs of 12 mm diameter and 1 mm thick were prepared by iso-axial pressing and sintering. Electrodes were made by coating opposite pellet faces with the platinum paste (ESL 5542). Measurements were conducted in mixtures of high purity gases: nitrogen dioxide and synthetic air of controlled concentrations. The precision mass flow controllers were used for obtaining gas mixtures composition. A constant gas flow of 100 sccm was maintained. Sensor was placed in a tube furnace. More detailed description of NASICON preparation procedure, sensor construction and measuring stand can be found in our earlier publications [3].

The measurements were performed using the electrochemical interface SI 1287 and a PC computer with suitable software for system control and data acquisition (CorrWare, Scribner Associates, Inc.). STCV technique is not supported by SI 1287. Staircase voltammetry was obtained by measuring a set of potentiostatic experiments. Controlling of potentiostatic experiment voltage and duration allowed obtaining desired staircase voltage excitation and measuring current response. Both voltage excitations used in experiments are presented in Fig. 1 left. For each temperature and gas mixture two measurements, CV and STCV, were conducted. In Fig. 1 right I-V response obtained at 200°C with both methods is compared. Characteristic for STCV seems to have more preferable shape, current peak is more distinct and higher, while measured currents for remaining part of curve are smaller.

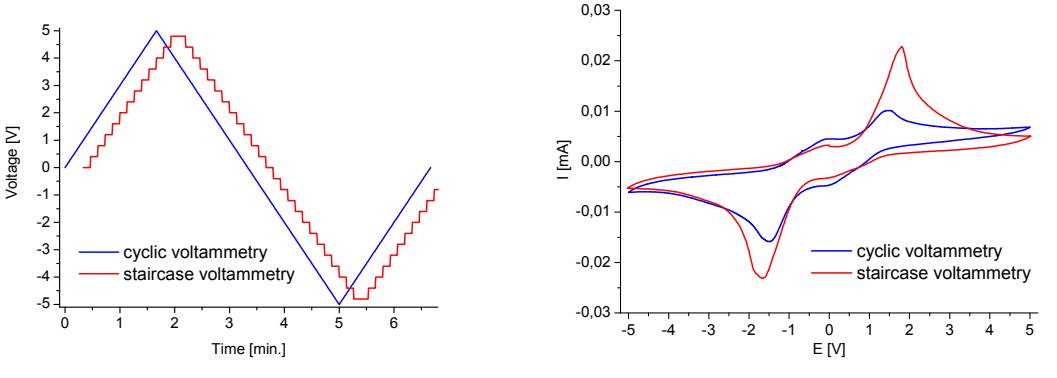

Fig. 1. (left) comparison of excitation signal of CV & STCV; (right) comparison of CV & STCV I-V response (synth. air, 20mV/s)

3. Results

Typical sensor response using CV and STCV to different nitrogen dioxide concentrations at 250°C is presented in Fig. 2. This temperature was chosen based on our earlier experience. Our previous reports proved that at this temperature high sensitivity for NO_2 and rapid, stable sensor response can be obtained [4]. In both cases two double symmetrical peaks near ±0.3 V and ±1.5 V are visible. With the increase of NO_2 concentration in the surrounding atmosphere the size of both peaks increases. Peaks for STCV are more distinct and steeper, but for CV and high nitrogen dioxide concentration measured currents are higher.

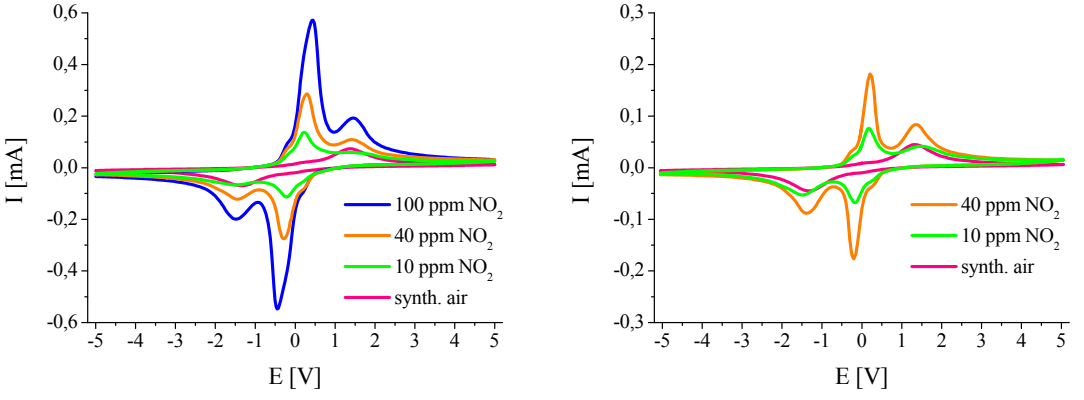

Fig. 2. Electrocatalytic sensors response (50mV/s) to different NO_2 concentrations (left) employing CV; (right) employing STCV

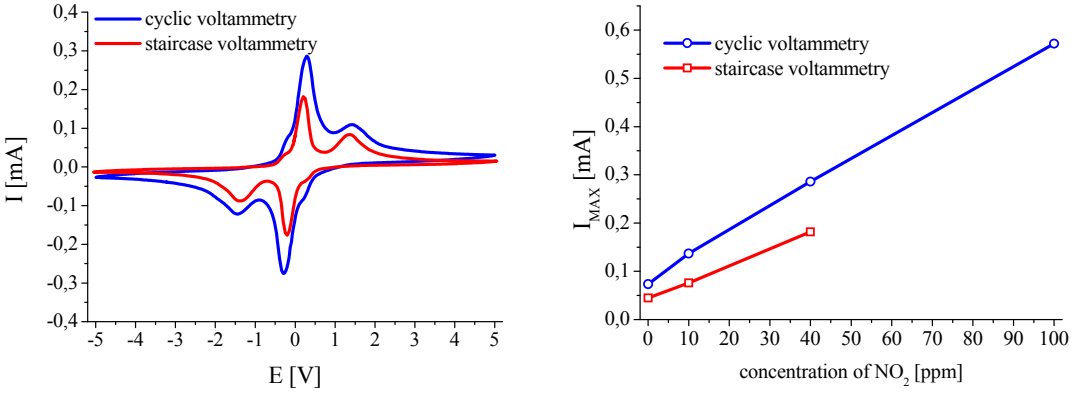

Fig. 3. (left) Comparison I-V responses (40 ppm NO_2, 50mV/s); (right) the current peak maximums

Direct comparison of plots for 40 ppm of NO_2 is presented in Fig. 3 left. In contrast to measurements obtained in synthetic air the peaks obtained in CV are higher than in STCV. Still, the peaks obtained in STCV are steeper than in CV. For the part of curve not directly related with nitrogen dioxide peak, namely for voltages from 2.5 V to 5 V, the measured currents in STCV are much lower. This proves that STCV technique helps reducing undesired capacitive current contribution.

The electrocatalytic gas sensor response in the form of current-voltage dependence does not give the possibility to obtain direct information about the concentration of gas in the vicinity of the sensors. A

maximum current at peak can be used as a measure of gas concentration. The maximum current as a function of carbon dioxide concentration, obtained for all measured and discussed earlier sensor responses, are presented in Fig. 3 right. In all cases almost linear dependence is observed. Unfortunately, sensitivity, which can is related to slope of presented curves, is higher for CV method.

4. Conclusions

The results of electrocatalytic gas sensors employing sodium ion conducting solid electrolyte (Nasicon) investigation were presented. Two techniques, namely standard cyclic voltammetry and staircase cyclic voltammetry, applied in electrocatalytic gas sensor were compared. It is demonstrated that all investigated types of the sensor excitations can be used for the detection of NO_2 concentration in synthetic air. The current-voltage response depends in a unique way on the type of gas and its concentration exposed to the sensor. The obtained results should be treated as preliminary. The STCV method allows easier peak separation than CV, what is more suitable for multigas measurements. In this case a few peaks are present in I-V plot and a peak position can be related to gas type. Application of the STCV method allows selecting desirable stair size. Therefore, this method it gives additional freedom in electrocatalytic sensor excitation optimization.

Acknowledgements

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