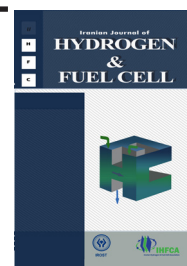


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Palladium nanoparticles supported on carbon black powder as an effective anodic catalyst for application in a direct glucose alkaline fuel cell

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Abstract

Palladium nanoparticles supported on carbon black powder (Vulcan XC-72) nanocomposite (Pd/C) were synthesized as the catalyst for the anodic oxidation of glucose for use in a direct glucose alkaline fuel cell (DGAFC). Characterization of the catalyst was carried out using physical and electrochemical methods. It was observed that Palladium nanoparticles are uniformly dispersed onto the carbon black powder nanocomposite support. The catalytic properties of the catalyst for glucose electro-oxidation were studied using electrochemical methods such as cyclic voltammetry and chronoamperometry. Cyclic voltammetry shows that this catalysts exhibited high electro catalytic activity for glucose oxidation. The Pd/Vulcan XC-72 /glassy carbon electrode exhibited a well-defined catalytic oxidation peak current increasing linearly with an increase in the glucose concentration in the range of 10 mM to 60 mM. Chronoamperometry indicated that Pd/Vulcan XC-72 exhibits a steady state activity for glucose oxidation. Results show that the prepared Pd/Vulcan XC-72 is an effective anodic catalyst toward glucose electro-oxidation. Therefore, this electrode is a good candidate for application in direct glucose alkaline fuel cells.

1. Introduction

Glucose is a stable fuel for application in fuel cells [1-5]. In the last decades the direct glucose fuel cell (DGFC) has been receiving much interest from researchers due to its renewability and environmental friendly characteristics [6-9]. DGFC can produce electric energy directly from chemical energy stored in glucose. The DGFC has several excellent features

such as: (1) a high energy generation ratio, (2) high energy conversion efficiency, (3) small impact on the environment, (4) and accessible fuel, which makes it an attractive fuel cell for various applications [6, 10-12]. Hence, research on low temperature DGFCs as a power source in transferable devices is being developed [1, 6]. Oxidation of glucose has been investigated on gold and platinum in diverse pH solutions. Electrocatalysts investigated for direct reaction in DGFCs have been

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mainly noble metals such as Pt, Pb, Au, Pd, Ni, Cu and Rh. Mediator metals oxides and their compounds, such as NiO, CuO, NiOx/MnOx and NiO/CuO, have a high capacity for glucose oxidation [1-3]. Low current density related to the glucose oxidation at the anode is one of the major challenges in the development of direct glucose fuel cells. Therefore, one of the keys to the improvement of DGFCs is to find more cost-effective catalysts with a higher stability and catalytic activity [6, 13-18]. Electrocatalyst materials plays an important role in fuel cell efficiency, and platinum (Pt) has long been a major and mandatory component for most anode catalysts including those used for DGFC investigation. Values of current density for glucose oxidation reaction (GOR) on PdPt/Vulcan XC72 and PtPdAu/Vulcan XC72 nano-catalysts have been previously reported at 2.6mAcm^{-2} and 3.4mAcm^{-2} , respectively [6].

Pt is a costly noble metal that is quickly self-poisoned by adsorbed intermediates, so other noble metals have been studied in an attempt to overcome this obstacle. Accordingly non-Pt based catalysts, for example palladium (Pd), have been recently studied for the electrocatalytic GOR in DGFC [6]. It was demonstrated that Pd can replace Pt in direct alcohol fuel cells as well as in DGFC. Since Pd is relatively cheaper compared to Pt and has high electrocatalytic activity for oxidation of many fuels (e.g. ethanol and glucose) in an alkaline medium, they explored Pd-catalyzed GOR as a promising field to employ for glucose fuel cells [6]. Other important points for determining the catalytic performance and catalyst employment in a fuel cell rely on the metal catalyst loading and distribution uniformity on the carbon support surfaces. It has been broadly demonstrated that the carbon support material can be as important as the catalyst itself for electro catalysis since it verifies the active surface area, dispersion of catalyst particles, electrical conductivity of the electrode, and synergistic role for catalysis all which affect the fuel cell performance [4, 6, 19-21].

In this present work, the synthesis of a Palladium nanoparticles catalyst supported on a Vulcan XC-72 were prepared by the chemical reduction method as

the catalyst for the anodic oxidation of glucose for use in a direct glucose alkaline fuel cell.

2. Experimental

Reagents

Glucose (Merck), KOH (Merck, 84% purity) and PdCl_2 (Alfa Aesar) were used as received. Carbon black powder (GP-3919, Cabot) was used as the support. NaBH_4 (CDH, India) was used as the reducing agent. All other chemicals were of analytic grade and used without further purification. All aqueous solutions were prepared with distilled water.

Preparation of Pd/C

Carbon black powder was used as a support for the catalyst [6]. The samples were synthesized by chemical reduction with sodium borohydride of PdCl_2 as follows: the carbon black was ultrasonically dispersed in a mixture of ultrapure water and 25 ml PdCl_2 . The PH value of the ink was adjusted by a NaOH solution to 10 and then its temperature was raised to $80\text{ }^\circ\text{C}$. Fifteen millilitres of 0/1 M solution of sodium borohydride was added into the ink drop by drop and then washed repeatedly with ultra-pure water. The catalyst powder was then dried for 3h at $120\text{ }^\circ\text{C}$.

Physical characterization

Morphology of the Pd nanoparticles on Vulcan XC-72 were characterized with a scanning electron microscope (SEM) (Model VEGAII, TESCAN) employed with an accelerating voltage of 15 kV.

Electrochemical experiments

All electrochemical experiments were performed in a three-electrode cell arrangement. A platinum sheet was used as the counter electrode, while all potentials were measured with respect to the Ag/AgCl electrode.

Electrochemical experiments were carried out using EG&G PARSTAT 2273 advanced potentiostat run by Power Suite software.

3. Results and discussion

Characterisation of catalyst morphology

Figure 1 shows the SEM image of the Pd nanoparticles on Vulcan XC-72. It can be seen that the Pd nanoparticles with a high density and diameters about 50–60 nm are distributed in an almost homogeneous manner at the Vulcan XC-72.

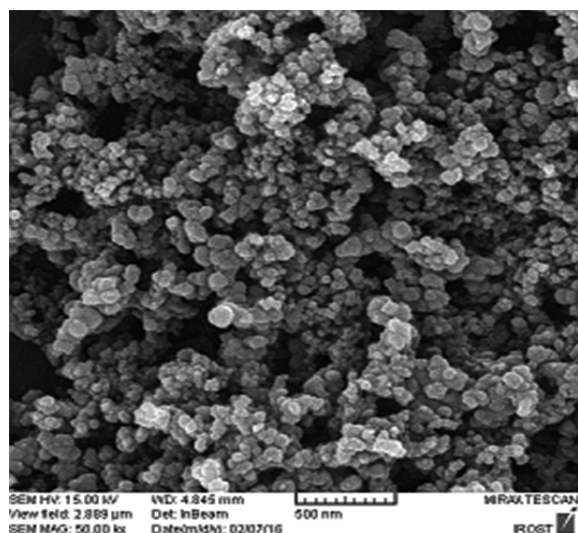


Fig. 1. SEM image of Pd nanoparticles supported on carbon black powder (Vulcan XC-72).

Electro-oxidation of glucose on Pd/Vulcan XC-72

The electro oxidation of glucose at the Vulcan XC-72/GCE and Pd/Vulcan XC-72/GCE were first studied by cyclic voltammetry. Cyclic voltammograms of two electrodes in 0.2 M KOH in the absence and presence of a 10 mM glucose aqueous solution are shown in Figure 2. The peak current for glucose electro-oxidation on Pd/Vulcan XC-72/GCE is greater than that observed for Vulcan XC-72/GCE. Figure 3 shows the cyclic voltammograms of the Pd/Vulcan XC-72/GCE in the presence of various concentrations of

glucose. The observed anodic peak current increases as the glucose concentration increased in the solution. This catalytic peak current showed a linear relationship with the concentration of glucose in the range of 10–60 mM with a correlation coefficient of $R^2 = 0.991$ (Fig. 4).

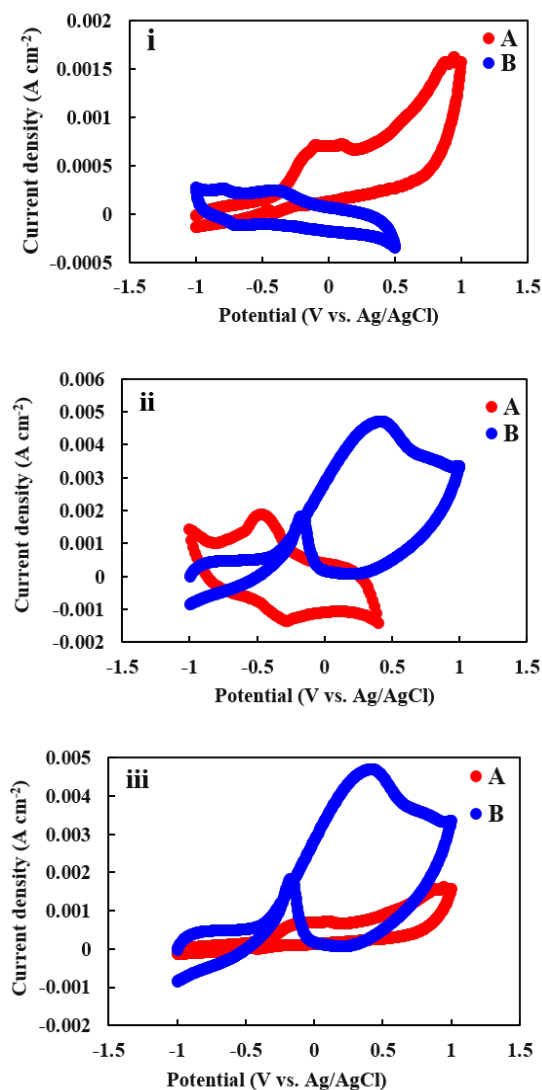


Fig. 2. Cyclic voltammograms: (i) Vulcan XC-72/GCE in 0.2 M KOH in absence (A) and presence 10 mM glucose (B) at 27 °C scan rate: 50 mV s⁻¹, (ii): Pd/Vulcan XC-72/GCE in 0.2 M KOH in absence (A) and presence 10 mM glucose (B) at 27 °C scan rate: 50 mV s⁻¹ and (iii): Vulcan XC-72/GCE (A), Pd/Vulcan XC-72/GCE (B) in 0.2 M KOH + 10 mM glucose at 27 °C scan rate: 50 mV s⁻¹.

Comparison of the proposed method with reported methods for the glucose electro oxidation

A comparison between the electrochemical characteristic of the Pd/Vulcan XC-72 and other previous reported methods for glucose electro

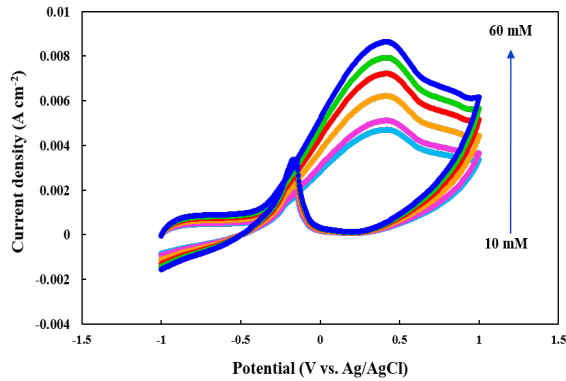


Fig. 3. The cyclic voltammograms of Pd/Vulcan XC-72/GCE in 0.2 M KOH with different concentrations of glucose.

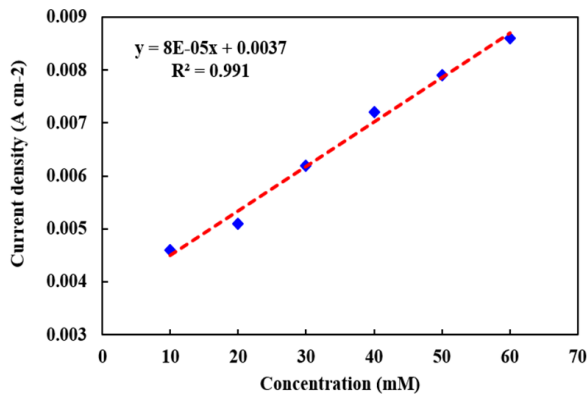


Fig. 4. The plot of glucose-electro oxidation peak current on the Pd/Vulcan XC-72/GCE versus concentration of glucose.

oxidation is shown in Table 1. It was found that the propose method showed a large anodic peak current density compared to the other methods.

In order to evaluate the stability of the electrocatalytic activity of the Pd/Vulcan XC-72 towards glucose electro-oxidation, chronoamperometric measurements were done [4]. Figure 5 shows the chronoamperometric curves of 10 mM glucose and 0.2 M KOH solution on the Vulcan XC-72 and Pd/Vulcan XC-72 for 100s. It was found that the current in the above electrode is

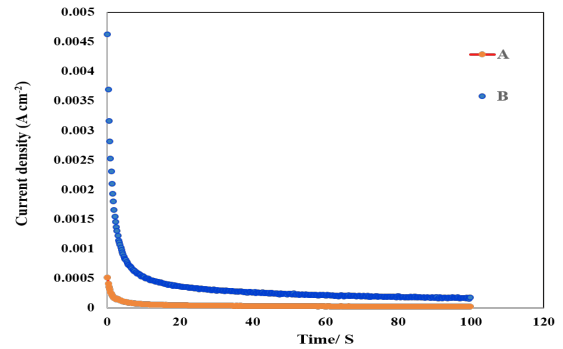


Fig. 5. Current-time curve for glucose oxidation on Vulcan XC-72/GCE and Pd/Vulcan XC-72/GCE in 0.2M + 10 mM glucose solution. Applied potential:-0.4 V and 0.5 V respectively (vs. Ag/AgCl electrode).

reduced with time for Vulcan XC-72 and Pd/Vulcan XC-72 reaching 0.02 mA and 0.17mA, respectively, at 100s. This results shows that the current represents less decay at the applied constant potential on the Pd/Vulcan XC-72 for a long duration (100s), indicating that Pd/Vulcan XC-72 exhibits a steady state activity for glucose electro-oxidation. Figure 6 shows chronoamperograms for different concentrations of glucose. The slope of I vs. $t^{-1/2}$ plot is shown in the inset of Figure 6. The diffusion coefficient of the glucose was calculated by the Cottrell equation [23]:

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} = Kt^{-1/2} \quad (1)$$

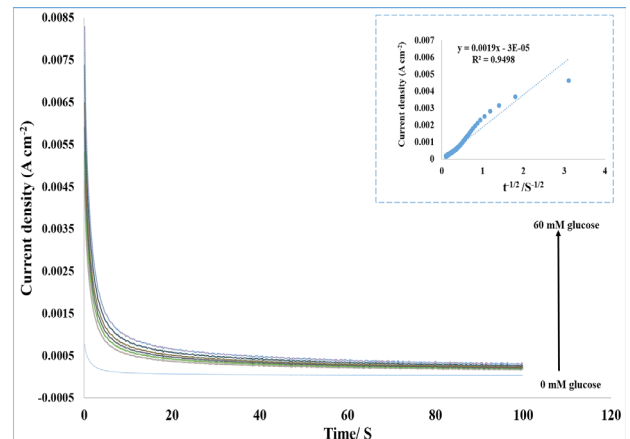


Fig. 6 Chronoamperogram of Pd/Vulcan XC-72/GCE in 0.2 M KOH with different concentrations of glucose. Applied potential: 0.5 V (vs. Ag/AgCl electrode). Inset show the corresponding I vs. $t^{-1/2}$ plot.

Table 1. Comparison of the proposed method with reported methods for the glucose electro oxidation in alkaline solution.

Electrode	Preparation method	anodic peak current density (Acm ⁻²)	Concentration of glucose (mM)	Scan rate(mV/S)	Ref.
Au/TiO ₂ /Ti electrode	Electro deposition method	0.0023	10	50	[22]
GC/MWNT/NiO	Chemical modified	0.0003	10	50	[23]
Pt-decorated nanoporous gold (NPG-Pt)	Chemical deposition method	0.0015	10	50	[25]
Pt-Au/C	Chemical reduction	0.0012	10	20	[26]
Pt/C	Chemical reduction	0.0038	10	20	[26]
Pd/Vulcan XC-72 / GCE	Chemical reduction	0.0046	10	50	Thiswork

where A is the real surface area, D is the diffusion coefficient, and C is the concentration of glucose. The diffusion coefficient was calculated to be $3.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (with $n=2$, $F=96485 \text{ C mol}^{-1}$ and $A=0.0314 \text{ cm}^2$).

The catalytic rate constant was calculated by equation [24]:

$$I_{cat}/I_L = \pi^{1/2} (k_{cat} C_0 t)^{1/2} \quad (2)$$

where, I_{cat} and I_L are the currents in the presence and absence of glucose, respectively. The symbol k_{cat} is the catalytic rate constant ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), C_0 is the bulk concentration of glucose ($10^{-5} \text{ mol cm}^{-3}$), and t is the elapsed time (s). I_{cat} , I_L and t were derived from the data of the chronoamperogram. The catalytic rate constant was calculated to be $1.645 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

4. Conclusion

Palladium nanoparticles supported on carbon black powder were successfully prepared by the chemical reduction method as the catalyst for the anodic electro-oxidation of glucose for application in a direct glucose alkaline fuel cell. We have demonstrated that

Pd nanoparticles with a size of 50-60 nm can be grown on the carbon black powder by chemical reduction of PdCl_2 .

The electro-catalytic activity of this catalyst for glucose electro-oxidation was evaluated by electrochemical voltammetric measurements and chronoamperometry. Results showed that the Pd nanoparticles have good performance data for glucose electro-oxidation, including the highest peak current density (0.0046 Acm^{-2}), an excellent diffusion coefficient ($3.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and a valuable catalytic rate constant for glucose ($1.645 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The electrocatalytic oxidation peak currents for glucose exhibited a good determination coefficient ($R^2=0.991$) depending on the glucose concentration in a range of 10–60 mM. Chronoamperometric measurements illustrated that Pd/Vulcan XC-72 exhibits steady state activity for glucose electro-oxidation. Therefore, palladium nanoparticles supported on carbon black powder are an effective anodic catalyst for electro-oxidation of glucose.

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