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Ionic Liquid Based Polymer Electrolytes for NO_2 Electrochemical Sensors

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Amperometric NO_2 sensors with a new type of printed solid polymer electrolyte and printed carbon working electrodes were developed. The electrolytes consisted of the ionic liquids 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [EMIM][N(Tf)$_2$], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF_3SO_3], and 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4], which were immobilized in a poly(vinylidene fluoride) (PVDF) matrix. The analyte, gaseous nitrogen dioxide, was detected by reduction at – 500 mV vs. the platinum pseudoreference electrode. The sensors showed linear behavior over the whole tested range, i.e., 0 – 5 ppm, and their sensitivities were in the order of hundreds of nanoamperes per one ppm of NO_2. The sensor sensitivity was influenced by the electrical conductance of the electrolyte; the higher the conductance, the greater the sensor sensitivity. The rise/recovery times were of the order of tens of seconds. The use of screen printing technology for the preparation of the solid electrolyte and the carbon working electrode simplifies sensor fabrication without a negative effect on sensor performance.

Keywords: nitrogen dioxide, electrochemical sensor, ionic liquid, electrochemistry.

1. INTRODUCTION

Many procedures in the industrial and ecological fields require fast, cheap and reliable gas sensors. As nitrogen dioxide is a toxic and environmentally unfriendly gas produced by humans in excess, it is necessary to detect and monitor it. One of the ways to manufacture cheap and reliable sensors sensitive to nitrogen dioxide is to use organic materials as the sensing media in chemiresistive sensors. However, these types of sensors are usually not stable over long periods of time (see e.g. [1] and references therein). Short exposures in the order of tens of seconds or units of minutes are usually described in the vast majority of published studies [2 – 7]. In recent times, some attempts have been made to prepare electrochemical NO_2 sensors [2 – 4]. A special group of these sensors are those containing ionic liquids in the electrolyte [8]. These sensors exhibit good stability over longer time periods as well as detection reproducibility.

The generally accepted overall reaction of NO_2 reduction at the working electrode is [5, 7, 9, 10].

$$NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O\,. \tag{1}$$

However, according to [5], two-step reduction with the formation of nitrite during the first step is more probable

$$NO_2 + e^- \rightarrow NO_2^-, \tag{2}$$

$$NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O\,. \tag{3}$$

The reaction mechanism may be quite complicated and depends on many factors, such as the structure of the electrolyte and the properties of the electrode materials.

Most probably, water is oxidized at the counter electrode

$$H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2\,; \tag{4}$$

and the complete reaction in the sensor can be written as

$$NO_2 \rightarrow NO + \frac{1}{2}O_2\,. \tag{5}$$

In this paper we present the results of a study concerning the influence of the electrical conductivity of the electrolyte on sensor sensitivity.

2. EXPERIMENTAL DETAILS

2.1. Preparation of sensors

The platinum counter electrode (3 in Fig. 1), Pt pseudoreference electrode (2 in Fig. 1), and Pt contact of the working electrode (1 in Fig. 1) were prepared by “lift-off” technology on an alumina ceramic substrate ($9 \times 7 \times 1$ mm^3). A polymer electrolyte (4 in Fig. 1) consisting of ionic liquid, poly(vinylidene fluoride) (PVDF), 1-methyl-2-pyrrolidone (1 : 1 : 3 weight), and some additives necessary for the preparation of the printing formulation was applied by screen printing onto the surface of the alumina substrate over both the platinum counter and pseudoreference electrodes. Then, the sensor

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was dried for 24 h at 25 °C and 40 % RH. Thereafter, the carbon working electrode (5 in Fig. 1) was deposited on top of the other layers by means of screen printing (carbon/graphite ink, GWENT GROUP). Three ionic liquids were tested: 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide $[EMIM][N(Tf)_2]$, 1-butyl-3-methyl imidazolium trifluoro-methanesulfonate $[BMIM][CF_3SO_3]$, and 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM][BF_4]$.

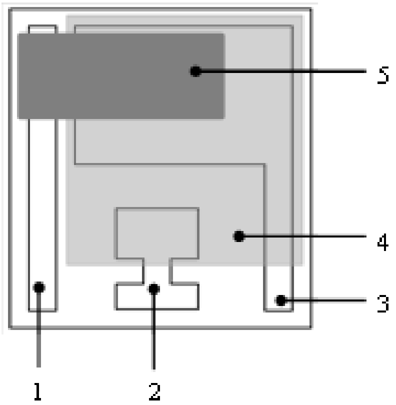


Fig. 1. Topology of sensors: 1 – Pt contact of the working electrode, 2 – Pt pseudoreference electrode, 3 – Pt counter electrode, 4 – solid polymer electrolyte, 5 – carbon working electrode

2.2. Apparatus for sensor testing

The testing apparatus for the measurement of electrochemical response during NO_2 exposure consisted of two gas tanks (one filled with a mixture of gaseous nitrogen dioxide and synthetic air at a concentration of 100 ppm, and the other one filled with pure synthetic air), three mass flow controllers, and a test chamber. The signal response was measured by the source-measure unit (KEITHLEY 2636). The required concentrations of the analyte (NO_2) were obtained by mixing the nitrogen dioxide mixture with humidified synthetic air. The analyte flow rate was 500 ml/min. The measurements were performed under laboratory conditions (25 °C, 40 % RH).

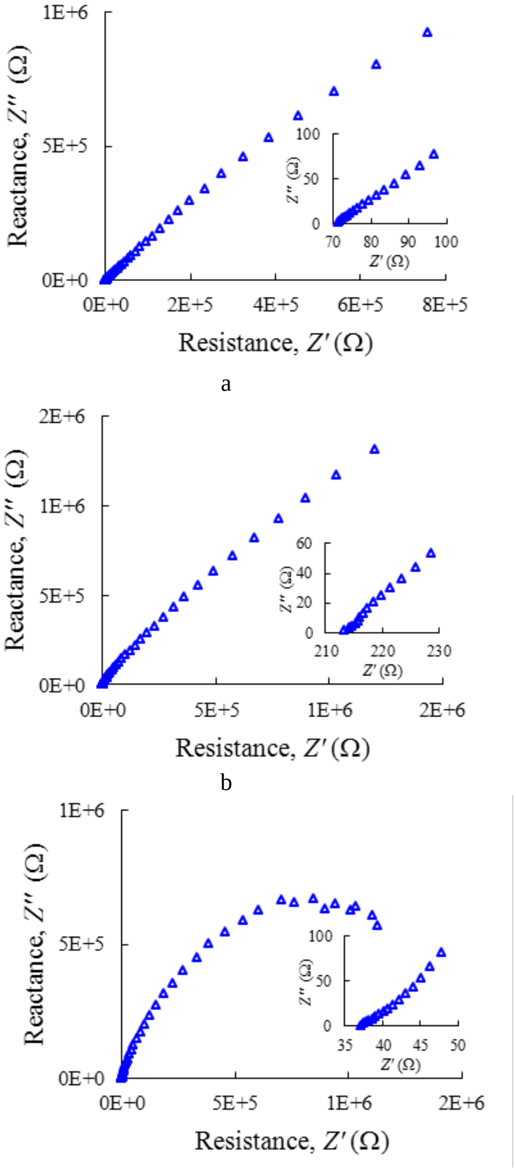
2.3. Impedance characteristics

The impedance characteristics of both the ionic liquids and the prepared sandwich sensors were determined using a PC controlled Solartron Analytical Impedance/Gain-Phase Analyzer (FRA, model 1260A) with dielectric interface (model 1296). From these, the AC conductances were determined for frequencies, where impedance phase shift was 0 (or close to 0). When phase shift is 0, imaginary part of impedance is also 0, therefore measured value of impedance is AC resistance of the sample [11]. The frequency dependence of impedance and impedance phase shift were measured using the following settings: frequency range from 1 MHz to 10 μHz; logarithmic sweep, 10 points per decade; AC modulation voltage of 200 mV; bias voltage of 0 V. The values of AC conductances were also determined independently by means of a Hioki 3511 HiTester.

3. RESULTS AND DISCUSSION

3.1. Ionic Liquids

The ionic liquids used in this study are shown in Fig 2. First, we characterized the ionic liquids by impedance spectroscopy. We used approximately 3 ml of ionic liquid. As electrodes, we used two parallel stainless steel plates 4 mm apart. The electrode area was 25 mm^2. The Nyquist plots, the dependences of the imaginary part of the impedance, *Z´´* (the "reactance"), on the real part of the impedance, *Z´* (the "resistance") of the respective ionic liquids are shown in Fig. 3. The resistances of the ionic liquids were determined from the intersections of the experimental dependences with the x-axis [11]. For greater accuracy the resistances were determined from detailed plots – see insets in Fig. 3.



a

b

c

Fig. 3. Nyquist plots for the tested ionic liquids: a – $[EMIM][N(Tf)_2]$; b – $[BMIM][CF_3SO_3]$; c – $[EMIM][BF_4]$. Insets: Details of the dependences of the imaginary part of the impedance, *Z´´*, on the real part of the impedance, *Z´*

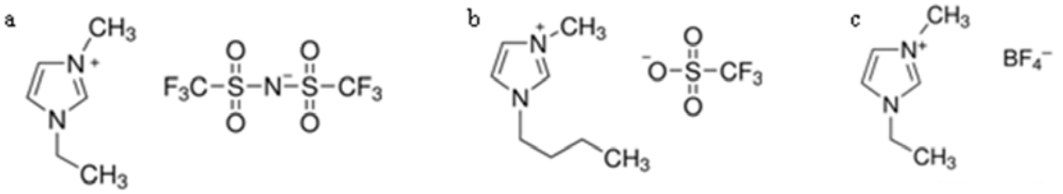


Fig. 2. Chemical structures of the ionic liquids used in this study: a – [EMIM][N(Tf)$_2$]; b – [BMIM][CF$_3$SO$_3$]; c – [EMIM][BF$_4$]

The AC resistances determined by the Solartron Analytical Impedance/Gain-Phase Analyzer together with the AC conductivities determined by the Hioki 3511 HiTester are presented in Table 1.

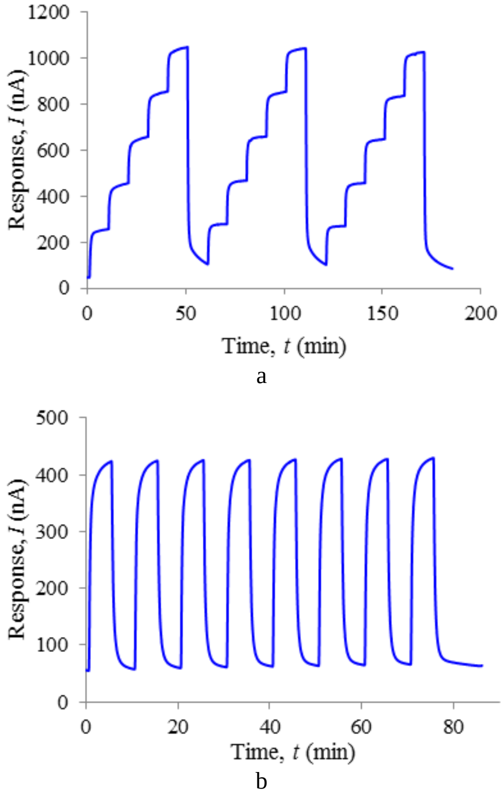
Table 1. Conductances of the ionic liquids under study

Ionic liquid	[EMIM] [N(Tf)$_2$]	[BMIM] [CF$_3$SO$_3$]	[EMIM] [BF$_4$]
AC Resistance * (Ω)	71	212	37
AC Conductance* (mS)	14.0	4.7	27.0
AC Conductivity** (mS/cm)	8.5	3.4	14.0

*Determined by the Solartron Analytical Impedance/Gain-Phase Analyzer.
**Determined by the Hioki 3511 HiTester.

3.2. NO$_2$ sensors

Fig. 4 a shows three consecutive kinetic sets of signal responses for the change in NO$_2$ concentration from 0 to 5 ppm in 1 ppm steps (the working potential was - 500 mV vs. the platinum pseudoreference electrode).



a

b

Fig. 4. Sensor with ionic liquid [EMIM][N(Tf)$_2$]:
a – dependence of reduction current (“response”) on time, the steps are for an NO$_2$ concentration change of 1 ppm;
b – kinetic curves for a 2 ppm concentration of NO$_2$

Note that the responses are fast and fully reproducible (see Fig. 4 b). The reproducibility is preserved even over long NO$_2$ exposures. The plots described above are for the ionic liquid [EMIM][N(Tf)$_2$]. Sensors incorporating the other tested ionic liquids behaved similarly.

From the data in Fig. 4 a, we determined average values of the current responses for each NO$_2$ concentration. The values were calculated using data from the saturation region of the current response for each NO$_2$ concentration. The value of the reduction current for a zero concentration of NO$_2$ was subtracted. These values were used for the creation of a calibration curve (dependence of the response on NO$_2$ concentration) – see Fig. 4. The sensitivity of the sensor with the ionic liquid [EMIM][N(Tf)2] was found to be 185 nA/ppm. The sensitivities of all sensors under study together with the respective values of the conductances of the electrolytes are summarized in Table 2.

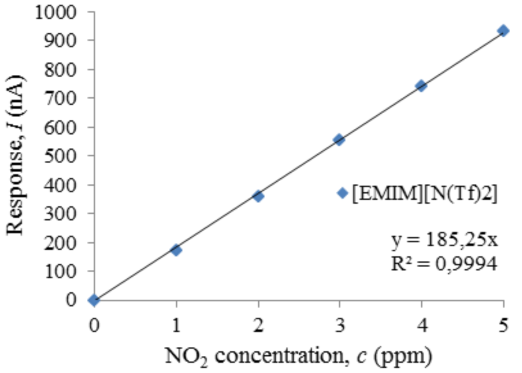


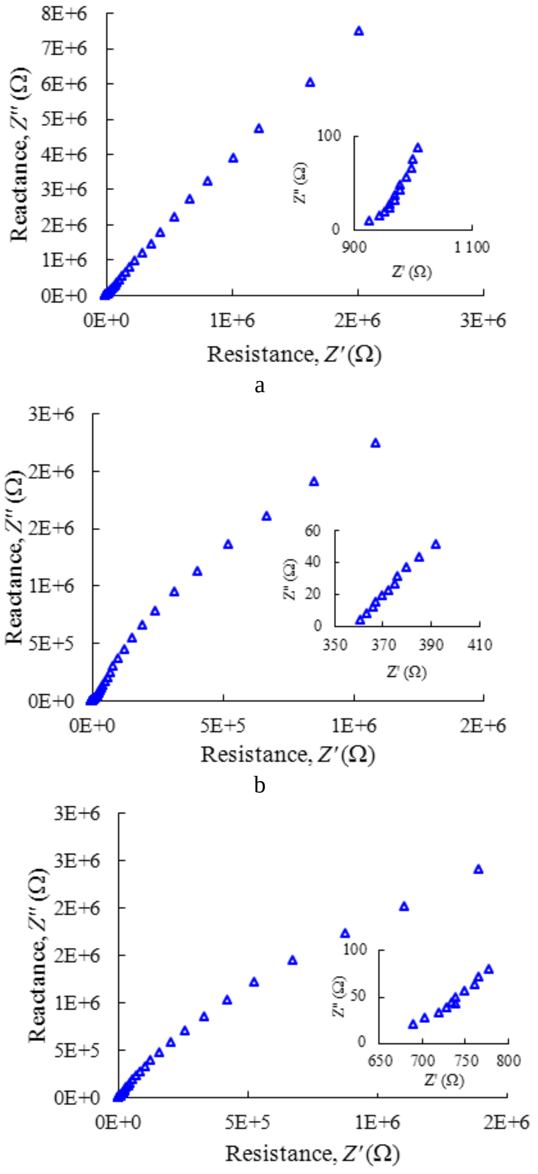
Fig. 5. Dependence of response (“reduction current”) on NO$_2$ concentration for the sensor with the ionic liquid [EMIM][N(Tf)$_2$]

Table 2. Sensitivities of sensors with various ionic liquids and the respective values of electrolyte conductances

Ionic liquid	[EMIM] [N(Tf)$_2$]	[BMIM] [CF$_3$SO$_3$]	[EMIM] [BF$_4$]
Sensitivity (nA/ppm)	185	302	286
AC Resistance * (Ω)	926	361	689
AC Conductance* (mS)	1.1	2.8	1.5

*Determined by the Solartron Analytical Impedance/Gain-Phase Analyzer.

The resistance values were obtained from the Nyquist plots (see Fig. 6) by same procedure as used in the case of ionic liquids (see Fig. 3). It follows from Table 2 that sensor sensitivity and electrolyte conductivity correlate: the higher the conductance of the electrolyte, the greater the sensor sensitivity. This is not true for the relationship between sensor sensitivity and the conductance of the ionic liquid (cf. Table 1 and Table 2). Thus, we can conclude that the morphology of the poly(vinylidene fluoride) with the ionic liquid additive plays an important role in electrolyte conductivity.



c

Fig. 6. Nyquist plots of electrolytes with different ionic liquids: a – [EMIM][N(Tf)$_2$]; b – [BMIM][CF$_3$SO$_3$]; c – [EMIM][BF$_4$]. Insets: Details of the dependences of the imaginary part of the impedance, Z´´, on the real part of the impedance, Z´

4. CONCLUSIONS

An electrochemical NO$_2$ sensor incorporating printed layers of a polymer electrolyte and a printed working electrode was developed. The polymer electrolyte consists of ionic liquid, poly(vinylidene fluoride), 1-methyl-2-pyrrolidone, and some additives necessary for the preparation of the printing formulation. The ionic liquids used were 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, and 1-ethyl-3-methylimidazolium tetrafluoroborate. The devices exhibit linear behaviour with respect to the dependence of sensor response on NO$_2$ concentration in the concentration range from 0 to 5 ppm as well as good response reproducibility. The rise/recovery time is in the order of tens of seconds. The sensor sensitivity is in the order of hundreds of nanoampers. The sensitivity depends on the electrical conductance of the electrolyte; the higher the conductance, the greater the sensor sensitivity.

Acknowledgments

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