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

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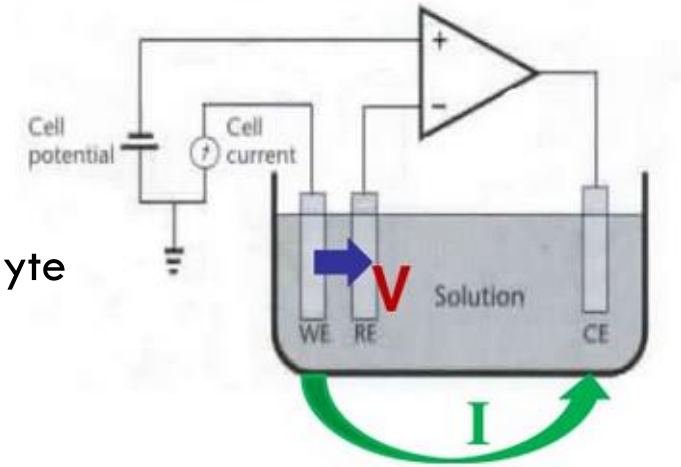
15 - 30 November 2020

7th International Electronic Conference on Sensors and Applications

ECSA-7

Motivation

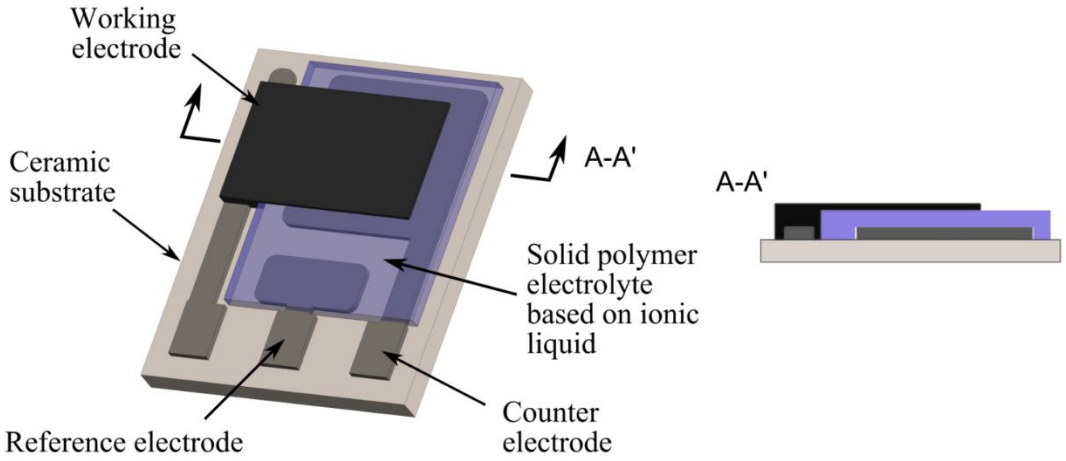
- Amperometric sensing principle
  - measurement of the current flow produced by an oxidation-reduction reaction,
  - After voltage between WE and CE across electrolyte is applied, WE reacting with gas generates a current flow as a function of concentration.



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

crystallinity of solid polymer electrolyte → ? → performance of amperometric sensor

Sensors layout and fabrication



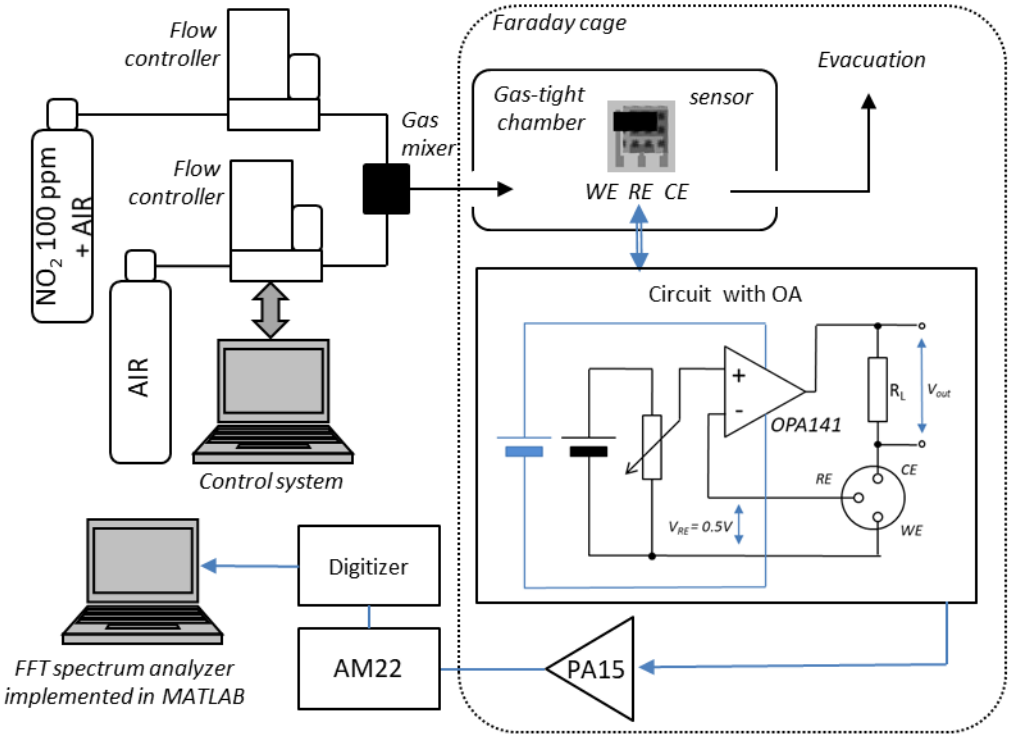
Solid polymer electrolyte (SPE) consists of
(i) ionic liquid [BMPYR][N(Tf)2],
(ii) Polymer matrix poly(vinylidene fluoride),
(iii) solvent 1-methyl-2-pyrrolidone.

- 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 sampe a at an appropriate temperature for a specific time,
  - and deposit working electrode by airbrushing of spherical glassy carbon powder.

Kuberský, P.; Syrový, T.; Hamáček, A.; Nešpůrek, S.; Syrová, L. Towards a fully printed electrochemical NO2 sensor on a flexible substrate using ionic liquid based polymer electrolyte. Sensors Actuators B Chem. **2015**, 209, 1084–1090

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 MΩ



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

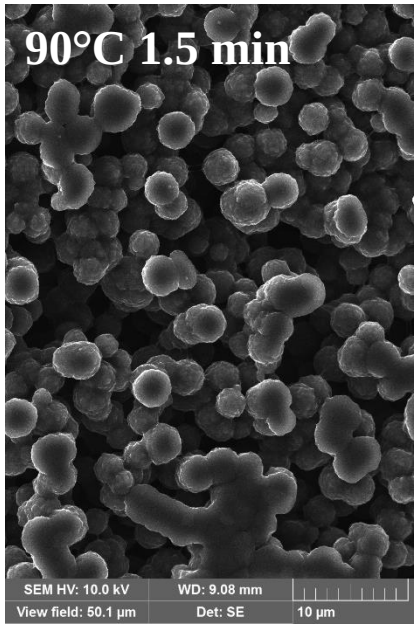
Sedlák, P.; Kuberský, P.; Mívalt, F. Effect of various flow rate on current fluctuations of amperometric gas sensors. *Sensors Actuators, B Chem.* **2019**, *283*, 321–328.
Sedlák, P.; Kuberský, P. The Effect of the Orientation Towards Analyte Flow on Electrochemical Sensor Performance and Current Fluctuations. *Sensors* **2020**, *20*, 1038.

SPE morphology

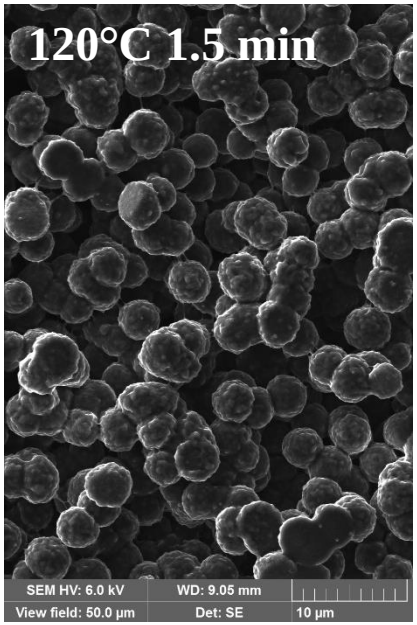
The surface of SPE consists of very small spherical SPE objects whose diameter increases with crystallization temperature, thus the lower value of this temperature results in higher porosity of prepared SPE.

diameters

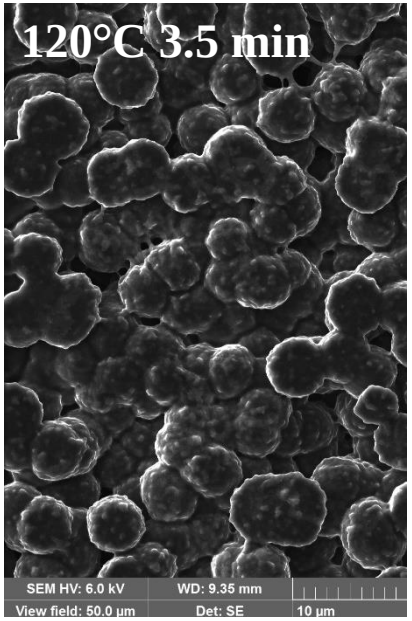
<3.04 ± 0.19> µm

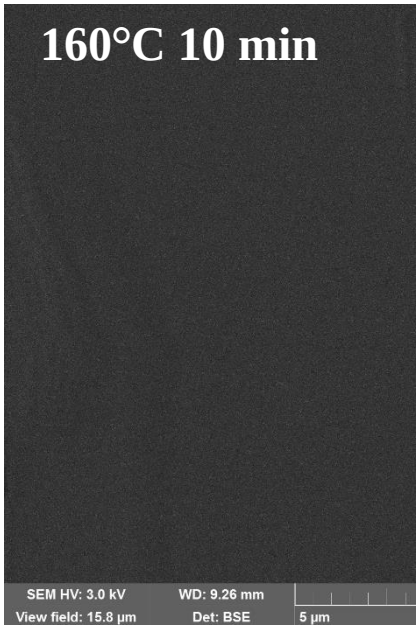


<3.64 ± 0.37> µm



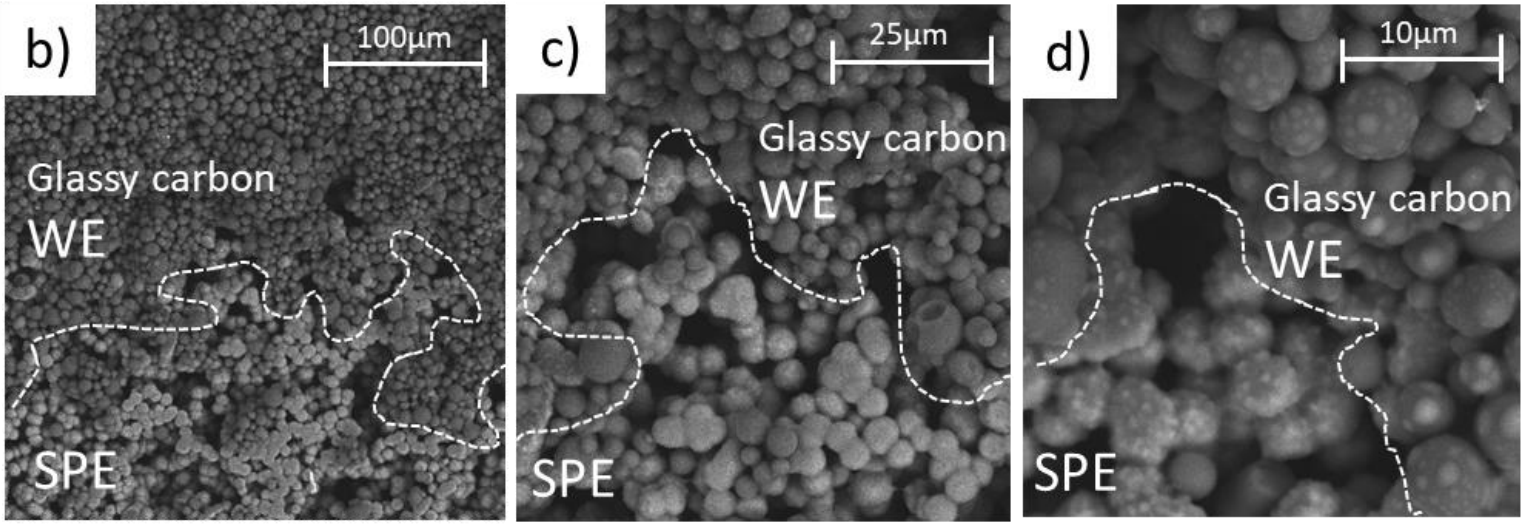
<4.94 ± 0.64> µm





Sedlak, P.; Gajdos, A.; Macku, R.; Majzner, J.; Sedlakova, V.; Holcman, V.; Kuberský, P. The effect of thermal treatment on ac/dc conductivity and current fluctuations of PVDF/NMP/ [EMIM][TFSI] solid polymer electrolyte. *Submitted to Scientific Reports*

WE/SPE morphology



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.

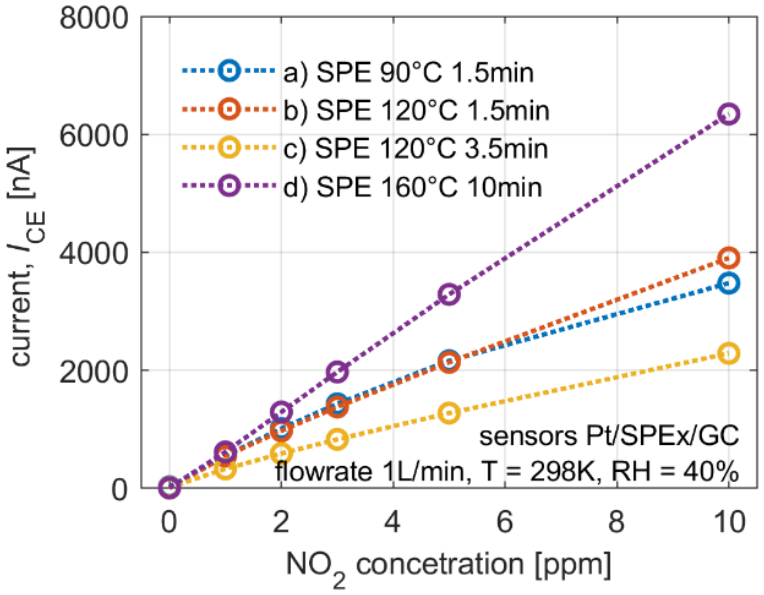


Figure dependences of DC current on NO2 concentrations .

Sedlak, P.; Gajdos, A.; Macku, R.; Majzner, J.; Sedlakova, V.; Holcman, V.; Kuberský, P. The effect of thermal treatment on ac/dc conductivity and current fluctuations of PVDF/NMP/ [EMIM][TFSI] solid polymer electrolyte. *Submitted to Scientific Reports*

Current fluctuations

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.

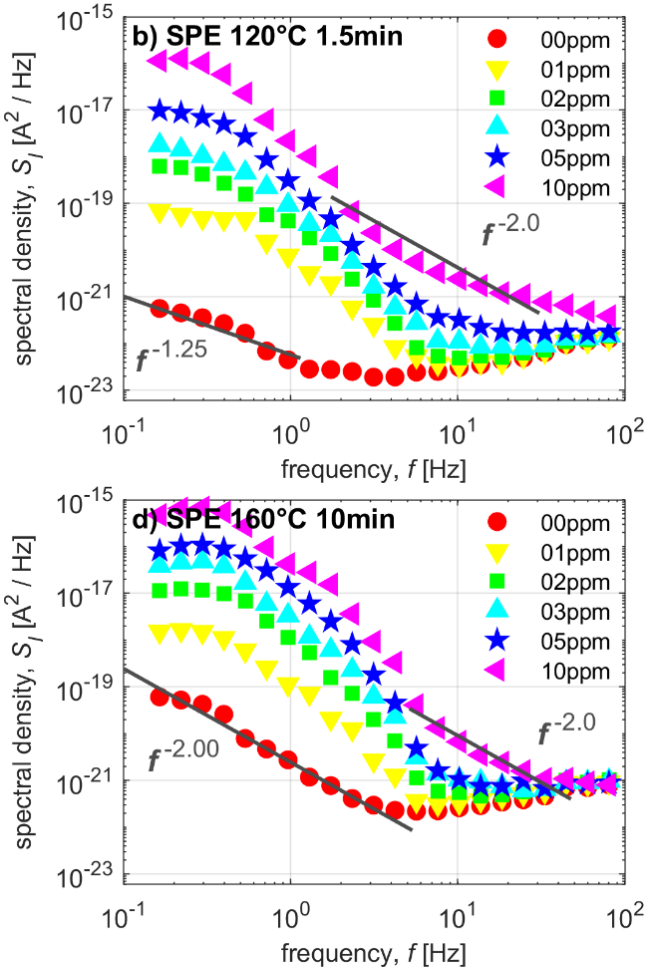


Figure Spectral densities of current fluctuations depending on NO_2 concentrations with SPE prepared at conditions (**a**) 90°C 1.5 min,, (**d**) 160°C 10min.

Results and discussion

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.

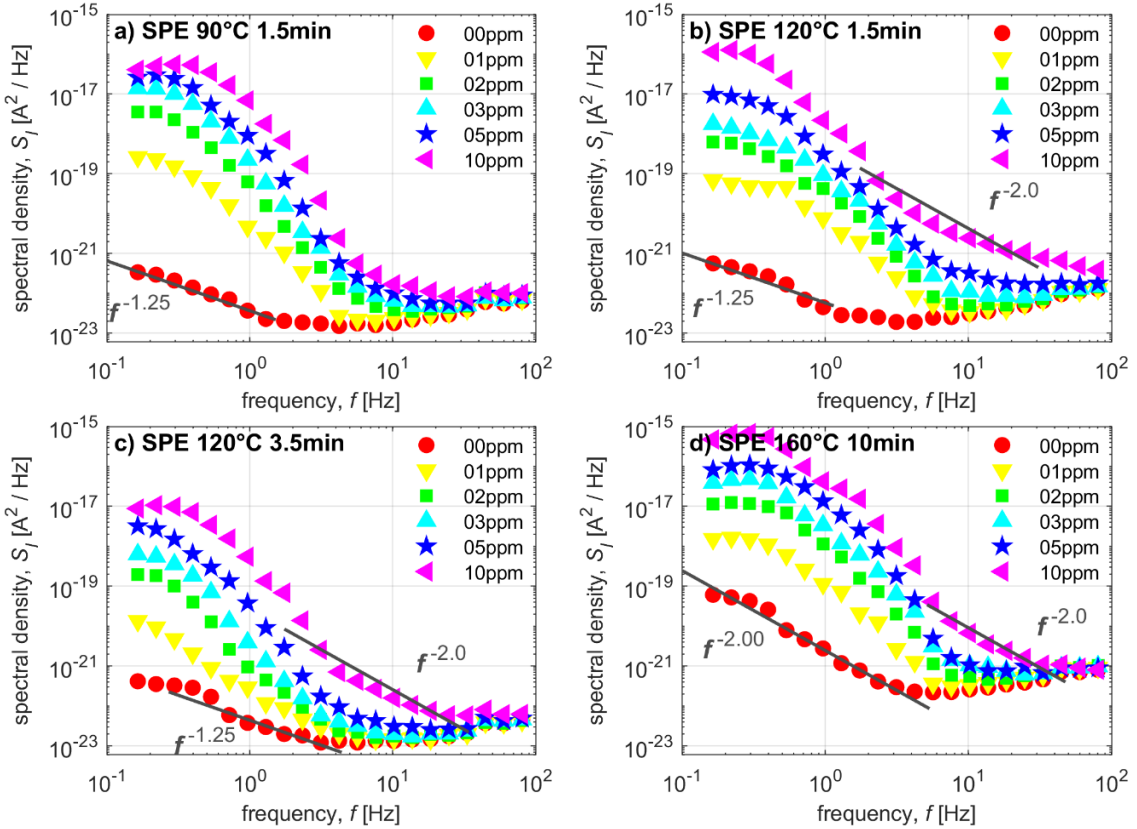


Figure Spectral densities of current fluctuations depending on NO_2 concentrations for the frequency range from 0.1 Hz up to 100 Hz for the sensors with SPE prepared at conditions (**a**) 90°C 1.5 min, (**b**) 120°C 1.5min, (**c**) 120°C 3.5 min, (**d**) 160°C 10min.

Limit of detection

- 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.

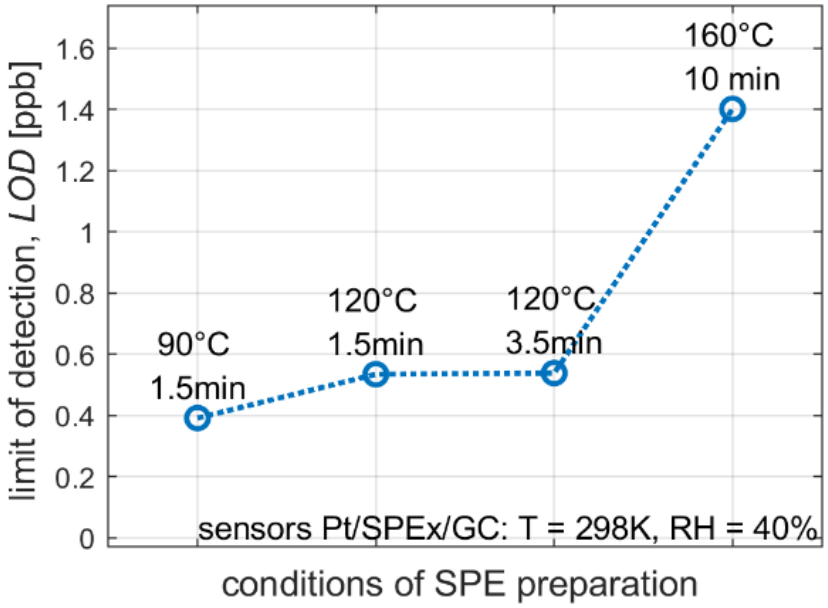
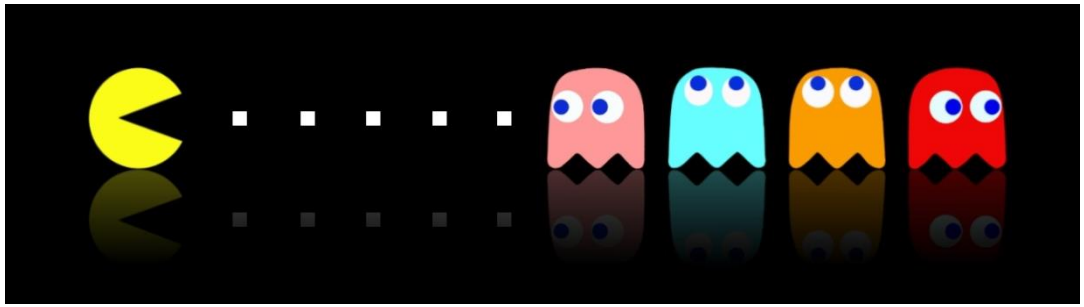


Fig. Limit of detection for four sensors of different SPE processed by different treatment conditions.

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 ??