EFFECT OF THE DIFFERENT CRYSTALLINITY OF IONIC LIQUID BASED SOLID POLYMER ELECTROLYTE ON THE PERFORMANCE OF AMPEROMETRIC GAS SENSOR

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## Motivation

- **Amperometric sensing principle**
  - measurement of the current flow produced by an oxidation-reduction reaction,
  - After voltage between WE and CE across electrolyte is applied, WE reacting with gas generates a current flow as a function of concentration.

- **Sensitivity connected to**
  - WE material
  - the morphology of the electrochemical active interface SPE/WE

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- Crystallinity of solid polymer electrolyte
- Performance of amperometric sensor
Sensors layout and fabrication

Fabrication steps:
- Preparation of platinum pseudo-reference electrode and the counter electrode on alumina substrate,
- SPE layer deposited by drop casting technique,
- Place substrate on a hot plate and kept the sample at an appropriate temperature for a specific time,
- And deposit working electrode by airbrushing of spherical glassy carbon powder.

Solid polymer electrolyte (SPE) consists of
(i) ionic liquid [BMPYR][N(Tf)2],
(ii) Polymer matrix poly(vinylidene fluoride),
(iii) solvent 1-methyl-2-pyrrolidone.

Experimental set-up

- **Noise measurement setup**
  - particular sensor – a part of potentiostat circuit,
  - battery as power sources,
  - $V_{RE} = 0.5\, V$,
  - sampling frequency 10 kHz and load resistance $RL = 1\, M\Omega$

- **Experimental setup**
  - PTFE testing chamber,
  - two gas tanks [AIR + 100 ppm NO2, AIR],
  - $T = 298\, \text{K}$, RH = 40%, analyte flow rate = 1 L/min.

SPE morphology

The surface of SPE consists of very small spherical SPE objects whose diameter increases with crystallization temperature, thus the lower value of this temperature results in higher porosity of prepared SPE.

diameters

- $<3.04 \pm 0.19> \mu m$
- $<3.64 \pm 0.37> \mu m$
- $<4.94 \pm 0.64> \mu m$

WE/SPE morphology

RESULTS and DISCUSSION

b) Glassy carbon WE

SPE

100μm

c) Glassy carbon WE

SPE

25μm

d) Glassy carbon WE

SPE

10μm
Sensor DC response

- The ionic conductivity of SPEs increases with increasing solvent evaporation temperature.

- As concentration increases, the DC component linearly increases for all orientations.

- The highest DC response corresponds to the SPE of the highest temperature and the longest interval of treatment after deposition.

Figure dependences of DC current on NO2 concentrations.

Current fluctuations

RESULTS and DISCUSSION

At zero concentration
- thermal noise,
- $f^{-1.25}$ noise component indicates diffusion-dominant electrode electrolyte interface,
- or $f^{-2.00}$ noise component indicates drift-dominant electrode electrolyte interface.

At higher NO$_2$ concentration
- noise component of Lorentzian-a-like spectra given by analyte flow around sensor,
- thermal noise,
- $f^{-2.00}$ noise component indicates drift-dominant electrode electrolyte interface.

**Figure** Spectral densities of current fluctuations depending on NO$_2$ concentrations with SPE prepared at conditions (a) 90°C 1.5 min, (d) 160°C 10min.
The sensor with the SPE of the highest temperature and the longest interval of treatment after deposition exhibits:

- the highest current fluctuations in the frequency range,
- the highest level of noise background level.

**Figure** Spectral densities of current fluctuations depending on NO$_2$ concentrations for the frequency range from 0.1 Hz up to 100 Hz for the sensors with SPE prepared at conditions (a) 90°C 1.5 min, (b) 120°C 1.5 min, (c) 120°C 3.5 min, (d) 160°C 10 min.
The limit of detection (LOD) is introduced as the ratio of the triple standard deviation of the background current noise (at zero concentration) and sensitivity (dc current pre ppm).

The sensor of the highest DC response (sensitivity) exhibit the worst LOD value.

Fig. Limit of detection for four sensors of different SPE processed by different treatment conditions.
Conclusions

- SPE of different crystallinity affects the performance of amperometric gas sensor from the point of view:
  - current response (sensitivity),
  - limit of detection,
  - and current fluctuations.

- The morphology of SPE has impact not only on its conductivity but also on sensor sensitivity due to morphology of the interface WE/SPE.
thank you for your attention

questions ??