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**Research Article**

# The investigation of the electrocatalytic effect of nanocomposites polyaniline films modified with platinum.

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**ABSTRACT**

Polyaniline (PAni) is relatively stable in the air even at very high temperatures. His indomitable nature is due to its instability, fragility, high pH dependence of the conductivity and electrochemical activity of the environment, and limitation of application. Therefore, efforts to change the structure of PAni have been made to deal with these problems. Between copolymers and composites, the yen has been considered as an important way to improve its properties. The use of conductive polymers as a support for catalytic platinum particles for the oxidation of hydrogen ions and small organic molecules has been the focus of many researchers, usually platinum is used as an ideal catalyst for these processes. The main reason for studying such composite materials is their extraordinary electrocatalytic activity, which is comparable to platinum electrode or even much more

**Keywords:** Polyaniline; Electrocatalytic effect, Platinum; Carbon Graphete

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## 1. Introduction

Electrically conductive polymers are among the most fascinating materials in modern technology due to their natural and diverse doping states. In the meantime, polyaniline has a special feature that may be due to its use in several different branches of technology. Although polyaniline is one of the most important conducting polymers of this era. Basically, polyaniline is known as a redox polymer. Chemical polymerization of aniline is carried out in an acidic environment. The acidic environment helps to dissolve the monomers in the formation of conductive polyaniline [1, 2].

Platinum is an extremely rare metal, Platinum is a shiny gray metal, and when it is pure, it is soft, malleable, and conductive [3]. This element is also used to make the cover of rockets, jet engine fuel. This metal, like palladium, has high hydrogen absorption properties. Platinum is used as a suitable catalyst for sulfuric acid production processes [4, 5]. Platinum is one of the main components of many metal products such as electrodes and is used as a catalyst in some chemical reactions. Platinum is usually used as a medicine in the treatment of cancer. The effects of platinum on health depend on the type of bonds formed and the level of immunity of the person [3, 6, 7].

The purpose of this study is Considering that platinum is an expensive metal, with the consumption of the least amount of platinum, the most analytical use was taken in the electrocatalysis of hydrogen reduction and ethanol oxidation.

## 2. Experimental

### Materials, Equipment, and Method

Aniline is distilled under low pressure in a nitrogen atmosphere and the resulting colorless liquid is kept at 5 degrees Celsius. Ethanol was also used in pure form. Platinum is used in the form of hexachloroplatinic acid hexahydrate  $H_2(PtCl_6)6H_2O$ . Mineral salt potassium chloride (KCL) and phosphoric acid ( $H_3PO_4$ ) have been used without purification. All the above items were labeled by the German company Merck.

Potentiostat/galvanostat model compactstat owned by Ivium Technologies, Netherlands was used for the synthesis and identification of nanocomposite. The Vega model electron microscope device of Tscan company (TESCAN) made in the Czech Republic and Slovakia, which has an Energy Dispersive X-ray analyzer, was used to check the morphology and size of the composite particles. The studies were carried out in a typical three-electrode electrochemical cell.

Graphite composite panels CG (1.8mm) 2B composite made by Gaj Educational Institute was used as working electrode and platinum electrode as auxiliary electrode and Ag/AgCl reference electrode. The reference electrode was prepared and used by placing a silver wire in saturated KCL solution along with a platinum electrode and connecting them to a DC current source and applying a voltage of 1.6 to 1.8 volts for 20 to 30 minutes. First, the electrochemical synthesis of polyaniline was performed on the tip of a graphite pencil; Polyaniline was synthesized by 10 ml of 50 mM aniline in 1 M phosphoric acid and 0.5 M potassium chloride solution on the working electrode (graphite pencil tip). The graphite

electrode was placed in the above solution and subjected to a potential of -0.4 to 1.2V according to Ag/AgCl reference with a scanning speed of 100 mV/s for 20 cycles by cyclic voltammetry method. Then, by potentiostatic electrochemical method (cyclic voltammetry), aniline-platinum composite (in different concentrations of platinum) was synthesized as a layered black deposit on the graphite electrode.

Electrosynthesis was performed by cyclic voltammetry method at a potential of -0.4 to 1.2V in the presence of silver electrode (Ag/AgCl) with a scanning speed of 100 mV/s.

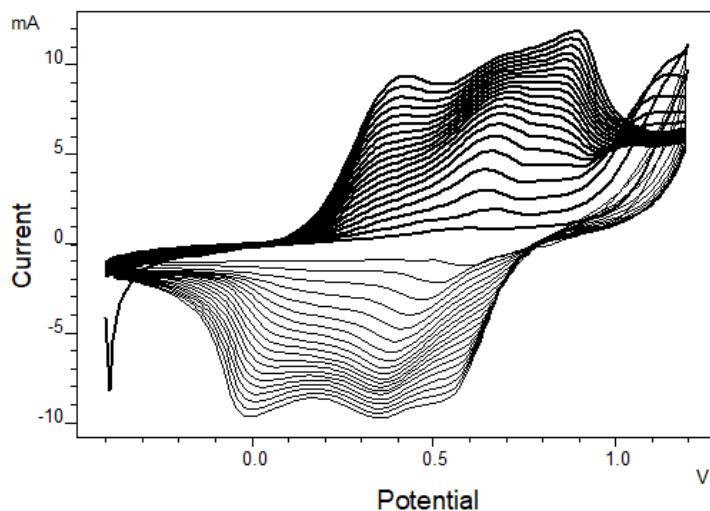
After the synthesis of the composite films prepared on the graphite electrode, the films were examined by SEM were studied and investigated. Graphite electrodes were placed inside different solutions. Solutions containing 10 ml containing 50 mM aniline in the presence of 0.5 M potassium chloride supporting electrolyte and 1 M phosphoric acid solution were applied to the electrode under a potential of -0.4 to 1.2V, then the above modified electrode (PAni was modified by platinum with different molar fractions of platinum. Then Solutions containing 10 ml, including 50 mM aniline with platinum (with different fractions, from 1 to 7 mM platinum) and in the presence of 0.5 M potassium chloride and 1 M phosphoric acid solution under a potential of - 0.4to 1.2 V were placed on the working electrode (CG). The working electrode (CG graphite) was placed in a 10 ml solution containing 4 mM hexachloroplatinic acid, the current Was applied, then the above electrode was placed in a 10 ml solution of aniline (50 mM) containing 1 M phosphoric acid and 0.5 M potassium chloride was entered. The above methods were used in order to select the best composite film with the highest distribution of platinum on the microlayer level and to study the electrocatalytic effect of that electrode on ethanol. Different molar fractions of monomers were used to examine polymer films for platinum diffusion on the electrode surface by SEM.

Then cyclic voltammetry method was used to measure ethanol in such a way that the above modified electrode was placed in solutions containing (0.5, 1, 2 M) of ethanol and the amount of current was measured according to the potential. The compactstat device was also used here.

### 3. Results and Discussion

#### *Electrochemical synthesis of polyaniline*

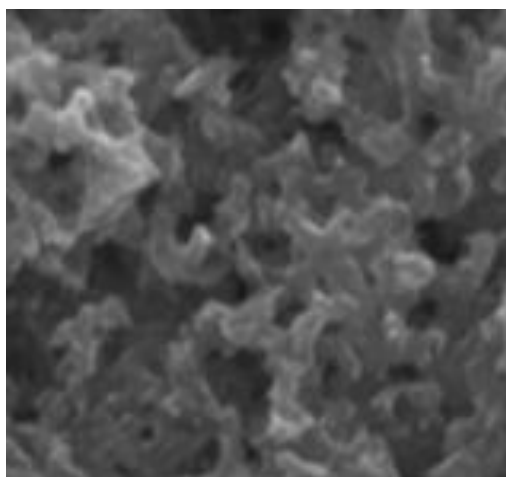
Polyaniline was subjected to a potential of -0.4 to 1.2V according to Ag/AgCl reference with a scanning speed of 100 mV/s up to 20 cycles by cyclic voltammetry method. Fig 1 shows cyclic voltammograms of 50 mM aniline in 1 M phosphoric acid containing 0.5 M potassium chloride on the tip of a graphite pencil.



**Fig 1.** Cyclic voltammograms of PANi with a scanning speed of 100 mV/s

#### *Analysis of surface and structure of polyaniline film*

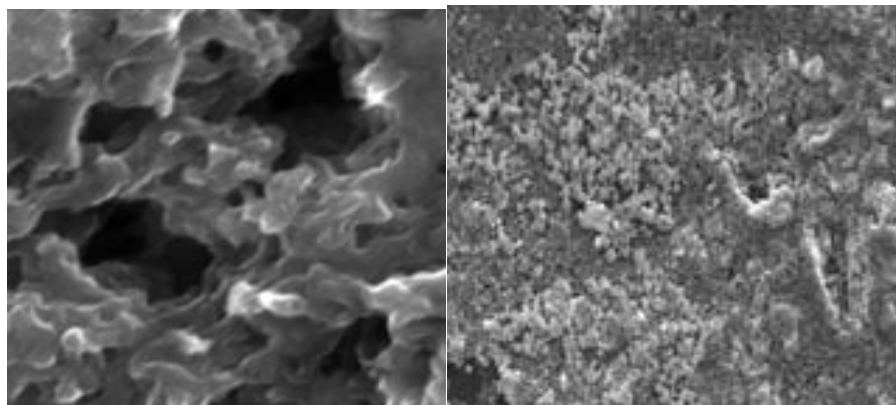
The SEM image (Fig 2) show the polyaniline film obtained from a 50 mM monomer solution in phosphoric acid containing potassium chloride, which proves that polyaniline is doped with ions. It is phosphate [8, 9].



**Fig 2.** SEM (a) of polyaniline obtained from 50 mM monomer solution in phosphoric acid.

### ***Scanning electron microscope image (SEM) of the electrode surface***

When aniline is added together with platinum (simultaneously) to the graphite electrode surface (Fig 3). As can be seen, platinum is placed in the form of spherical circles in the interior of the polymer, but compared to the previous case when platinum was synthesized on the polymer (Pt/PAni), it has less spread and dispersion. Checking and identifying the modified electrode by scanning electron microscope (SEM). The resulting images showed that only aniline polymerization has taken place and there is no trace of platinum particles on the surface.



**Fig 3.** Scanning electron microscope images of the surface of Pt / PAni /CG

The SEM image taken in the presence of platinum not only proves the formation of the composite, but also shows the formation of nano-sized particles. (The presence of causes the reflection of transparent points on the surface of the microlayer). The results confirmed the presence of platinum in the microlayer [10, 11]. According to the pictures (Fig 4), the presence of platinum in the polymer has been confirmed by SEM, which proves the doping of

polyaniline with platinum ions. As can be seen in the resulting images, this state has the highest distribution of platinum at the microlayer level and has a high and uniform distribution on the surface of the modified polyaniline electrode and contains a high percentage of platinum [12, 13].

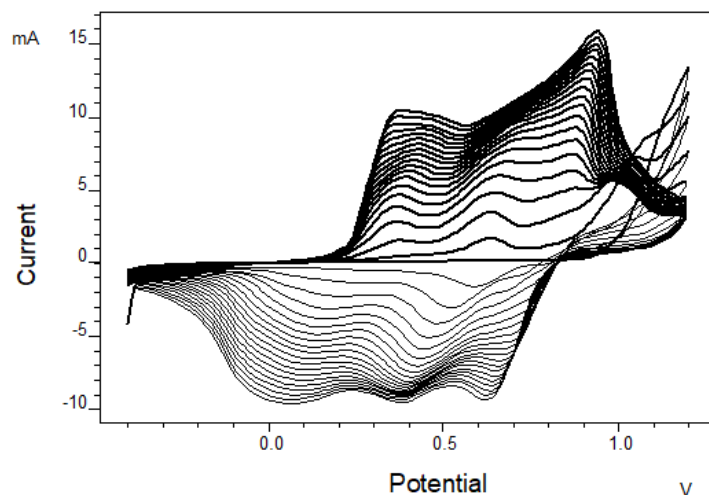


**Fig4.**Spreading platinum on the surface of the polyaniline modified electrode

By spreading platinum on the PANi film, the size of the platinum particles reaches less than 100 nm. When the particles reach nanometer dimensions, their contact surface increases significantly. As a result, by distributing platinum on the film, it is possible to cover the surface with a much smaller amount of platinum. More calls were received. With this, the amount of platinum used will reach the lowest level and more platinum level will be available. In addition, due to the reactions between platinum and the substrate, the electronic structure of platinum atoms is probably improved, which can increase the catalytic activity [14, 15].

#### ***Electropolymerization of aniline in the presence of platinum by graphite electrode***

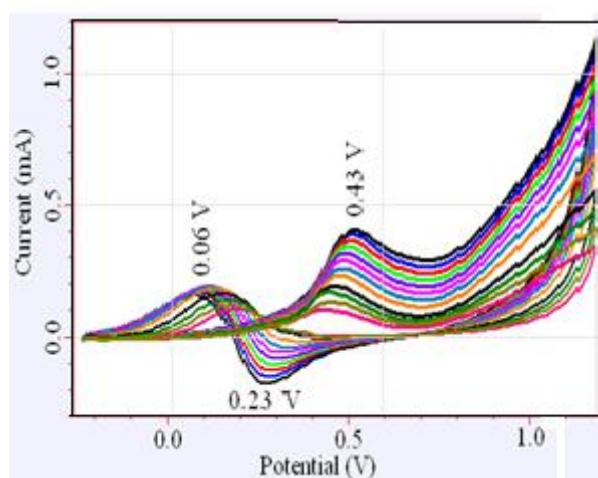
Solutions containing 10 ml, including 50 mM aniline along with platinum (simultaneously) in the form of hexachloroplatinic acid in the presence of 0.5 M and 1 M potassium chloride Of  $H_3PO_4$  was placed under a potential of -0.4 to 1.2V by graphite electrode. In all the above cases, the solution was performed by the cyclic voltammetry method at a potential of -0.4 to 1.2V in the presence of Ag/AgCl with a scanning speed of 100 mV/s. The studies showed that increasing the mole fraction of platinum increases the anode peak potential. It can be said that the synthesis of polyaniline was done on the electrode more than platinum.



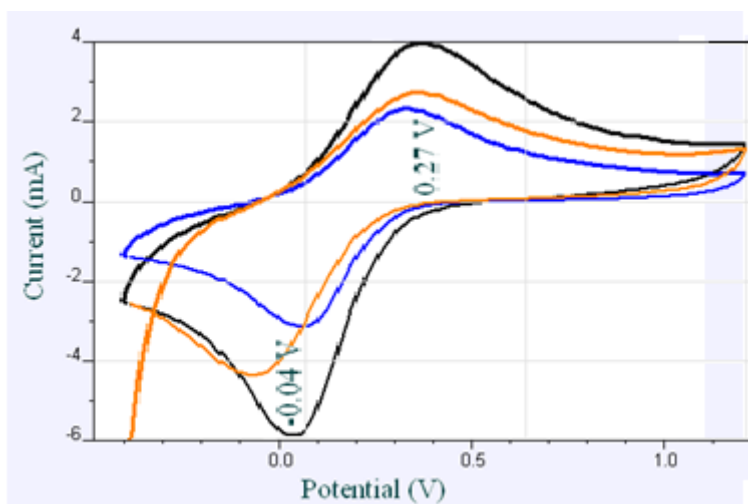
**Fig 5.** Cyclic voltammograms of aniline with platinum by a graphite electrode with a scanning speed of 100 mV/s up to 20 cycles

### *Electrocatalytic effect of modified electrode of ethanol*

Fig. 6. Cyclic Voltammetry (CV) shows different concentrations of ethanol by graphite electrode. As it is evident, the potential of anodic peaks by the unmodified graphite pencil tip appears at 0.43 V on the above electrode. Fig 7. Different concentrations of ethanol (2, 1, 0.5 M) in phosphoric acid in the potential range of -0.4 to 1.2V are measured using cyclic voltammetry method using modified CG electrode/PAni/Pt. As it is evident, in case of using the modified CG-PAni-Pt electrode, the anode peaks appeared at 0.27 V, which indicates a negative shift of 0.16 V compared to the unmodified electrode. Meanwhile, the current of anodic peaks is directly proportional to the increase in ethanol concentration and confirms the electrocatalytic effect of the modified CG-PAni-Pt electrode on ethanol [16-18].



**Fig 6.** Cyclic voltammetry (CV) and linear scan voltammetry (LSV) of different concentrations of ethanol by graphite electrode



**Fig 7.** Cyclic voltammetry (cv) of different concentrations of ethanol by modified graphite electrode CG/PAni/Pt

As the increase in the current of the anodic peaks is directly proportional to the increase in ethanol concentration and confirms the electrocatalytic effect of the modified CG-PAni-Pt electrode on ethanol.

#### 4. Conclusion

In this research, the electrosynthesis of platinum-modified polyaniline film nanocomposite was carried out on the tip of a graphite pencil (CG-PAni-Pt) in 1 M phosphoric acid environment, which included potassium chloride electrolyte support. The main reason for choosing graphite as a substrate is the unique properties of this material, including: cheap price, high electrical conductivity, high corrosion resistance and good chemical stability.

According to the scans performed and the results obtained from the voltammograms of the modified electrodes, we found that the absence of aniline on the graphite composite substrate causes platinum to not have an electrochemical reaction with graphite, and in other words, the synthesis of metal-based nanocomposite is not possible; According to the images taken from the surface of the micro layer, its presence causes the polymerization process and the uniform distribution of platinum on the surface of the modified polyaniline electrode, which is probably due to the increase in the conductivity of polyaniline compared to graphite.

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