



Study of synergism effect in platinum – Gold alloy electrocatalyst for glucose oxidation in direct glucose alkaline fuel cell

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Abstract:

Glucose can be used as an energy source for production of electricity in daily activities. Bio fuel cell systems can be consumed glucose as a fuel for electricity production. For doing that noble electrocatalysts must be used to facilitate glucose oxidation in anode. Gold and platinum nanoparticles on carbon Vulcan (Au-Pt/ C) are synthesized at various ratios (20:80, 40:60, 50:50, 60:40, 80:20) as the catalyst for the anodic oxidation of glucose for use in a direct glucose alkaline fuel cell (DGAFC). Characterization of the catalyst is carried out using physical and electrochemical methods. It is observed that gold nanoparticles are uniformly dispersed onto the carbon support. Linear Sweep Voltammetry was shown that the prepared Au-Pt/ C catalysts exhibit higher electro-catalytic activity for glucose oxidation than pure catalysts. The synergism effect in 50% platinum electrocatalyst in alloy form can provide the better performance for glucose oxidation in prepared electrocatalysts. It was confirmed by impedance spectroscopy results, also.

Keywords: Bio fuel cell, Alloy electrocatalysts, Gold – Platinum electrocatalyst, synergism

Introduction:

Glucose is an idea renewable fuel because it can be produced by photosynthesis in plants such as sugar cane or corn and by a large amount of waste biomass that is generated by agricultural activities [1,2]. Studies on electro-catalytic oxidation of glucose are of high interest to the fuel cell community for various reasons. Firstly, glucose is easily available, cheap and non-toxic bio-fuel. Electro-oxidation of glucose and fructose on PtRu/C catalyst, are studied using cyclic voltammetry in alkaline medium to study the reason for deactivation of glucose fuel cell. A simple direct glucose fuel cell with PtRu/C as anode and activated charcoal as cathode was constructed and operated to study the effect of different temperature and concentration of glucose and KOH solution [3].

A more systematic study of the thermodynamics and kinetics of glucose electro-oxidation should provide useful data for better evaluating the energy performances, which will be absolutely necessary to guide the exploitation of the direct glucose oxidation or idiotically catalyzed [4] fuel

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cells [5]. The investigation of direct carbohydrate oxidation fuel cells started in 1964 [6] and continued as a promising approach to autonomous energy supply for medical implants [4]. Until the coming of the lithium batteries, a dozen years later.

[8] Mallou and co-workers [7] investigated the glucose oxidation on the alloy electrodes of Pt, Pb, Au, Pd, and Rh, and reported that Pt–Pb alloy catalyzed the glucose oxidation in neutral solutions, generating more stable and larger responses than pure platinum. Electrochemical oxidation of glucose on gold–platinum nanocomposite electrodes and platinum-modified gold electrodes was investigated with cyclic voltammetry. The gold–platinum nanocomposite electrodes display high electrocatalytic activity for the glucose oxidation in alkaline solution. The results of experiments indicate that both gold and platinum act as the dehydrogenation site and gold also functions to regenerate platinum from poisoned platinum [8]. Gold nanoparticles supported on MnO₂-carbonnanocomposite (Au/MnO₂-C) are synthesized as the catalyst for the anodic oxidation of glucose alkaline fuel cell (DGAFC) [9].

Effects of different carbon sources and carbonized carbon contents during carbon riveting process (CRP) on the stability of Pt/C catalysts have been systematically studied. Experimental results show that the carbon riveted Pt/C catalysts treated by different carbon sources have different stability due to different properties of Pt and carbon after the CRP [10].

Experimental:

Materials:

Carbon powder Vulcan XC-72R was used as support. K₂PtCl₆ and HAuCl₄ from Merck were used as platinum and gold precursor, respectively. NaBH₄ (Merck) was used as reducing agent. All aqueousolutions were prepared using ultrapure water during catalyst preparation. Propan-2-ol (>99% purity) (Quailed Fine Chemicals) was used as solvent for making a dilute solution of prepared catalyst Catalyst-coated carbon paper (Toray 90 T) was used as working electrode. D-glucose (>99% pure) and KOH (>85% assay, flakes purified) (Merck) were used as fuel and electrolyte, respectively.

Preparation of electro catalyst:

Bimetallic Pt-Au/C (metal ratio 1:1, total metalw10% wt.) was prepared by immobilizing platinum and gold sols on carbon [12,11]. Aqueous solutions of HAuCl₄ and K₂PtCl₆ (100 mg/l) were prepared and glucose was added as protecting agent (metal: glucose 1:50 w/w) in the mixture of precursor sols. A freshly prepared 0.1 M NaBH₄ solution was added (metal: NaBH₄ 1:1w/w) drop wise under vigorous stirring condition and a blackcolloidal dispersion was obtained. The metal particles were immobilized by adding carbon to the metal dispersion under heater-stirring. The slurry was kept overnight and when the solutionbecame clear, it was filtered. The solid obtained was washed many times with distilled water and air dried for 24 h. The oven in 80°C dried catalyst was used for characterization.

Preparation of the gold-platinum electrode:



The anode was prepared using prepared Pt-Au/C. The loading of catalysts in each electrode is 3 mg cm⁻² for fuel cell operation. The catalyst slurry was prepared by dispersing required amount of catalyst powder in distilled water and 2-iso propanol with 1:1 ratio and 30% w/w poly tetra flour ethylene mixture for 30 min using an ultrasonic. The fairly well-mixed catalyst slurry was coated on a carbon paper (cut to size of the electrode) using a brush. The catalyst-coated carbon paper was dried in an oven for an hour at a temperature of 200C. The area of each electrode is 1.13 cm² [13].

Electrochemical measurements:

Three-electrode cell assembly connected to a potentiostat-galvanostat (Zahner) was used for LSV and EIS studies. Ag|AgCl (saturated with KCl) electrode was used as reference electrode and platinum electrode was used as counter electrode. The catalyst-coated carbon paper was used as working electrode (Azar Electrode). The electrodes were dipped into 100 ml 0.5 M KOH solution with 0.2 M glucose.

Result & Discussion:

Physical characterization:

XRD analysis:

The crystal structures of prepared Pt-Au/C and Pt/C and Au/C catalyst powders were studied using XRD as shown in Fig. 1. All electro-catalysts showed a broad peak at about $2\theta = 25^\circ$ which is associated with carbon support [11].

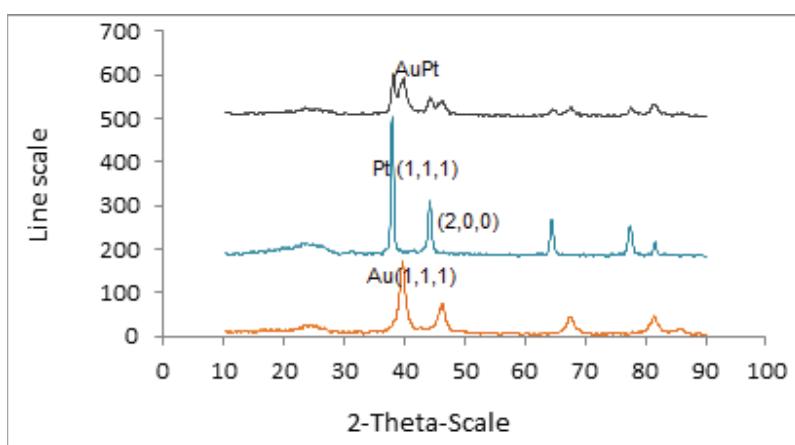


Fig. 1 - XRD pattern of Pt/C, Au/C, AuPt/C catalyst powder samples

The pattern of the AuPt/C, Pt/C and Au/C exhibited diffraction peaks of (1 1 1), (2 0 0), (2 2 0), which indicates that the metals are present in the face centered cubic (fcc) structure [11, 20].



The peaks are found for Au/C at $2\theta = 38.2, 44.4, 64.6, 77.5, 81.8$ and for Pt/C at $2\theta = 40^\circ, 46.2, 67.6, 81.4, 86$. The single diffraction peak of (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) at $2\theta = 25^\circ, 40, 46.2, 67.6, 81.4, 86$ for AuPt/C confirms the formation of alloy.

The calculated metal composition for PdPt/C catalysts is 78.8: 21.2, which is very close to the assumed nominal ratio of 3:1 of Au to Pt in Au Pt alloy nanoparticles.

Electrochemical characterization:

LSV analysis:

In the presence of glucose, the usual peak of electroxidation at platinum electrodes is presented. The glucose molecule is first electrochemically absorbed at the surface of the electrode by dehydrogenation.

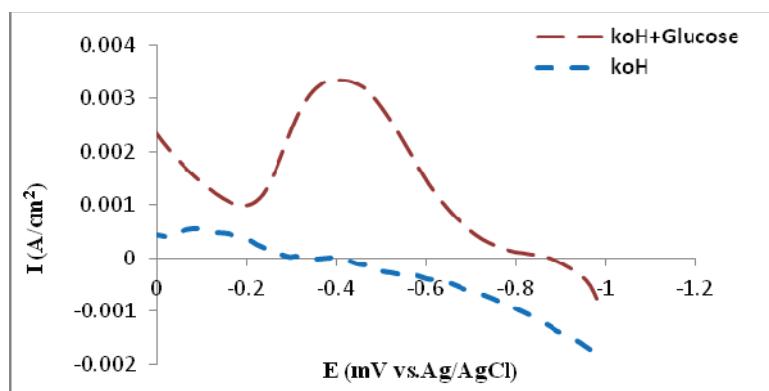


Fig. 2 – Effect of electrolyte in oxidation of glucose in alkaline media

Fig. 2 shows a typical linear sweep voltammogram of glucose electroxidation in alkaline solution. The LSV from -1 to 0.0V with Ag/AgCl (sat.KCl) reference electrode at 1mVs^{-1} scan rate with Au-Pt/C catalyst in KOH and Glucose electrolyte.

The aim of the present work is to understand the influence of physical synergism in the alloying method.

Electrocatalytic activity of an electrode towards the glucose oxidation is mainly reflected by oxidation potential, i.e., the higher the electrocatalytic activity of the electrode is, the lower the oxidation potential is. The glucose oxidation on the Au-Pt/NPs electrode and the Pt electrode is shown in Fig. 1. The peak potential of the Au-Pt/NPs electrodes appeared at -0.29V , which means about 0.06V negative shift in peak potential as compared with that of the Pt electrodes. The difference in peak potential is remarkable, showing high catalytic activity of the Au-Pt/NPs electrodes. The high catalytic activity of the Au-Pt/NPs electrodes is attributed to platinum and the interaction between gold and platinum species in the reaction, and the detailed mechanism of this reaction needs further investigation. We can see maximum current with 8.22 mA and -0.27 mV related to Ag/AgCl reference electrode.

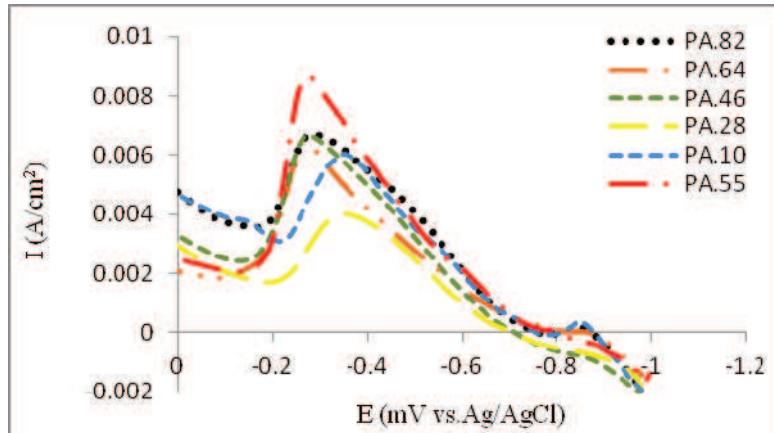


Fig.3 Polarization study of fabricated electrodes at various platinum content for glucose oxidation

EIS analysis:

EIS measurements were used to understand the role of the phosphate buffer on the conductivity of the solution and the mechanism of the reaction. The conductivity of the solution also influences the amount of usable electrode. In fact, a higher conductivity of the solution permits an easier transport of the current inside the electrode and consequently a higher portion of the electrode to be active. The measurement can be used to optimize the thickness of the electrode as a function of the working conditions.

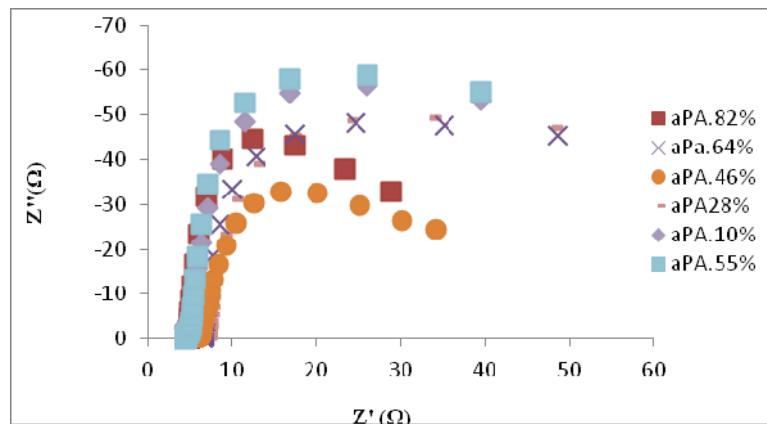


Fig.4 – Impedance Spectroscopy of fabricated electrodes for glucose oxidation in -0.5 v potential



Conclusion:

In this work, alloy method for preparation of electrocatalysts was studied. For these purpose platinum and gold noble metals was used as an alloy form. The simultaneous presence of two metals being together can provide especial situation for creating synergism effect. The percentage of each catalyst in alloy form influences on performance of electrocatalyst for glucose oxidation in gas diffusion electrodes. In this research, the 50:50 proportion percentage of each catalyst is the best ratio for electrocatalytic activity of fabricated electrodes. In this state, the best current density for glucose oxidation reaction was observed. This current density is higher than pure platinum and gold electrocatalysts for desired reaction. Therefore, according our results, the synergism effect was shown in alloy form of platinum and gold electrocatalysts in especial ratio.

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