Use of Palladium-Modified Polyaniline Electrode as a Sensitive Element of Fire Sensor

Igor Ryshchenko[1,a], Larisa Lyashok[1,b], Alexey Vasilchenko[2,c*], Vitalii Asotskyi[2,d], Leonid Skatkov[3,e]

[1]National Technical University «Kharkiv Polytechnic Institute», 2, Kyrpychova str., 61002, Kharkiv,Ukraine

[2]National University of Civil Defence of Ukraine, 94, Chernishevska st., Kharkiv, Ukraine, 61023

[3]Ben Gurion University of Negev, 2/1220 Eliyahu ha-Navi Street, Beer Sheva, Israel, 8455006

[a]ryshchenko@kpi.kharkov.ua, [b]larisa.lashok1947@gmail.com, [c]avas2006@ukr.net, [d]asotskiy@nuczu.edu.ua, [e]leonid.skatkov1961@gmail.com

Abstract. Results of the development of a method for immobilizing nanosized palladium into an electrochemically synthesized polyaniline (PAn) electrically conductive porous matrix to create a sensitive element of an ignition sensor are presented. Two methods of manufacturing a sensitive element in the form of an electrode are investigated. The first method consists in the co-precipitation of polyaniline and palladium on a graphitized butyl rubber substrate in a mode of cycling of potential. It was shown that this method can be used to obtain a volume-porous electrode in which palladium nanoparticles are embedded in a polyaniline matrix. The second method involves the deposition of palladium on a polyaniline film formed on graphitized butyl rubber. It was shown that micron-sized island palladium conglomerates on the surface of a polyaniline film can be obtained by this method. The conclusions made are confirmed by physical research methods and the results of scanning electron microscopy. Investigations of the electrocatalytic properties of the electrode in the sensor model showed that with a change in the H_2 concentration formed upon ignition, occurs change in the hydrogen concentration on the surface of metal-catalyst (Pd) and a linear change in the current of electrochemical reaction. Comparison of a composite volume-porous polyaniline electrode with embedded palladium showed its superior efficiency compared to a compact palladium electrode and an electrode in which palladium is deposited on the surface of a polyaniline film. The possibility of using an electrochemical detector based on polyaniline with immobilized palladium nanoparticles for a gas amperometric sensor of low hydrogen concentrations and a fire hazard detector is shown.

1 Introduction

Existing fire detectors (light, heat, smoke) are able to register a fire as a fait accompli, since the operation of their sensors is based on physical principles such as light, heat or smoke detection. A much more effective way to prevent a fire could be to register events prior to a fire. This can only be done by establishing constant control over the gas-dynamic composition of the indoor air environment. Such control will make it possible to take adequate measures to prevent fire and its elimination in the first stage.

A reliable way to prevent fire at an early stage preceding a fire is to control the chemical composition of air, which changes dramatically due to thermal decomposition of overheated or smoldering combustible materials [1].

It is known that at the stage of smouldering during the pyrolysis of wood, paper, plastic and other hydrocarbon materials, hydrogen is released. Moreover, its concentration, even at a considerable distance from the ignition site, can reach 10-100 ppm (background hydrogen content in the air is about 0.5 ppm). Due to the high diffusion rate, hydrogen spreads very quickly even from enclosed

spaces. Thus, based on the detection of low concentrations of hydrogen, it is possible to create a sensor that can detect the threat of fire long before the open fire stage [1, 2, 3].

In industry, gas sensors are widely used to control technological parameters and control air quality, ensuring compliance with the process and increasing technological safety [4, 5, 6, 7].

From the literature data it is known that there are some complaints to many existing environmental analysis gas analysis tools (in particular, manufactured hydrogen detectors). To control the air environment or use as fire detectors, electrochemical, thermocatalytic and other sensors are either too expensive, or bulky, or do not have sufficient sensitivity [1, 2].

The cost of gas detectors was reduced with the introduction of fire detectors based on semiconductor chemical sensors. Currently, small-sized semiconductor sensors of two types have been developed, metal oxide (based on aluminum oxide) and structural (based on silicon MIS structures and Schottky diodes). They are able to determine the concentration of hydrogen in the air in the range from 0.001 % to units of percent and at the same time require an electric power of 150...500 mW. A feature of semiconductor chemical sensors is an action with a frequency of 6...10 s, associated with the need to heat the sensor to 120...500 °C [1, 2].

The products of such companies as Nemoto (Japan), Dynament, Alphasense, Sixth Sense (Great Britain), Membrapor (Sweden) are presented on the market. Nemoto is a leader in the manufacture of thermocatalytic and electrochemical sensors for the detection and determination of the concentration of combustible and toxic gases. However, they are inaccessible and expensive.

It is also possible to minimize the dimensions and reduce the cost of fire detectors through the use of electrochemical sensors, which are based on the interaction of hydrogen with a noble metal - palladium. It is known that a convenient method for the manufacture of a catalytically active electrode is the immobilization of palladium in a conductive polymer matrix [8, 9].

The optimal conditions when a metal is included in a matrix of a conductive polymer are created when palladium is in a highly dispersed state, and the polymer matrix provides good electronic and ionic conductivity. Due to its high porosity, hydrogen diffuses easily through it without interacting with it. At the same time, the consumption of the noble metal decreases sharply, and substrates made of base metals, glassy carbon and graphitized materials can be used as current taps. The advantage of such sensor is a linear dependence of the measured current on the hydrogen concentration and the possibility of working at normal temperature [8, 10].

2 Features of Obtaining a Polyaniline Electrode with Embedded Palladium Nanoparticles

It is known that the conditions of PAN-Pd system formation affect the distribution of metal particles in the polymer matrix and the electrochemical properties of the system [11, 12].

The aim of this work was to develop a method for immobilizing nanosized palladium into an electrochemically synthesized conducting porous polyaniline (PAN) matrix to use its catalytic properties in the detection of hydrogen.

Experimental studies were carried out on the basis of previously tested methods [13, 14, 15, 16].

The co-precipitation of palladium and aniline was carried out from a solution of 0.002 M $PdCl_2 + 0.1$ M $C_6H_5NH_2 + 1.0$ M H_2SO_4, by cycling the electrode potential from 0.1 V to 1.0 V. The coated sample was then washed in distilled water and 1.0 M H_2SO_4 solution. This procedure was repeated 3 times with the change of washing solutions. The resulting sample was dried in an oven and placed in a desiccator.

Catalytic activity of the synthesized composite PAN–Pd electrode was evaluated in a hydrogen oxidation reaction using measurements of potentiostatic polarization. The Kipp gas generator was used as a dispenser for the hydrogen-air mixture in the laboratory. The ionization of hydrogen was carried out in a three-electrode cell. As the working electrode used a composite electrode PAN–Pd. A lead mesh was used as the auxiliary electrode. The argentum chloride electrode was used as the reference electrode. The electrodes are separated by a proton electrolyte composition: polyvinyl alcohol (PVA) – boric acid – water in a mass ratio of 1:3:0.5. The activity of the PAN–Pd system was determined from the voltage dependence of the current. The ionization of hydrogen was performed in a potentiostatic mode at a potential of 0.5 V. To select the optimum saturation time of

the working electrode, the composite PAN–Pd electrodes were saturated with hydrogen for 10, 20, 30 min. The optimum palladium content was determined by varying the palladium content in the electrode at a constant time of hydrogen saturation.

In Fig. 1, the potentiodynamic dependences of obtaining a system graphitized butyl rubber–polyaniline + palladium (GBR–PAN+Pd) are presented. Cyclization of potential of the GBR electrode in a solution of $2 \cdot 10^{-3}$ M $PdCl_2$ + 0.1 M $C_6H_5NH_2$ + 1.0 M H_2SO_4 was carried out in the potential range of 0.0…1.0 V.
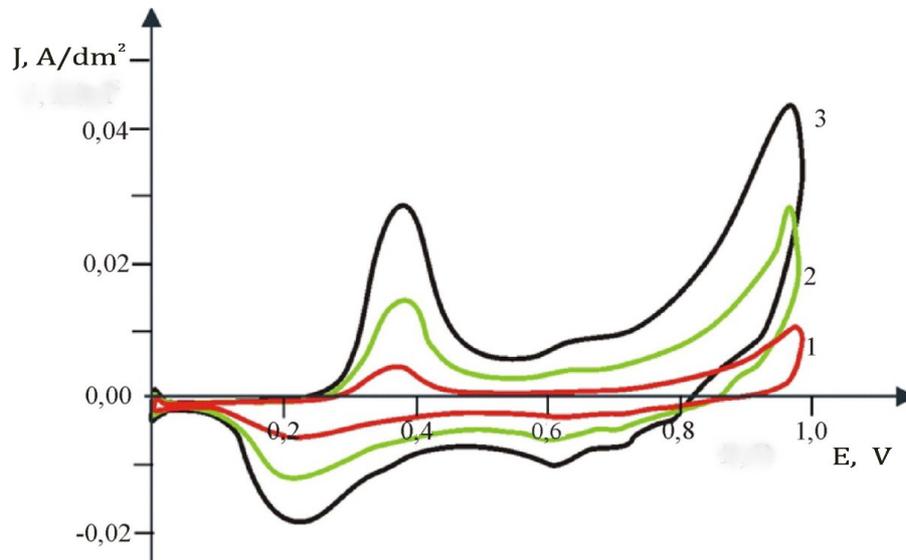
Fig. 1. Cyclic voltammograms of obtaining the system GBR–PAR+Pd in solution $2 \cdot 10^{-3}$ M $PdCl_2$ + 0.1 M $C_6H_5NH_2$ + 1.0 M H_2SO_4 during, min: 1 – 15; 2 – 30; 3 – 60

Composite electrode of GBR–PAN+Pd can be characterized by cyclic voltammograms (CVA), which shows that when the potential is deployed in the region of positive values, the PAN film grows, and when the potential reverses into the cathodic region, the salt in the volume of polymer is restored to a finely dispersed palladium (area between the peaks $E = 0.6…0.25$ V).

The CVA shows that there is a rapid advanced increase in anode current, which characterizes aniline oxidation, which increases from cycle to cycle. Recovery to metallic palladium occurs in the region of potentials from 0.6 to 0.25 V, and oxidation to Pd^{2+} at the reverse of the potential to the anode side – from 0.6 to 0.9 V. Such a large potential difference, from 0.2 to 0.6 V, indicates that the recovered Pd^0 is on the working electrode in the form of adsorbed clusters. It should be noted that in this potential range, from 0.3 to 0.6 V, the PAN is in an electrically conductive state (in the form of emeraldine), which indicates that the polymer matrix provides conditions for charge transport [17, 18].

The graph in Fig. 2 shows that by varying the conditions of electrodeposition, films with different content and thickness distribution of metal particles can be obtained.

Linear nature of the dependence means that the process can be easily adjusted and the results can be predicted in advance.

3 Features of Electrodeposition of Palladium on Polyaniline

Of particular interest is the study of electrochemical behavior of the PAN–Pd system obtained by palladium deposition on a polyaniline film previously synthesized on the electrode surface (graphitized butyl rubber) and comparison with the properties of GBR–PAN+Pd electrodes obtained by the method of potential cycling in mixed solution $PdCl_2$ + $C_6H_5NH_2$ + H_2SO_4.

Synthesis of the GBR–PAN,Pd system is dramatically different from the previous system. When palladium precipitates are formed in electrically conductive polymers, electrodeposition of the metal catalyst directly onto the polymer is possible.
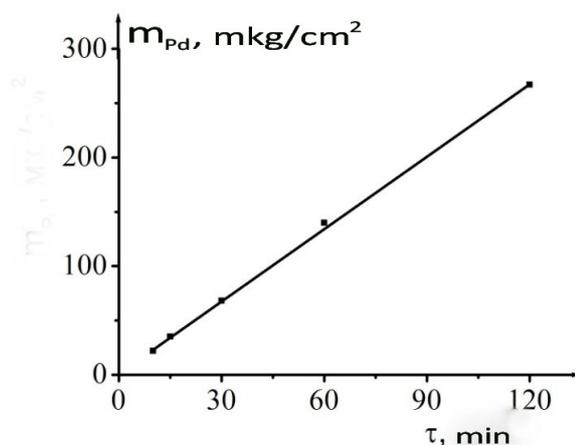
Fig. 2. Dependence of mass of the embedded Pd on time for the system GBR–PAN+Pd

For research, the PAN film was initially deposited on a substrate of graphitized butyl rubber by a previously worked out method [8, 13, 14]. Modification by palladium was carried out in a solution of $2 \cdot 10^{-3}$ M $PdCl_2$ + 1.0 M H_2SO_4 in the sequence:

1) in potentiodynamic mode by cycling the electrode potential from 0.1 to 1.0 V (Fig. 3);

2) in potentiostatic mode at potential of 0.1 V (moreover, electrode GBR–PAN pre-kept for about 3 min at 0.8 V in a sulfuric acid solution of palladium because no palladium deposition was observed at this potential value).
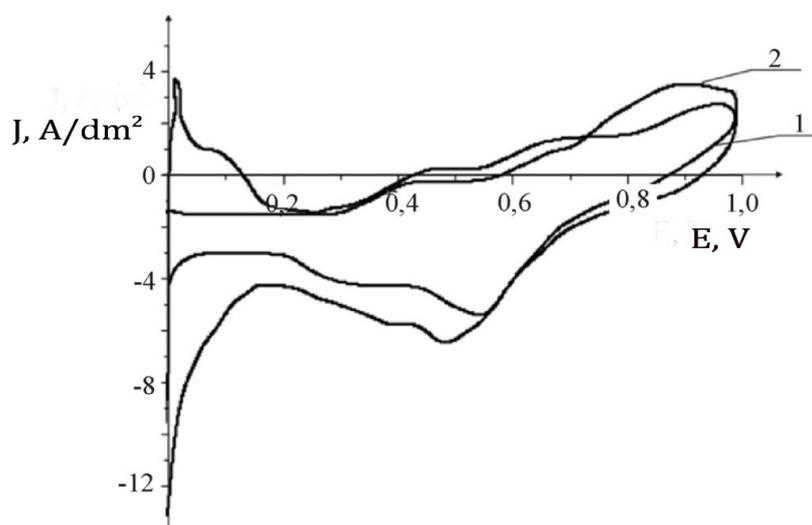
Fig. 3. Cyclic voltammograms of obtaining the system GBR–PAN,Pd in solution $2 \cdot 10^{-3}$ M $PdCl_2$ + 1.0 M H_2SO_4 during, min: 1 – 30; 2 – 60

In Fig. 3 shows that with increasing electrolysis time the height of the anode and cathode peaks increases, indicating an increase in the size and number of palladium crystals. This assumption is confirmed by the obtained images of scanning electron microscopy (SEM) of a PAN electrode surface with electrodeposited Pd particles for 30 and 60 min, as shown in Fig. 4. At $\tau = 30$ min, nanometer-sized metal particles are formed on the surface of the electrode. As the electrolysis time increases from 30 to 60 min, micrometer-sized conglomerates are formed on the surface.

a)   b)   c)
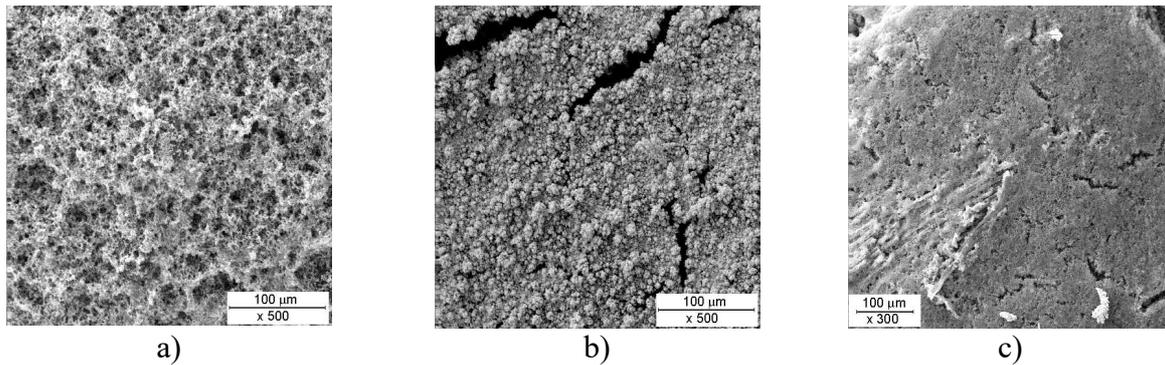
Fig. 4. SEM images of surfaces of GBR–PAN (a) and GBR–PAN,Pd (b, c) electrodes with palladium content ($\mu g \cdot cm^{-2}$ geometric surface): b – 100; c – 250. Thickness of the PAN film is 1500 nm

Previously, it was found that the deposition of metal directly on the polymer also occurs at the "non-conductivity" potential of the polymer. In [11], using atomic force microscope (AFM) palladium particles were detected on the surface of a rather thick polyaniline film at palladium deposition potential of 0.10 V, when the volume of deposited metal was more than an order of magnitude smaller than the pore volume. Palladium deposition after polyaniline dedoping is explained by the relatively small voltage drop in the thin (~500 nm) film. The SEM images of the surface of GBR–PAN,Pd electrodes (Fig. 4, b, c) with deposited palladium indicate, on the one hand, the globular structure of the electrochemically obtained films, and, on the other hand, the appearance on the surface micro-quantities additional smaller particles, even when electrodeposition of palladium (Fig. 4, b). As their number increases with increasing amount of deposited palladium (Fig. 4, c), it is safe to say that these are palladium particles. In the table 1 can be traced as the amount of palladium metal increases, depending on the deposition time.

Table 1. Characteristics of the system GBR–PAN,Pd

Deposition time, τ [min]	Dispersion of particles Pd, δ_{Pd} [nm]	Specific content of Pd on geometric surface, m_{Pd} [mkg$\cdot$cm^{-2}]
10	11.2	30
15	16.7	40
30	37.5	80
60	95.8	185
120	187.5	387

As the amount of precipitated Pd increases, the specific surface area of the precipitate decreases, which may be associated with a gradual decrease in the dispersion of the growing particles and some smoothing of the surface during growth. This phenomenon is due to a change in the features of the diffusion growth of the deposited palladium upon the transition from the hemispherical form to linear.

4 Electrocatalytic Properties of Pd Electrodes Modified with Pd

Studies of electrocatalytic properties of the GBR–PAN+Pd electrode (in which palladium nanoparticles are embedded in the volume of a polyaniline matrix) in the sensor model showed that a change in concentration H_2 results change of concentration of hydrogen on the surface of metal-catalyst (Pd). This process corresponds to a linear change in the current of electrochemical reaction in the range from 0.1 to 30 vol.% H_2. A linear dependence of the current is also traced by varying

the number of catalyst metal nanoparticles in the electrode volume, as shown in Fig. 5. These results are consistent with the results of the work [19].
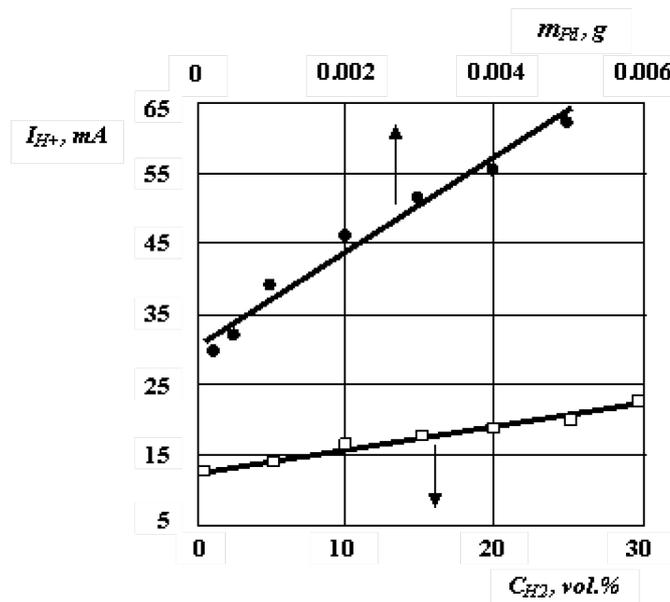
Fig. 5. Change in ionization current from the hydrogen concentration and amount of immobilized Pd into the polymer matrix

The work of the composite volume-porous GBR–PAN+Pd electrode was studied in comparison with the GBR–PAN,Pd electrode (in which palladium was deposited on the surface of a polyaniline film).

As can be seen from fig. 6, in the hydrogen ionization reaction after passing a constant-composition gas mixture through the electrode system, the ionization current at the volume-porous electrode with embedded palladium is higher than on the electrode with deposited palladium.
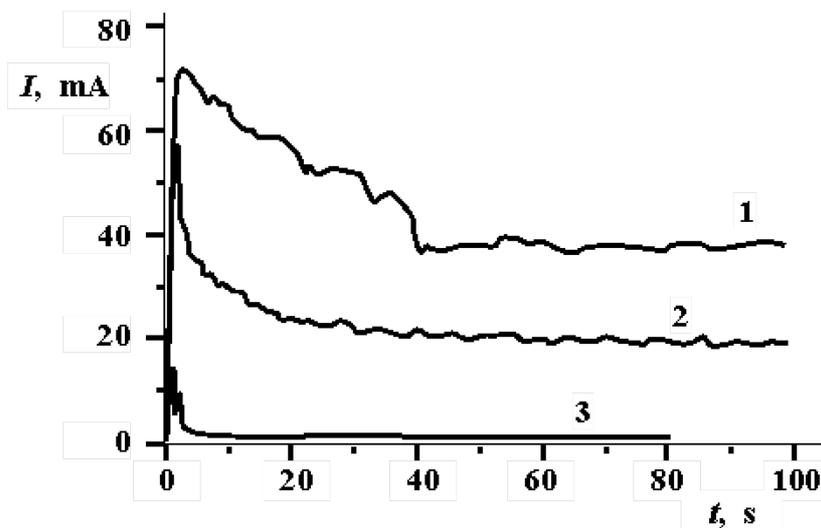
Fig. 6. Change in hydrogen ionization current at the electrodes: 1 – volume-porous GBR–PAN+Pd electrode, 2 – GBR–PAN,Pd electrode; 3 – background current

The same is observed when comparing a volume-porous electrode with a compact palladium electrode [8, 11]. This means that the volume-porous electrode is more active than the electrode with deposited palladium and the compact palladium electrode. It should be noted that the GBR–PAN+Pd electrode contains an order of magnitude less catalyst metal than the GBR–PAN,Pd electrode. The obtained effect is explained by the more developed total working surface of palladium nanoparticles in the GBR–PAN+Pd electrode compared to the GBR–PAN,Pd electrode.

When recalculating the volume of ionized hydrogen per 1 g of palladium contained in the electrodes, it turns out that this indicator for the GBR–PAN+Pd electrode is 110 ml, while for the GBR–PAN,Pd electrode it does not reach 10 ml.

5 Conclusion

Thus, methods for producing electrode systems based on a conductive polymer (polyaniline) with immobilized palladium are proposed.

Samples of the sensory system were developed using a palladium nanodispersed particles embedded in a polyaniline matrix. It is shown that variation in the number of palladium and the morphology of matrix makes it possible to create sensor systems designed to detect different amounts of hydrogen.

As a result of an experimental study of the sensor model, it was shown that the composite volume-porous PAN+Pd electrode with palladium embedded in the volume of the polyaniline matrix has maximum catalytic activity and is much more efficient than the deposited palladium electrode and compact palladium electrode.

The obtained linear dependence of measured current on the hydrogen concentration indicates that, based on the porous PAN+Pd electrode, it is possible to create a series of indicator electrodes for gas amperometric sensors capable of detecting presence of any hydrogen concentrations at normal temperature and being sensors of fire hazard detectors.

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