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Synthesis of Graphitic Crude Glycerol-Based Carbon for Potential Energy Conversion and Storage Based Material

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Abstract **-** In this study, phosphorus-doped on crude glycerol-based carbon was synthesized via acid pyrolysis. As a sustainable approach, crude bioglycerol produced from the transesterification of waste canola oil was utilized as the carbon source, and phosphoric acid served as the acid dehydrator as well as a phosphorus source. The as-prepared phosphorus-doped carbon (P-CGBC) shows a remarkable specific capacitance of 381 F/g at 0.5 A/g current density and an energy density of 53 Wh/kg. P-CGBC was also employed as a support material with palladium (Pd-P-CGBC) for ethanol electro-oxidation and showed comparable properties as an anodic material. These results suggest that crude glycerol-based carbon can be a potentially promising electrode material for energy conversion and storage applications.

Keywords**:** Bioglycerol, Phosphorus, Energy conversion, Supercapacitor, Direct Ethanol Fuel Cell, Carbon

1. Introduction

The biodiesel sector has expanded significantly during the past decades [1]. However, its manufacture necessarily results in the generation of 'glycerol' as a by-product. The global crude glycerol output is predicted to increase to 6 million tons by 2025 [2]. The discovery of high-value-added products from glycerol would considerably increase the profitability and sustainability of this industry. Glycerol has been identified as a promising 'green construction' material for the chemical industry. Various instances [3] of glycerol conversion via oxidation, hydrogenolysis, dehydration, esterification/etherification, pyrolysis/gasification, and steam reforming have been documented [4]. Because they maintain their stability in a variety of electrolytes, from the most acidic to the most alkaline, carbons are appropriate electrode materials. The capacitance characteristics of several types of carbon, including carbon aerogels [5], xerogels [6], carbon nanostructures [7], and activated carbons [8, 9], have been studied. Additionally, activated carbons' high capacitance characteristic is widely known and has attracted a lot of interest [10-12]. The surface area and pore volume of activated carbons are the main determinants of their capacitance [12], which may be improved by adding a heteroatom to the carbon matrix. The pseudo-capacitive effect is thus created as a result [5]. Contrary to more traditional precursors for activated carbon, such as natural organic solids or agricultural wastes, crude glycerol is significantly less researched among the precursors for carbon materials even though it is greatly produced in the biodiesel sector [13]. Additionally, only a small number of research have examined the conversion of crude glycerol-based carbon [14], whereas the majority of studies [15, 16] concentrate on using purified and commercially available glycerol. In light of the foregoing, the purpose of this study is to investigate graphitic crude glycerol-based carbon materials produced by acid dehydration of crude glycerol (P-CGBC) as the carbon precursor for potential energy conversion and storage-based material. This research primarily serves as a platform for investigating the utilization of waste crude bioglycerol as a carbon source to synthesize exceptionally conductive graphitic carbon materials.

2. Methodology

All chemicals were purchased from Sigma-Aldrich and used as received without prior purification or treatment.

2.1. Synthesis procedure of crude glycerol-based carbon

A dehydration of crude glycerol resulted in the production of crude glycerol-based carbon. A 4:1 ratio of concentrated phosphoric acid to crude glycerol was used during synthesis. The acid was progressively added to weighed crude glycerol in a 500 mL capacity beaker. The latter was heated from 25 °C to 180 °C using a hot plate magnetic stirrer. The hue of the initial combination shifted from brown to black when the temperature was raised. When the foaming stopped after 20 minutes, the heating was turned off. The obtained black paste was calcined at 600 °C for one hour. The product was washed with distilled water until neutral pH and dried in the oven at 100 °C. The dried was collected and labelled as P-CGBC. The material was characterized with SEM,/EDs, TEM, XRD, Raman spectrometer, and SAED.

For the energy conversion application, Pd-P-CGBC was prepared by sonicating PdCl and P-CGBC (40:60 weight ratio) in ethanol for 3 hours The solvent was evaporated land the product was calcined at 350 °C for 1 hour.

2.2. Electrochemical analysis

Biologic potentiostat equipped with a three-probe electrode was employed. Pt wire, and Ag/AgCl (KCl saturated) were employed as counter and reference electrodes respectively. Graphite sheet was used as the current collector and 1 M NaOH as the electrolyte. The working electrode was prepared by drop casting of sample ink on the graphite sheet using 5% Nafion solution as the binder and dried in the oven at 70 °C for 12 hours.

3. Result and Discussion

3.1. Morphological characterization

In the pursuit of advanced materials for supercapacitors and energy conversion applications, the characterization of P-CGBC emerges as a critical step. This article delves into the comprehensive characterization of P-CGBC, focusing on its potential in supercapacitance and ethanol electrooxidation.

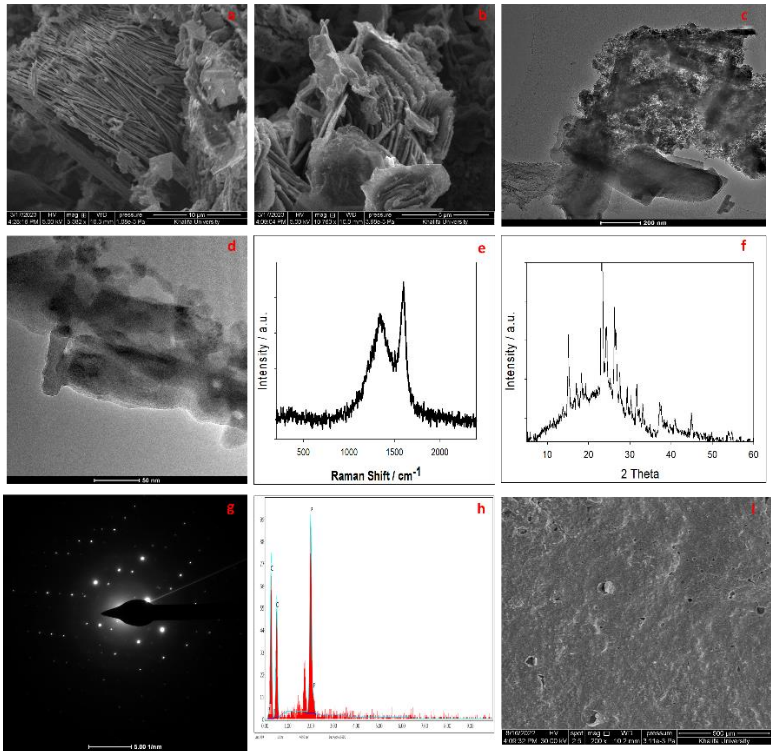

Fig. 1: SEM image (a,b), TEM image (c,d), Raman spectral (e), XED pattern (f), SAED pattern (g), and EDS spectrum (h) of P-CGBC, and SEM image Pd-P-CGBC.

SEM and TEM analysis were carried out to explore the material morphology, as shown in Figures 1a-1d, both techniques confirm the graphitic nature of P-CGBC with stacked sheets observed. Raman spectroscopy (Figure 1e) reveals essential structural aspects of P-CGBC. The D and G band peaks in the Raman spectra signify key characteristics. The D mode suggests a disordered carbon structure, while the G band points to the presence of *sp*^{2} hybridized carbons within the graphitic layer. The intensity ratio (ID/IG) below 1 also suggests a graphitic structure, enhancing electronic conductivity, a crucial factor for supercapacitance and electrooxidation applications.

Furthermore, X-ray diffraction (XRD) patterns (Figure 1f) offer insights into the crystallographic structure of P-CGBC. A diffraction peak at ~23° signifies reflections from (002) planes. The interlayer spacing (d002) provides critical information, measuring at 0.39 nm. Additionally, P-CGBC reveals a 001 peak at ~15°, indicating a high level of oxidation and a d001 interlayer distance of 0.59 nm. This distinctive pattern suggests a graphitic oxide nature, vital for supercapacitance.

The SAED patterns (Figure 1h) show the polycrystalline nature of P-CGBC, while energy-dispersive X-ray spectroscopy (EDS) (Figure 1h) confirms the presence of phosphorus alongside carbon and oxygen in P-CGBC, critical for its tailored properties. The Pd deposited on the P-CGBC SEM image shown in Figure 1i shows a slightly porous and agglomerated deposition of Pd on the surface of P-CGBC. Overall, the graphitic structure, electron conductivity as a result of phosphorus doping, and tailored morphology make it a promising material in the realm of energy conversion and storage.

3.2. Electrochemical analysis

The electrochemical analysis of the as-prepared material as an anode material were studied using a three-probe electrode system via cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) cycling with applied current density ranged from 1 A/g to 10 A/g.

a. Supercapacitor Study

CV characterization at different scanning rates was performed to evaluate the specific capacitance of the phosphorus-doped crude glycerol-based carbon. As shown in Figure 2a, the leaf-like shape of the voltammogram at lower scanning rates implies an increase in resistivity. The specific capacitance decreases with an increasing scanning rate (Figure 2b). This is due to the ions' occupancy at the surface of the carbon material at a higher scanning rate. However, lower scanning rates allow the ions to diffuse inside the pores and enhance the chances of the double layer's formation within the holes of the electrode material.

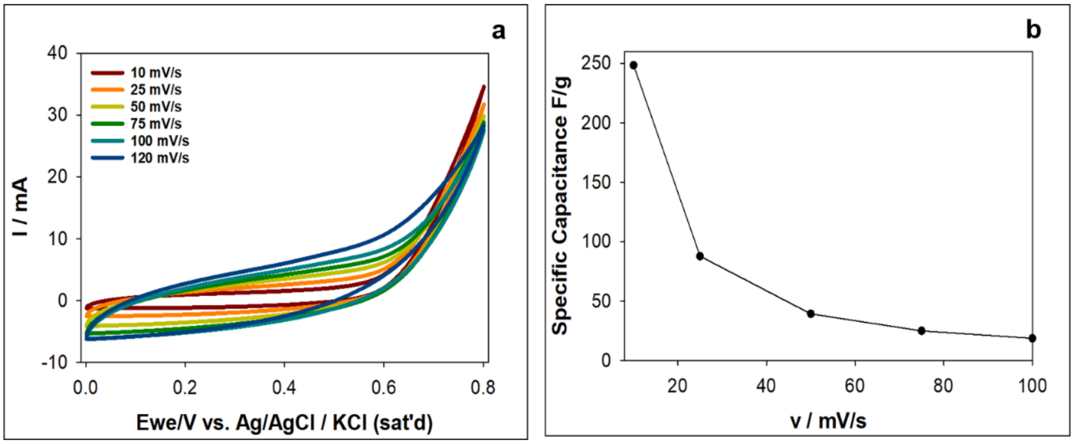

Figure 2. Cyclic voltammetry profile of P-CGBC in 1 M NaOH at different scanning rates (a), and variation of specific capacitance as a function of scanning rates of P-CGBC (b).

The crude glycerol-based carbon electrodes were further characterized for their electrochemical properties using galvanostatic cycling with potential limitation (GCPL). The presented GCPL curves are asymmetrical triangular shapes. This is a result of the capacitive and reversibility properties of the electrodes [14, 17]. Furthermore, there was no significant change in the behaviour of the electrodes after twenty cycles.

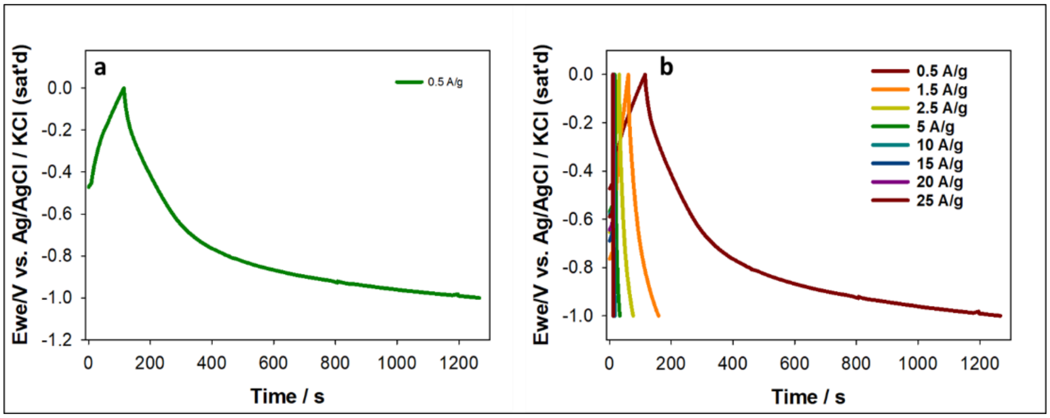

Figure 3. GCPL curve at the applied current density of 0.5 A/g (a) and at different applied current densities (b) of P-CGBC.

As shown in Figure 3, the GCD curve is in agreement with the trend observed in the CV curve as different current densities. There is a slight deviation at an applied current density of 0.5 A/g which shows the longer discharge timing and therefore signifies that the electrode material has a specific capacitance [17]. The estimated specific capacitance of the phosphorus-doped crude glycerol-based carbon (P-CGBC) is approximately 381, 158, 108, 85, and 15 F/g at current densities of 0.5, 1.5, 2.5, 5, 10 A/g, respectively (Figure 3a). A maximum energy density of approximately 53 Wh/kg at a power density of 294 W/kg, while retaining the power density of 5000 W/kg at an energy density of 2 Wh/kg was estimated.

Table 1: Comparison of specific capacitance, current density, and energy density of this work and those reported in the literature. .

Carbon Source	**Heteroatom**	**Electrolyte**	**Specific Capacitance**	**Current densities (A/g)**	**Energy density (Wh/kg)**	**Ref**
Coconut shell		1 M Na_2SO_4	154 F/g	10 mV/s	NR	[18]
Graphene	-	6 M KOH	283 F/g	0.1	NR	[19]
Glycerol (pure)	S (from H_2SO_4)	0.5 M Na_2SO_4	291 mF/cm2	10 mV/s	NR	[15]
Cow margarine	S	6 M KOH	337 F/g	1	37.9	[20]
Crude glycerol	**P**	**1 M NaOH**	**381 F/g**	**0.5**	**53**	**This Work**
Crude glycerol	S (from H_2SO_4)	1M NaCl	96.7	1 mV/s	-	[14]

Compared to the previously reported biomass-based activated carbon or nanoparticle, P-CGBC exhibit a remarkable specific capacitance, energy density, as well as power density (**Error! Reference source not found.**). These results suggest that P-CGBC can be a potentially promising electrode material for energy storage applications.

b. Ethanol Electro-oxidation

The electrocatalytic performance of palladium loaded on crude glycerol-based carbon (Pd-P-CGBC) catalyst electrodes towards ethanol electro-oxidation was analyzed using cyclic voltammetry in 1 M NaOH with 1 M ethanol. CV is the common technique used to evaluate the electrocatalytic activity of catalysts, rate of electron transfer, as well as redox reaction potentials [21-24].

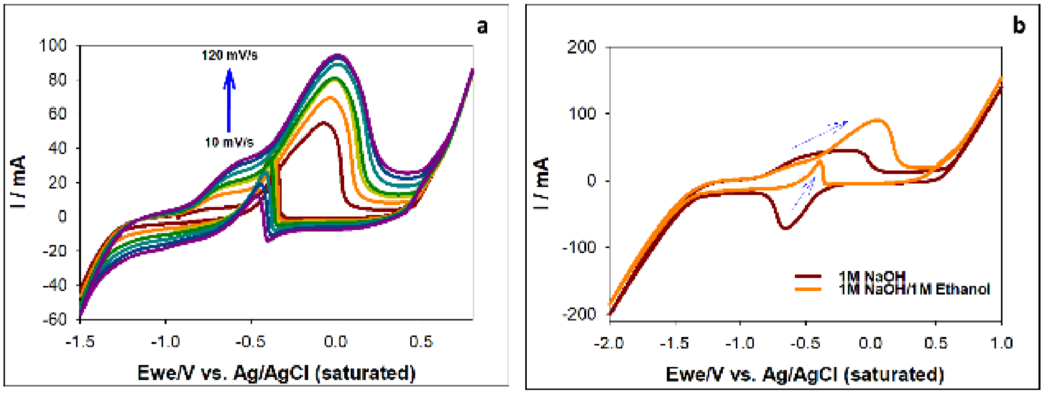

Figure 4. CV curve of Pd-P-CGBC at different scan rates in 1 M NaOH + 1 M ethanol (a), and with and without 1 M ethanol (b) at 50 mV/s scan rate.

The profile of the CV curve (4) for the as-prepared catalyst is in agreement with that reported in the literature [25-27]. The CV analysis at different scan rate were carried out to determine the electrochemical process taking place on the surface of the graphite sheet substrate (10 mV/s – 120 mV/s]. 4a shows the increase in the ethanol oxidation peaks with increasing scan rate, and Figure 4b shows two distinct oxidation peaks in reverse and forward scans. These oxidation peaks can be ascribed to the ethanol electro-oxidation compared to the CV curve without ethanol (4b).

Table 1 .Comparison of Pd-P-CGBC with other Pd-based electrocatalyst for ethanol oxidation reactions.

Material	**Electrolyte**	**[Ethanol]**	**Substrate**	**ECSA/j_p**	**Reference**
Pd-Co nanotube	1 M KOH	1 M	Carbon cloth	501.3 cm^2/mg	[28]
Pd-Co	1M KOH	0.5 M	Ni Bowl	95.65 cm^2/mg 240.1 mA/cm^2	[26]
Pd-P-CGBC	**1 M NaOH**	**1 M**	**Graphite sheet**	**255.6 cm^2/mg**	**This Work**
Pd-Co/GO	1 M KOH	1 M	GCE	64.2 mA/cm^2	[29]
Pd-Co/MWCNT	1 M KOH	1 M	GCE	198 cm2 1734 mA/mg	[30]

The modified electrode's electrocatalytic activity of the prepared catalyst for ethanol oxidation reaction was compared compared with some earlier works. The electrochemical surface area (ECSA) of the modified electrode was compared with with other outcomes for various catalysts in the literature that utilized Pd-based bimetallic catalysts or conductive substrate substrate as anode material.

Table 1 demonstrates that the Pd-P-CGBC modified electrode performs well and that the findings are comparable to those reported in the literature. As a result, it can support the ethanol oxidation process as an active electrocatalyst.

4. Conclusion

In summary, we have effectively synthesized phosphorus-doped graphite, such as crude glycerol-based carbon (P-CGBC), and successfully loaded palladium onto P-CGBC without the need for pre-treating the waste crude bioglycerol. This synthesis involved the use of phosphoric acid as both the dehydrator and phosphorus source, followed by thorough characterization. The fabricated P-CGBC electrode exhibit a high specific capacitance 382 F/g and a remarkable energy density of 53 Wh/h. Similarly, the findings show that the Pd-P-CGBC can significantly increase the current density and ECSA of ethanol electro-oxidation in an alkaline medium, indicating a promising anodic catalyst potential for DEFCs. These results suggest that graphitic crude glycerol-based carbon (CGBC) can be a potentially promising support material for energy conversion and storage applications.

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