Materials Research Express

PAPER

Investigating the effect of carbon support on palladium-based catalyst towards electro-oxidation of ethylene glycol

Katlego E Raseruthe, Thabo Matthews, Sandile S Gwebu, Kriveshni Pillay and Nobanathi W Maxakato

Department of Chemical Sciences, University of Johannesburg, Doornfontein, 2028, South Africa

E-mail: nmaxakato@uj.ac.za

Keywords: electrocatalyst, alcohol electrooxidation, carbon nanotubes, carbon nanodots

Abstract

Palladium-based catalysts serve as promising electrocatalysts for the oxidation of ethylene glycol to produce electrical energy that can be used to address the continuous worldwide energy demand increments along with the depletion of fossil fuels which serve as the main energy source. For optimal catalysts performance, carbon nanotubes and carbon nanodots were investigated as palladium catalyst support materials to address difficulties in oxidizing and breaking the C–C bonds in ethylene glycol, cost of electrocatalyst, and complex reaction mechanism that is restraining rapid development and applications of direct ethylene glycol fuel cells (DEGFC). Utilization of palladium catalysts supported on carbon nanotubes (CNT) and carbon nanodots (CND) as support materials resulted in spontaneous ethylene glycol oxidation. The Pd/CNT catalyst showed greater stability compared to Pd/CND during the oxidation of ethylene glycol, and it is not easily poisoned by carbon monoxide intermediates formed during ethylene glycol oxidation as shown by a slow current decay on chronoamperometry.

1. Introduction

To save the mother earth from pollution and simultaneously solve the growing energy demand, renewable environmentally friendly energy systems need to be implemented. Among different energy systems, direct ethylene glycol fuel cell (DEGFC) has been extensively studied as an ideal direct alcohol fuel cell (DAFC) that has the potential to generate energy for application in stationary, mobile and portable devices via the conversion of chemical energy stored in ethylene glycol directly to electrical energy giving out heat and water as by-products [1–4]. This cell has the benefits of emitting low to zero levels of harmful pollutants in the atmosphere and benefits of using ethylene glycol as a fuel include its availability in the supply chain, its high boiling point of 198 °C, the high theoretical energy capacity of 4.8 Ah ml⁻¹ and its ability to be easily transported, handled, and distributed [5, 6]. As for methanol as a fuel, its production of intermediates such as carbon monoxide (CO) that are poisonous to the catalyst material makes the cell to degrade severely under long operation terms. Methanol is also subjected to severe methanol crossover from anode to the cathode side of the cell during operation while ethanol as a fuel normally results in the formation of acetic acid with a very low electron transfer rate of 33% [7–9].

With all the benefits of using DEGFC, it is still far from successful commercialization due to challenges in finding a durable, cost-efficient catalyst with high catalytic activity [8]. To date, platinum has been the most used metal catalyst for DAFCs because of its unique and excellent catalytic properties. However, Pt has disadvantages which include its expensive nature, reservoirs depleting and susceptibility to CO poisoning which is an intermediate formed during ethylene glycol oxidation, consequently leading to a sharp decrease in its electrocatalytic activity [10–12].

Challenges faced by platinum as a catalyst have been addressed by the use of palladium as it is an abundant metal with catalytic activity comparable to that of platinum, cheaper than platinum, and offers improved alcohol
oxidation kinetics in alkaline media with a decrease in catalyst surface poisoning by adsorbed CO intermediates [13–15]. This study was aimed at obtaining the best catalytic performance with the usage of little amounts of the catalyst material. For this to happen, the introduction of support material to the catalyst will reduce the catalyst price and enhance some of the catalyst’s properties like catalytic activity.

A support material needs to have high electrical conductivity, high surface area to provide the maximum possible active sites for electrooxidation, and high electrochemical stability to remain intact during alcohol oxidation [15, 16]. Carbon-based catalyst–support materials are easily available, have high stability in basic and/or acidic media, are relatively cheap, and can be easily recovered after use as they are burnt off easily making them the best support material [14, 15]. The role played by carbon materials as support materials for catalysts includes enhancement of electroactive area with great nanoparticle dispersion; promotion of electronic transfer and improvement of the rate of diffusion of electroactive species through the porous structure of carbon support [6, 17]. Different carbon material supports include carbon nanotubes (CNT) [18], carbon black [16], mesoporous carbon [18], graphene [15, 19], carbon dots (CND) [20]. Among these carbon materials, carbon nanotubes have earned their respect in the carbon material industry due to their great catalytic activity, high surface area, electrical conductivity, and mechanical stability which makes them a good support material and carbon nanodots are new carbon materials that need to be investigated thoroughly for their ability as an alternative good supporting material [18–20]. In this study, we investigated the performance of different carbon support materials for palladium nanoparticles as a catalyst that is synthesized with the hydrothermal method.

2. Experimental section

2.1. Materials and reagents

Pristine multi-walled carbon nanotubes (CNT), palladium chloride (PdCl2, 10% wt. %Pd), Nafion solution (20 wt.%), and potassium bromide (KBr, ≥99.9%), sulphuric acid (H2SO4, 98%), nitric acid (HNO3, 65%), sodium borohydride (NaBH4, 98%), Pd/C (10% wt. %Pd) commercial standard, potassium hydroxide pellets (KOH, ≥85%), ethanol (>99.9%), ethylene glycol (>99.9%) and methanol (>99.9%) were all purchased from Sigma Aldrich. Double distilled water was used in all experiments for the preparation of solutions and all reagents used were of analytical grade unless stated otherwise. Platinum wire, glassy carbon electrode (GCE) with a diameter of 3 mm) and the Ag/AgCl reference electrode saturated with 3 M KCl were purchased from BAS Inc.

2.2. Methods

2.2.1. Preparation of carbon nanodots

Carbon nanodots (CND) were synthesized by pyrolysis of oats in which 10 g of oats was left to carbonize in a muffle furnace for 2 h at 400 °C as reported by Shi et al [19]. CND were then cooled down to room temperature, mechanically ground and washed with distilled/purified water several times, and dried at 80 °C for 24 h, respectively.

2.2.2. Preparation of carbon nanotubes

Commercial multi-walled carbon nanotubes (CNT) were functionalized with acid treatment [12]. Briefly, CNT amounting to 0.6 g were sonicated (at 750 W and 20 kHz/watts) in a mixture of concentrated H2SO4 and HNO3 (3:1, v/v) for 4 h. The acid solution was then centrifuged to separate functionalized CNT (fCNT) and washed with 3 M NaOH and bi-distilled water to neutralize the acid that may still be left in the fCNT. The fCNT were then dried in an oven at 60 °C overnight.

2.2.3. Preparation of palladium on carbon nanodots (Pd/CND) and palladium on carbon nanotubes (Pd/CNT)

A specific amount of CND/CNT was dispersed in 20 ml of water with an addition of 0.5 g of palladium chloride (PdCl2), under sonication for 30 min. The solution was then transferred into an autoclave and heated at 180 °C for 10 h and centrifuged to get Pd/CND or Pd/CNT which were washed repeatedly with distilled water and ethanol then The solid product was dried overnight at 80 °C.

2.3. Characterization

The techniques used for characterizations are a high-resolution transmission microscope (HRTEM), x-Ray Diffractometer (XRD), and frontier transmission infrared spectroscopy (FTIR). The samples for HRTEM (JOEL JEM-2100, Japan) analysis were prepared by dispersing the catalyst in ethanol using a sonicator. A drop of the suspension was then deposited on a standard copper grid for catalyst morphological studies. The Phillips X-PertPro XRD was used to obtain the XRD patterns of all catalysts using a Cu Kα x-ray source (λ = 0.15443 nm, 40 kV, and 40 mA). The FTIR was used to obtain the FTIR spectrum by KBr-sample pelletization technique making use of using a Perkin Elmer FTIR spectrophotometer.
2.4. Electrochemical measurements
All electrochemical experiments were carried out at room temperature in a three-electrode cell (DropSens \(\mu\)STAT8000 potentiostat using Dropview 8400 software). Platinum wire, glassy carbon electrode (GCE), and Ag/AgCl saturated with 3 M KCl were used as counter, working, and reference electrodes, respectively. Electrocataylst was prepared through dissolving 10 mg of Pd/CNT or Pd/CND in 2.5 ml of double distilled water and 4 drops of Naion where 10 \(\mu\)l of the electrocatalyst sample solution was dropped onto the surface of GCE working electrode for electrochemical measurements.

3. Results and discussion

3.1. Structural characterization

3.1.1. TEM analysis
The morphology of the synthesized carbon nanodots (CND) and Pd/CND was firstly studied using HRTEM. Figure 1 shows the HRTEM images (A&C), EDS spectrum (B), and particle size distribution plots (B&E) of CND and Pd/CND catalysts, respectively. The CND synthesized with the pyrolysis of oats consist of homogeneous spherical CND as shown on the TEM image (A). A successful synthesis of Pd/CND catalyst using palladium chloride as a precursor is supported by the notable difference in TEM images of pristine CND (A) with that containing palladium shown in (C) in figure 1. This difference is brought by spherical palladium (Pd) nanoparticles that are huge as compared to the CND as can be seen in figure 1, image (C) and the Pd nanoparticles are on top of the CND. The presence of palladium was then elucidated by the EDS spectrum in figure 1(D) which shows a broad Pd peak spectrum at 3 keV. The particle size distribution histogram curves of the CND and Pd/CND catalysts were plotted giving average particle sizes: 7,7938 nm for CND and 39.68 nm for the Pd nanoparticles in Pd/CND. CND sizes ranged from 0–10 nm, typical of the CND sizes [18] and Pd nanoparticles had a wide range of large particle sizes ranging from 27–50 nm.

Figure 2 shows the successful synthesis of Pd/CNT catalyst prepared via hydrothermal synthesis elucidated by HRTEM images below. The successful synthesis has further supported the presence of palladium on the EDS spectrum of the Pd/CNT catalyst. The synthesized material was found to have a particle size distribution of Pd nanoparticles to be 38.65 nm.

3.1.2. XRD analysis
Figures 3(A) & (B) shows XRD spectra of CND support, and Pd/CND catalyst (A), CNT support, and Pd/CNT catalyst (B). Amorphous materials are characterized by broad peaks as seen from the XRD spectrum of CND with a broad peak observed at 24.85° thus CND are amorphous carbon material [20]. Crystalline materials are characterized by sharp peaks on the XRD spectrum as seen by the sharp peaks evident on the spectra of Pd/CND & Pd/CNT catalysts. Strong sharp peaks at 41°, 46°, 69°, and 83° were observed for Pd/CND and Pd/CNT catalysts, which are indexed as (1 1 1), (2 0 0), (2 2 0), and (3 1 1) respectively for the face-centered-cubic (fcc) lattice crystal structure facets of the Pd [21]. The Pd (1 1 1) shows the strongest diffraction peak, assigned to oxidation of an active facet of small organic small molecules [22–24]. The incorporation of Pd on both CND and CNT supports did not change the structure of the support materials as the peaks for both CND and CNT are retained with a decrease in intensity in figure 3 and the sharp diffraction peaks are due to the high crystallinity of Pd nanoparticles. Debye–Schererr equation \((D = k\lambda/\beta \cos \theta)\) was used to evaluate the average size of samples, where \(D\) is the diameter of the sample material, \(k\) is the shape factor (0.90), \(\lambda\) (Cu K\(\alpha\)) = 0.154059 nm, and \(\beta\) is the full width at half maximum of the diffraction peaks in radians [21, 25]. The size of Pd nanoparticles in Pd/CNT and Pd/CND were derived from the full-width half-maximum (FWHM) of the strongest intensity Pd(1 1 1) peak reflection and found to be calculated to be 37.4263 nm and 39.1386 nm respectively [22]. The sizes of the Pd nanoparticles in both Pd/CNT and Pd/CND are comparable to one another and to the sizes noted in HRTEM. The large size of the Pd nanoparticles is as a result of the sintering of palladium nanoparticles [22, 23]. There are also several reasons that contributed to the large Pd crystallite size which include XRD reflecting even particles that are smaller than 0.5 nm as a result of their XRD pattern, the XRD peak broadening is not only caused by the crystallite size but it is also caused by factors such as the grain boundaries, chemical heterogeneities, stacking faults, dislocations, micro stresses, twinning, etc. [26, 27].

3.1.3. FTIR analysis
Functional groups are used to facilitate the attachment of metal nanoparticles on the surfaces of carbon materials. FTIR was conducted to investigate changes in the functional groups of CND and CNT supports after functionalization by strong acids and incorporation of palladium on their surfaces [28]. Spectra were taken in the range between 500 to 4000 cm\(^{-1}\) and both spectra are very much similar which is expected as carbon nanomaterials possess similar functional groups. In both spectra shown in figure 4, the band between 3126 and
3461 cm$^{-1}$ is attributed to the O–H stretch of the hydroxyl group due to the oscillation of the carboxyl group formed during oxidation or functionalization of CNT [27]. The peaks on the O–H stretch may also be due to water or moisture adsorbed by the KBr, which was used for FTIR analysis. Although the KBr was heated at 80 °C for 24 h before analysis, moisture or water may have not been completely eliminated from the sample thus leading to the assumption of most O–H vibrations originating from moisture in the sample rather than from the functional groups attached to the surface of the CNT [29]. The band at 1726 cm$^{-1}$ is associated with the C=O vibrations of carboxyl or carbonyl groups. The peak at 1384 cm$^{-1}$ is associated with C–O or C–O–C vibrations of ether, ester, carbonyl, or carboxyl groups [27, 28]. It can be seen from figure 4 that the intensity of this peak increased after the treatment of both CND and CNT with strong acids indicating successful functionalization of these carbon nanomaterials and an increase in the number of active species that allow for bonding with other species. Weak shoulder peaks appearing between 2836 and 2990 cm$^{-1}$ can be associated with –CH$_2$ or –CH$_3$ stretching vibrations [30].

Figure 1. (A&C) HRTEM images, (B&E) particle size distribution curves of CND and Pd/CND respectively, and (D) EDS plot of Pd/CND.
Figure 2. (A) TEM image, (B) EDS plot, and (C) particle size distribution curve of Pd/CNT catalyst.

Figure 3. XRD images of (A) CND and Pd/CND, (B) CNT and Pd/CNT.

Figure 4. FTIR images of (A) CND, fCND (functionalized carbon nanodots), and Pd/CND, (B) CNT, fCNT (functionalized single walled carbon nanotubes), and Pd/CNT.
3.2. Electrochemical characterization

3.2.1. Cyclic voltammetry

Cyclic voltammetry (CV) was used to determine the electrocatalytic activity of carbon-supported Pd-based catalyst, the rate of electron transfer processes, and potentials at which redox reactions occur [29–31]. The electrocatalytic activity of the Pd/CNT and Pd/CND catalysts synthesized and the commercially bought Pd/C catalyst for ethylene glycol oxidation in alkaline media was studied by cyclic voltammetry (CV). The CV of the catalysts on the glassy carbon electrode in 1 M KOH are shown in figure 5(A). In all plots, OH\textsuperscript{−} adsorption peak was observed from the −1.5 V to 1.00 V potential window while the PdO reduction peak was observed from the 1.00 V to −1.5 V potential window. Pd/CNT has the highest oxygenated species reduction peak at lower potentials that are beneficial for ethylene glycol oxidation [31]. These CV curves were used to determine the electrochemically active surface areas (EASA) of the prepared electrocatalysts (Pd/CNT, Pd/CND, and Pd/C). EASA of the electrode materials were calculated using the formula:

\[ \text{EASA} = \frac{Q}{s/l} \]

where Q is coulombic charge obtained by integrating the area under the PdO reduction peak, s is the proportionality constant (405 μC cm\textsuperscript{−2}) and l is the palladium loading (g cm\textsuperscript{−2}) [32].

The EASA values for Pd/C, Pd/CNT, and Pd/CND were calculated to be 98.09 cm\textsuperscript{2} mg\textsuperscript{−1}, 175. 15 cm\textsuperscript{2} mg\textsuperscript{−1} and 314.07 cm\textsuperscript{2} mg\textsuperscript{−1}, respectively. The CV currents were normalized to the electrode surface area and EASA as shown in figure 5(B). The Pd/CNT catalyst gave the highest current response of 1799 mA mg\textsuperscript{−1} indicating the best catalytic activity followed by Pd/C and Pd/CND. The high catalytic activity of Pd/CNT is a result of the high electroactive surface area for ethylene glycol oxidation and the high catalytic activity nature of CNT as a support material in comparison to other carbon support materials [15, 31].

To determine the electrochemical processes taking place at the glassy carbon electrode surface (adsorption or diffusion), different scan rate studies (10 to 100 mV s\textsuperscript{−1}) were performed as shown in figure 6. Figure 6(A) shows an irreversible peak because only the oxidative peak of ethylene glycol oxidation is observed. This irreversibility may be due to an inactive or insufficient charge transfer rate to maintain the surface equilibrium. Pd/CNT (B) and Pd/C (C) plots show the behavior of a quasi-reversible plot with peak potential drifting to more extreme potentials as the peak current increases with the scan rate [33]. This shift in potentials may be attributed to the build-up of poisonous intermediates formed during the oxidation of ethylene glycol on the electrode surface. Although poisonous species may slow down the catalyst activity, the lower the oxidation onset potential, and the higher the peak current density, the better the catalytic activity of the catalyst.

The peak current of each scan rate was plotted against the square root of the scan rate to determine the processes occurring at the electrode surface. For a fast electron transfer process with diffusion-reaction taking place, the peak current will be proportional to the square root of the scan rate as described by the Cottrell equation [34]. The straight-line plot of Pd/CNT as seen in figure 7(B) implies that electron transfer reactions occur in a homogenous manner. The plot of Pd/CND and Pd/C catalysts in figures 7(A) & (C) do not have a perfect linear fit graph, due to electron transfer reactions occurring between the electrode and adsorbed molecules on the electrode surface as ethylene glycol is oxidized. To further investigate what occurs on the electrode surface, log peak current and log scan rate plots were plotted as shown in figures 7(D)–(F) which gave the slopes of 0.3220, 0.01688, and 1.0567 for Pd/CNT, Pd/CND, and Pd/C respectively. The slope of Pd/CNT is close to a theoretical value of 0.5 for a diffusion-controlled ideal reaction at the electrode surface [33].

![Figure 5](image-url)
Figure 6. Cyclic voltammograms of (A) Pd/CND, (B) Pd/CNT, and (C) Pd/C catalysts respectively at different scan rates in 1 M KOH + 1 M ethylene glycol.

Figure 7. Peak current as a function of the square root of scan rate (graph A, B, and C) and the log-log plot of the absolute value of the peak current versus scan rate (graph D, E, and F) for the of Pd/CND, Pd/CNT, Pd/C respectively at 10 mV s$^{-1}$ to 100 mV s$^{-1}$ in 1 M KOH + 1 M ethylene glycol.
3.2.2. Chronoamperometric analysis

Electrochemical kinetics, stability, and durability form part of the properties of a good catalyst which generally means that for a cell to operate for longer hours, it must have high stability that will allow it to run longer for commercial practical purposes [35–37]. The stability of Pd/CND, Pd/CNT, and Pd/C catalysts for ethylene glycol oxidation was investigated with chronoamperometry at 0.40 V. From chronoamperometric plots in figure 8, the current density of Pd/CND catalyst instantly decays at a faster rate than that of Pd/C and Pd/CNT catalysts. This spontaneous decay may be due to the formation of poisonous species such as CO during ethylene glycol oxidation [38]. From the curve, the Pd/CNT catalyst curve decays slower with high initial and steady-state current densities compared to the other two catalysts thus it is more stable. This shows that CNT is better support material for ethylene glycol oxidation than CND and activated carbon due to its high mechanical stability and tolerance to poisonous species formed during ethylene glycol oxidation. Considering that the Pd loading into the carbon materials was the same, the high activity performance of Pd/CNT catalysts could also be due to the interactions of positively charged Pd with negatively charged CNT leading to no agglomerations and non-uniform size distribution of Pd nanoparticles. This interaction improved the stability of the catalyst and the little number of Pd nanoparticles incorporated into CNT led to improved catalytic activity as the smaller the particle, the higher the activity [35–40].

3.2.2.1. Electrochemical impedance spectroscopy (EIS)

EIS is the technique used to check the properties of modified electrodes in-depth looking at the solution interface reactions [41]. The impedance response of the Pd/CND, Pd/CNT, and Pd/C catalysts are illustrated in

[Figure 8. Chronoamperometric detection of Pd/CND, Pd/CNT, and Pd/C catalysts at 1000 s in 1 M KOH + 1 M ethylene glycol.]

[Figure 9. (A) Nyquist plots of Pd/CND, Pd/CNT, and Pd/C catalysts obtained in 1 M KOH + 1 M ethylene glycol.]
figure 9. Generally, the presence of a capacitance double layer between the electrolyte and the electrode interface is characterized by the presence of the semicircle at high-frequency regions whereas the diffusion-limited processes are characterized by the linear segment in the lower frequency region [42, 43]. For these various catalysts, observed were semicircles in the high-frequency region for Pd/CND and Pd/C catalyst in comparison to the Pd/CNT, indicating the occurrence of charge transfer reactions on the surface of the catalyst of Pd/CND and Pd/C catalyst as indicated in figure 8. The results given by EIS are in agreement with the CV results acquired and reported above. Theoretically, an increase in charge transfer resistance ($R_{ct}$) leads to an increase in the semicircle diameter which results in a slow charge transfer rate [44–46]. The order of semi-circle diameters is $Pd/CNT < Pd/C < Pd/CND$, meaning that the rate at which ethylene glycol was oxidized on the electrode surface was faster in Pd/CNT modified electrode than in Pd/C and Pd/CND catalysts.

4. Conclusion

The successful synthesis of fCND, fCNT, Pd/CND, and Pd/CNT, was validated by HRTEM coupled with EDS that showed the presence of palladium on the palladium-based catalysts. The particle size distribution was found to be 0.5635 nm and 0.9395 nm for Pd/CND and Pd/CNT respectively using the images acquired from TEM. The catalytic activity of Pd/CNT was higher than that of Pd/CND and Pd/C for the oxidation of ethylene glycol. The oxidation of ethylene glycol on Pd/CNT occurred fast as validated by the directly proportional relationship of peak current with the square root of the scan rate of Pd/CNT meaning that the rate at which ethylene glycol was oxidized on the electrode catalyst as indicated in figure 8, fiCND and Pd/CND catalysts.

Acknowledgments

The authors would like to thank the Centre for Nanomaterials Science Research, University of Johannesburg, South Africa, National Research Foundation of South Africa grant number [NRF-TTK 118148] and Department of Science and Technology and National Nanoscience Postgraduate Teaching and Training Programme (NNPTTP).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Katlego E Raseruthe orcid.org/0000-0002-1618-1956
Thabo Matthews orcid.org/0000-0002-9766-2144
Sandile S Gwebu orcid.org/0000-0002-4365-4077

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