# HYDROGEN GAS SENSORS AS TOOLS FOR EXPLOSIVE ATMOSPHERE SAFETY

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The importance of detecting hydrogen gas stems from its flammability and ability to explode in mixtures with air, at an extremely wide range of concentrations (flammability limit 4÷75% vol. hydrogen in air; explosive level 18.3÷59% vol. hydrogen in air) [1,2]. Hydrogen sensors are recently extensively studied for many significant applications in: safety systems, automotive industry, chemical processing, energetic industry and many others where $H_2$ is using as an fuel and product of the reaction. Numerous branches of technology include processes, in which hydrogen gas either evolves or is handled directly, such as: fabrication and operation of fuel cells, glass and steel manufacturing, refining of petroleum products, charging of lead batteries and atomic hydrogen / oxyhydrogen welding.

The high flammability and ability to explode of $H_2$ restrict many applications because both international and national regulations for dealing with possible explosive atmospheres require the monitoring of hydrogen concentrations in air at any relevant sites, in the case of an accidental hydrogen release [3-5]. At the same time, this precludes many types of $H_2$ sensing solutions, primarily due to the fact that $H_2$ sensors tend to operate at elevated temperatures, posing a risk as possible ignition sources. Consequently, it is crucial to achieve sensing methods which will operate properly at room temperature in a wide range of concentrations of $H_2$ [6].

$H_2$ monitoring is also very important in the case of oils used in energetic transformers, as well in hydrogen fuel-cells exportation level [7]. Thus, it is very important to develop sensors, which may measure $H_2$ concentrations in liquids and particularly in oils. Such sensors may replace currently used and very time- and cost-intensive methods like gas-chromatography.

The most important $H_2$ gas sensing methods like: metal-oxide based sensors, metal thin film transistors, pellistors are very effective and fast in determining $H_2$ gas concentrations in air, hoverer they all require high temperatures of operation (normally 200°C or more) [8]. In recent time many attempts of application of conducting polymers as gas receptor structures have been undertaken. The results available in the literature show that conducting polymers have a huge potential as novel room temperature gas sensing materials [9,10].

Polycarbazole (PCz) and its derivatives are well-known electroactive and photoluminescent polymers, finding application as active layers in organic photovoltaics [11,12], corrosion protection [13], anion [14] and gas sensors [15–17]. PCz shows good thermal and photochemical stability, high triplet energy and relatively high p-type conductivity [18,19]. Both carbazole (Cz) and PCz have been investigated as potential materials for the chemical storage of hydrogen [20–22]. This application stems from the fact that in the presence of a catalyst both the monomer and polymer can undergo reversible hydrogenation. Interestingly, despite such reports and the varied use of PCz-based $NH_3$ and $H_2S$ gas sensors, no attempts to utilise PCz or its derivatives as hydrogen sensing materials have heretofore been reported, with the exception of our last communication [23].

In this article, we have presented a proof of concept for room temperature hydrogen sensing using electropolymerised PCz on Pt electrodes (Fig. 1). The proposed configuration showed significant and fast decrease in the electrical conductivity of PCz films upon exposure to $H_2$ gas and fast reversibility of this response (Fig. 2).

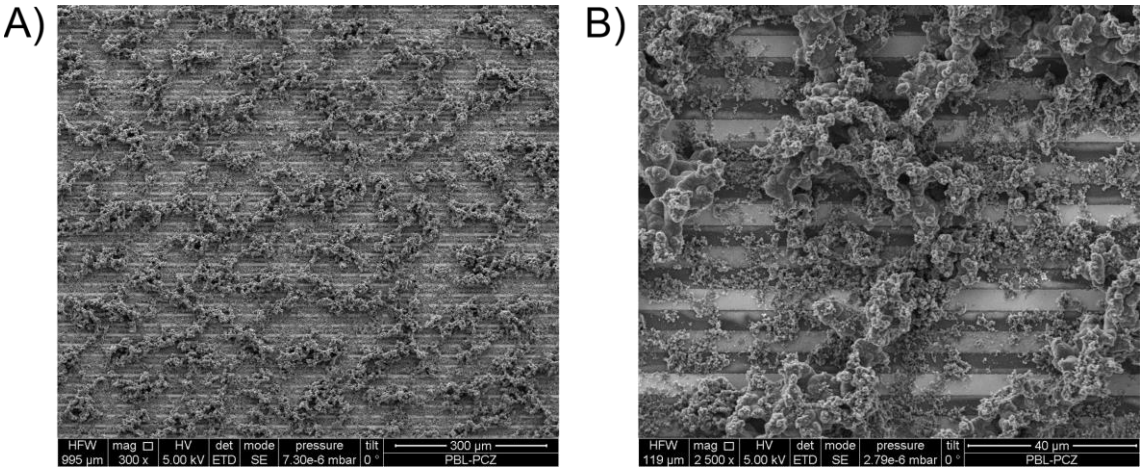


Figure 1 SEM images showing polycarbazole layer on the interdigitated electrode A) magnification 300 B) magnification 2500

As our proposition of sensing hydrogen gas using PCz is a scientific novelty, there is lack of any scientific works detailing this sensing mechanism. This is why deep basic research has to be conducted, in order to obtain knowledge about the nature of the physico-chemical interactions between PCz, $H_2$ and possibly, the transducer metal, acting as a catalyst of those interactions.

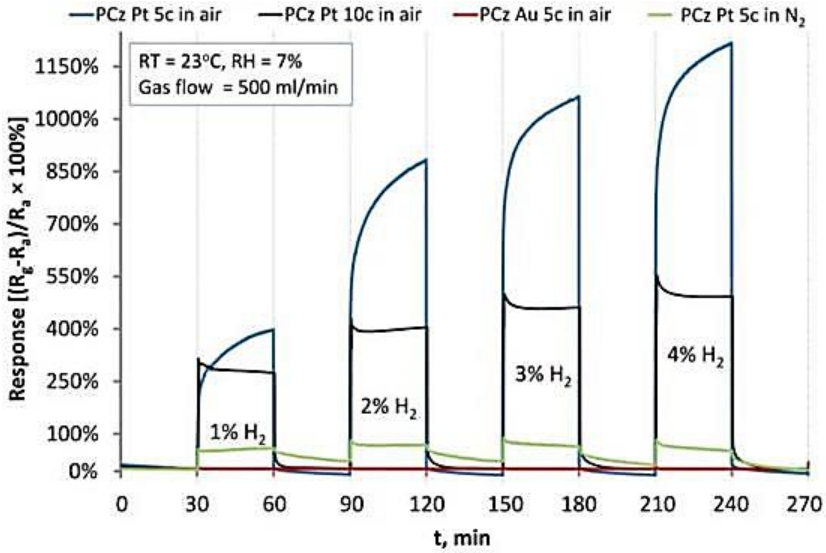


Figure 2 polycarbazole sensors on platinum (PCz Pt) and golden (PCz Au) electrode response to hydrogen gas.

We hypothesise that the sensing mechanism is a reversible hydrogenation of PCz in the presence of a catalytic metal. In contrast to typical conducting polymer active layers,

in which changes of physico-chemical properties take place via redox reactions generating and decomposing positive charge carriers (doping / dedoping), in our case we suspect the occurrence of conjugation breaks in the PCz chains, caused by the hydrogenation of double bonds forming the conjugated bond system (Fig. 3). Recovery of the sensor would rely on dehydrogenation of the film.

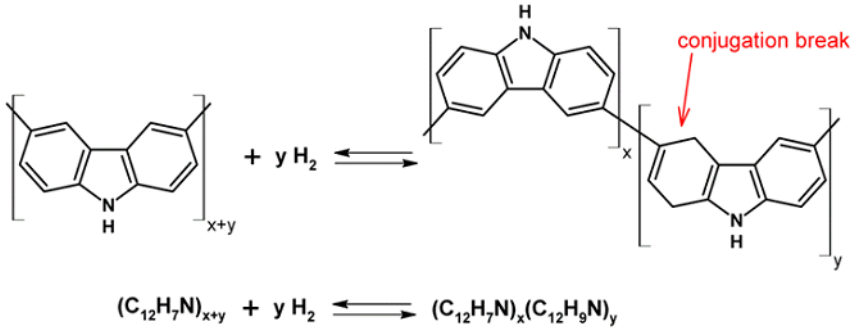


Figure 3 Possible mechanism of PCz-based sensor operation, based on our initial investigations and the reported properties of PCz

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3 Gaseous hydrogen land vehicle refuelling connection devices 2012, ISO 17268:2012

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