



Pecan shell-derived nitrogen-doped porous carbon as a sustainable metal-free electrocatalyst for the oxygen reduction reaction

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ABSTRACT

Increasing energy demand and rapid environmental deterioration are major challenges of modern times. Proton exchange membrane fuel cells and metal-air batteries are considered as the most promising alternatives. Both technologies rely critically on the oxygen reduction reaction (ORR) at the cathode, and its efficiency determines the overall efficiency of the fuel cell. At present, platinum-based materials are regarded as the benchmark electrocatalysts for ORR due to their high catalytic activity and favorable reaction kinetics. Despite their potential, the high cost and scarcity of platinum-based ORR catalysts remain a challenge for these systems. Biomass-derived carbon materials have attracted considerable attention as one of the viable alternatives explored in recent years due to their renewability, low cost, environmental friendliness, and natural abundance of carbon. In this work, nitrogen-doped carbon derived from pecan shell was synthesized by ZnCl_2 activation and melamine doping at three mass ratios (1:0.125, 1:0.25, 1:0.5) and characterized by SEM, EDS, Raman spectroscopy, BET surface area analysis, XRD, and XPS. ORR activity was evaluated in 0.1 M KOH using cyclic and linear sweep voltammetry. The 1:0.25 melamine-doped sample exhibited the optimal ORR performance, with the major part of the positive onset potential and the highest limiting current density among all three tested catalysts. These results demonstrate the potential of pecan shell as a biomass precursor for metal-free ORR electrocatalysts.

1. Introduction

The demand for clean and sustainable energy technologies is growing globally at a rapid rate, leading to research on electrochemical energy conversion systems such as fuel cells and metal-air batteries. These systems are considered alternatives to fossil-fuel-based energy sources on account of their energy conversion efficiency and environmentally friendly operation. However, the practical performance of these devices is strongly limited by the sluggish kinetics of the oxygen reduction reaction (ORR) occurring at the cathode [1]. Therefore, the advancement of highly active, stable, and cost-effective ORR electrocatalysts remains an ongoing challenge in the field of sustainable energy conversion.

At present, platinum-based materials are taken as standard electrocatalysts for ORR based on their high catalytic activity and favorable reaction kinetics. However, the widespread commercial use of Pt-based catalysts is hindered by low natural abundance, high cost, poor long-term stability, and susceptibility to methanol crossover and CO poisoning [2]. Beyond noble-metal catalysts, a range of non-precious metal systems have

also been extensively investigated as ORR electrocatalysts, including single-atom catalysts [3,4], Fe-N-C and metal-nitrogen-carbon materials [5,6], transition-metal-nitrogen-carbon hybrids [7], and computationally guided carbon-based electrocatalysts [8]. These drawbacks have spurred efforts to discover sustainable alternatives for ORR applications, such as abundant metal and carbon-based electrocatalysts.

Among a number of alternatives explored in recent years, biomass-derived carbon materials have gained attention because of their renewability, low cost, environmental friendliness, and naturally abundant carbon content [9]. In addition, biomass-derived carbons frequently contain naturally occurring heteroatoms such as nitrogen, oxygen, sulfur, and phosphorus, which enhance catalytic activity after carbonization and activation processes [10]. Different biomass sources that include pine needles [11], microalgae [12,13], hemp [14], and other plant-based biomass feedstocks have been widely investigated as carbon precursors for ORR electrocatalysts. Agricultural and lignocellulosic residue-derived Fe-N-C electrocatalysts [6,15] and iron-nitrogen co-doped carbon composites [16] showed similar ORR activity. While iron-phthalocyanine functionalized biomass carbons [17] have

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expanded the range of precursors. Nanostructured architectures from biomass, such as engineered carbon nanosheet composites [18] and hierarchically porous carbon aerogels [19], have further expanded the structural diversity of this class of materials. The broad scope and diversity of biomass-derived electrocatalysts have been achieved through nitrogen-doped carbons from wood [5] and biomass processing routes assisted by ultrasound and ball-milling [20,21]. Biomass feedstocks have been extensively reviewed for their wide applicability in the development of sustainable electrocatalysts [1,22].

The catalytic activity of biomass-derived carbon materials can be improved through heteroatom doping and chemical activation strategies. Among different heteroatoms, nitrogen doping has been widely recognized as a potent approach to strengthen ORR performance. Nitrogen incorporation modifies the electronic structure and introduces structural defects. These changes improve electrical conductivity and generate active sites for oxygen adsorption and electron transfer [2]. In particular, pyridinic and graphitic nitrogen species are considered to be beneficial for ORR activity due to their ability to redistribute the charge within the carbon framework and to improve the kinetics of oxygen reduction [12,23,24]. Fundamental studies show that nitrogen configuration is critical for ORR selectivity, with pyridinic-N and graphitic-N playing complementary roles in the 4-electron pathway [8,25]. Along with nitrogen doping, chemical activation with ZnCl_2 has been reported to be an effective method to produce highly porous carbon structures with large specific surface area and improved mass-transport properties [26]. ZnCl_2 activation promotes pore formation during carbonization and increases exposure of catalytically active sites, improving electrochemical performance.

Recent work shows that the combined effects of porous carbon frameworks, defect engineering, and heteroatom doping can lead to high ORR activity in biomass-derived carbon electrocatalysts. For example, ZnCl_2 -activated porous biomass carbon shows an improved onset potential, high limiting current density, and good methanol tolerance in alkaline media [27]. Similarly, nitrogen-doped porous carbon materials derived from various biomass precursors have increased defect density and the presence of nitrogen-containing active sites [17], which enhanced ORR activity [19]. Biomass-derived catalysts exhibiting bifunctional ORR/OER activity coupled with better stability further underscore the versatility of this class of materials. Additionally, biomass-derived carbon structures incorporating transition-metal nitrogen functionalities show competitive performance in ORR [7,18]. Despite these advances, the exploration of pecan-shell-derived porous carbon materials for ORR applications remains limited, particularly in systems combining ZnCl_2 activation and melamine-assisted nitrogen doping.

In this study, nitrogen-doped porous activated carbon is synthesized from pecan shell biomass via ZnCl_2 -assisted activation. Melamine is then added to achieve nitrogen doping for oxygen reduction reaction (ORR) electrocatalysis in an alkaline medium. The prepared materials are meticulously characterized using scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and electrochemical measurements to elucidate their structural, surface, and catalytic characteristics. The relationship between porosity, defect structure, nitrogen functionalities, and ORR performance is also examined. This study aims to provide a cost-effective approach for converting agricultural biomass waste into functional electrocatalysts for sustainable energy applications.

2. Experimental

2.1. Materials

Pecan shells (*Carya illinoensis*) were collected from the Southern University and A&M campus, Baton Rouge, Louisiana, and used as the biomass precursor. Zinc chloride (ZnCl_2 , 98%, Sigma-Aldrich, USA) was used as the chemical activating agent. Melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99%, Sigma-

Aldrich, USA) served as the nitrogen precursor for heteroatom doping. Potassium hydroxide (KOH, ACS grade, 88% assay, Mallinckrodt Chemicals, USA) was used to prepare the alkaline electrolyte. 5 wt% Nafion solution (Alfa Aesar, Ward Hill, MA, USA) was used as the electrode binder. Litmus paper was used to monitor the pH of the washing solutions. All solutions were prepared with deionized water, and all chemicals were used as received.

2.2. Materials characterizations

The morphology and surface structure of the synthesized materials were investigated using scanning electron microscopy (SEM, Thermo-Fisher Helio G5 Xe PFIB/SEM). X-ray diffraction (XRD) patterns were recorded using a Bruker D8 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) over a 2θ range of 10° – 80° at a scan rate of 2° min^{-1} . The graphitization degree and defect density were determined using a Renishaw Raman microscope by analyzing the D and G bands. X-ray photoelectron spectroscopy (XPS, ScientaOmicron ESCA 2SR) was used to determine elemental composition and nitrogen bonding configurations within the carbon framework. Energy-dispersive X-ray spectroscopy (EDS) was additionally used to confirm elemental distribution.

Electrochemical measurements were performed using a Princeton Applied Research VersaSTAT 3 potentiostat/galvanostat in an alkaline electrolyte. Catalyst ink was prepared by dispersing 5 mg of synthesized carbon material in 1 mL deionized water and 20 μL 5 wt% Nafion solution, followed by ultrasonication. Then, 20 $\mu\text{g cm}^{-2}$ of homogeneous catalyst ink was drop-cast onto the glassy carbon electrode (GC, 5 mm diameter), which served as the working electrode. Hg/HgO and platinum wire were used as reference and counter electrodes, respectively. Linear sweep voltammetry (LSV) measurements were performed at 600–2400 rpm at 10 mV s^{-1} in oxygen-saturated 0.1 M KOH electrolyte to evaluate ORR performance. All the measured potentials vs. Hg/HgO reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the following Nernst equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591 * \text{pH}. \quad (1)$$

The stability and methanol tolerance tests of the synthesized carbon were performed using the chronoamperometric method at a fixed rotation speed of 1600 rpm in 0.1 M KOH electrolyte. The onset potential, limiting current density, and electrocatalytic behavior were analyzed to investigate ORR activity.

2.3. Synthesis of pecan shell-derived carbon

The collected pecan shells were washed thoroughly with deionized water at room temperature to remove surface impurities and dust particles. The cleaned shells were dried in a vacuum oven (Isotemp, Model 281A, Fisher Scientific, USA) at 60°C for 24 h. The dried shells were ground into fine powder using a 400, a high-speed multi-function comminutor (motor speed 25,000 r/min, 1800 W) and sieved through a 50 mesh (0.355 mm) sieve to collect uniform fine particles. The sieved powder was carbonized in a tube furnace (Across International, NJ, USA) at 800°C for 2 h under a continuous argon atmosphere at a heating rate of $10^\circ \text{C min}^{-1}$. The resulting sample was denoted as PSC.

2.4. ZnCl_2 activation process

Pecan shell powder was mixed with ZnCl_2 at a weight ratio of 1:3 in 25 mL of deionized water and stirred with a magnetic stirrer until a homogeneous mixture was obtained. The mixture was dried in a vacuum oven at 60°C for 12 h. The dried mixture was transferred to a tube furnace and heated to 800°C at a heating rate of $10^\circ \text{C min}^{-1}$ under a continuous argon atmosphere and held for 2 h. After cooling to room temperature under argon, the product was washed repeatedly with deionized water to remove residual ZnCl_2 and other impurities until a

neutral pH was reached, as confirmed by litmus paper. The washed carbon was dried at 60 °C for 12 h and ball-milled to obtain a uniform fine powder, denoted as PAC.

2.5. Synthesis of nitrogen-doped pecan shell-derived carbon

Nitrogen doping was carried out using melamine as the nitrogen precursor. The activated carbon and melamine were thoroughly mixed by ball milling and subjected to secondary thermal annealing under an inert atmosphere. PAC was mixed with melamine at three carbon-to-melamine mass ratios (1:0.125, 1:0.25, 1:0.5) and then ball-milled to ensure homogeneous mixing. Each mixture was subjected to thermal treatment in a tube furnace at 800 °C for 2 h under continuous argon at a heating rate of 10 °C min⁻¹. The resulting nitrogen-doped carbon samples are denoted as NPAC-0.125, NPAC-0.25, and NPAC-0.5, corresponding to the three melamine ratios.

3. Results and discussion

3.1. Morphological analysis

The SEM images of the pecan shell-derived carbon samples at different stages of synthesis are shown in Fig. 1. The PSC shows a relatively dense and compact surface structure with limited visible porosity Fig.1(a). After ZnCl₂ activation, the surface of PAC changed significantly, showing a highly porous and interconnected network with a sponge-like morphology Fig. 1(b). The ZnCl₂ activation introduced abundant micro- and mesopores into the carbon matrix during the high-temperature carbonization process. After melamine treatment, the surface of NPAC retained its porous backbone, while additional granular and flake-like features were observed on the surface Fig. 1(c), which can be attributed to the incorporation of nitrogen-containing functional groups into the carbon framework [28].

The elemental composition of the synthesized carbon samples was examined by EDS. The ZnCl₂-activated carbon before nitrogen doping (PAC) consists mainly of carbon (92.82 at %) and oxygen (5.87 at %). Minor amounts of Ca, K, and Mg were also detected, reflecting the natural mineral content of pecan shell biomass. A trace Cl signal (0.32 at %) was observed, attributed to residual ZnCl₂ from the activation step. After melamine treatment, a clear N signal was detected in NPAC-0.25 with a nitrogen content of 2.45 at % (Fig. S1), confirming successful nitrogen incorporation into the carbon matrix. The oxygen content decreased to 2.30 at.% after doping, indicating further decomposition of surface oxygen groups during the second pyrolysis at 800 °C [12,29].

The X-ray diffraction (XRD) patterns of PSC, PAC, and NPAC-0.25 are shown in Fig. 2a. Two characteristic broad diffraction peaks are observed at approximately $2\theta \approx 23^\circ$ and $2\theta \approx 44^\circ$, corresponding to the (002) and (100) reflection planes of graphitic carbon, respectively [11, 26]. The minor peaks are present in the PSC before ZnCl₂ activation and acid wash, which may be due to the presence of impurities and silica. After activation and doping in the sample, no minor peaks were

observed, indicating successful synthesis of carbon without impurities.

The degree of graphitization and disorder in the PSC, PAC, and NPAC-0.25 were analyzed by Raman spectroscopy. Two characteristic bands, the D band around 1337 cm⁻¹ and the G band around 1589 cm⁻¹, were observed (Fig. 2b) in all three samples: the D band, associated with structural defects and disorder in the carbon, whereas the G band represents in-plane stretching vibrations of sp²-hybridized graphitic carbon. The intensity ratio of the D and G bands (i.e., I_D/I_G) for PSC, PAC, and NPAC-0.25 was 0.85, 0.73, and 0.76, respectively. Because PSC contains no activating agent, carbonization alone yields an amorphous, defect-rich, and poorly graphitic domain, resulting in a higher I_D/I_G ratio [14]. ZnCl₂ activation promotes rearrangement of the carbon layers, reduces defect density, and alters the pore structure, resulting in a lower I_D/I_G ratio. After N-doping, the I_D/I_G increases because nitrogen atoms have a different size and bonding geometry than carbon. This doping disturbs carbon symmetry and creates defects.

XPS was performed to investigate the surface chemical composition and nitrogen bonding configurations of the synthesized catalysts. The combined XPS survey spectrum (Fig. 2c) confirms the presence of carbon and oxygen peaks in both PSC and NPAC-0.25. In addition to this NPAC-0.25 show the addition of a nitrogen peak, confirming the synthesis of N-doped carbon. The atomic percentage of C, N, and O in PSC is 87.43, 0.40, and 10.65, respectively. It also contains other impurities like Cl, Zn, K, and Ca in the atomic percentages of 0.59, 0.03, 0.28, and 0.62, respectively. After doping and activation, there was a change in the atomic percentages of each element. The NPAC-0.25 shows atomic percentages of C, N, O, and Zn as 94.01, 2.28, 2.75, and 0.46, respectively. The high-resolution C 1 s spectrum (Fig. 2d) was deconvoluted into five components: sp²-hybridized C=C (284.8 eV), sp³-C/C-N (285.4 eV), C—O—C (287.5 eV), C=O/C=N (289.4 eV), and -COOH (291.1 eV). The dominant sp²-C peak confirms the graphitic character of the carbon framework, while the C—N peak reflects successful incorporation of nitrogen functionalities into the carbon matrix.

The O 1 s spectrum (Fig. 2e) was deconvoluted into two components corresponding to C=O (532.2 eV) and C—O—C (533.5 eV). Similarly, the N 1 s spectrum (Fig. 2f) was deconvoluted into three peaks: pyridinic N (398.6 eV), pyrrolic N (400.5 eV), and graphitic N (404.6 eV). Pyridinic N, located at the edge sites of the carbon lattice, is widely regarded as the most catalytically active nitrogen configuration for ORR, facilitating O₂ adsorption and promoting the 4-electron reduction pathway. Graphitic N substituted into the bulk carbon framework improves electrical conductivity and charge delocalization, contributing to improved electron transfer kinetics during ORR [23,24].

N₂ adsorption-desorption isotherms and BJH pore size distributions for PSC and PAC are shown in Fig. 3. PSC displays a Type I isotherm with a flat adsorption plateau and no hysteresis loop. The flat plateau and absence of hysteresis are consistent with a predominantly microporous carbon framework. PAC shows a composite Type I/IV isotherm with steep N₂ uptake at low relative pressure ($P/P^\circ < 0.1$) and a hysteresis loop from $P/P^\circ = 0.4$ to 0.9, attributed to the coexistence of micropores and mesopores formed during ZnCl₂ activation [26,30]. The BET surface

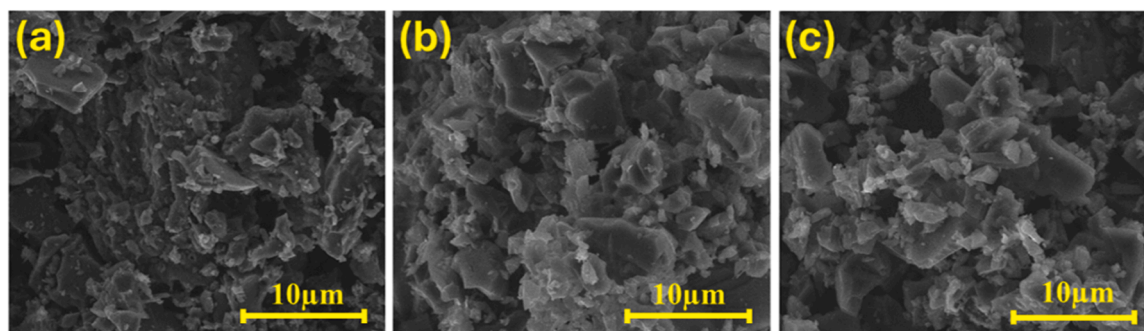


Fig. 1. SEM images of (a) PSC, (b) PAC, and (c) NPAC-0.25.

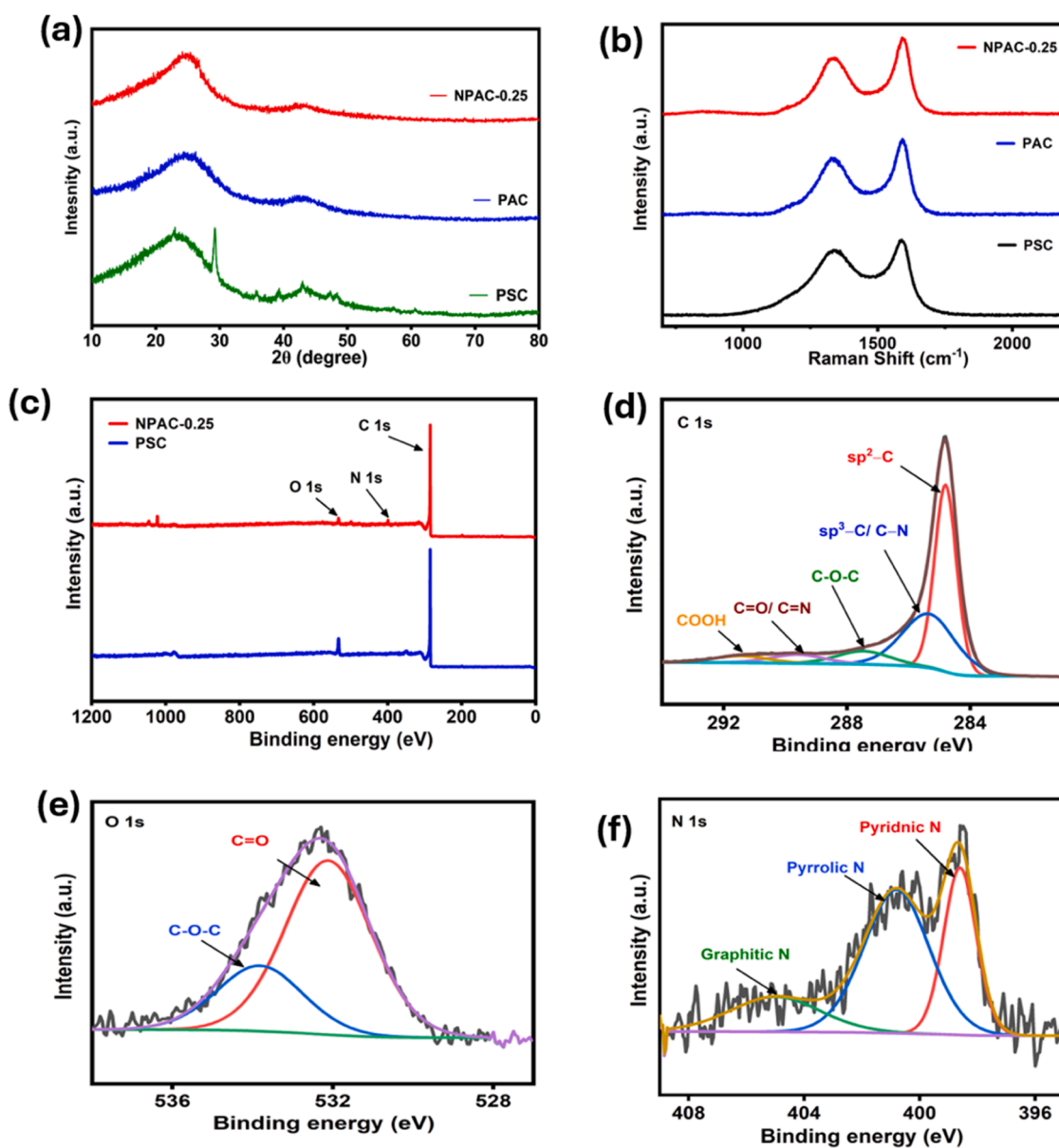


Fig. 2. (a) XRD patterns; (b) Raman spectrum; (c) comparative XPS survey spectra of PSC and NPAC-0.25; high-resolution XPS spectra of NPAC-0.25: (d) C 1 s, (e) O 1 s, and (f) N 1 s.

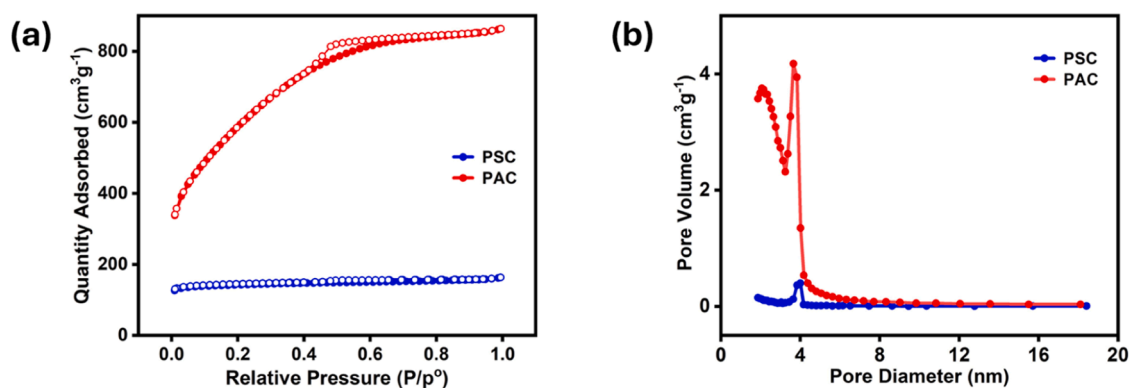


Fig. 3. (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distributions of PSC and PAC.

area of PAC is $2156.4 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of $1.322 \text{ cm}^3 \text{ g}^{-1}$ and a BJH average pore diameter of 2.73 nm . By contrast, PSC has a BET surface area of $488.8 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of $0.245 \text{ cm}^3 \text{ g}^{-1}$, and a BJH average pore diameter of 3.82 nm . ZnCl_2 activation raised the BET surface area 4.4-fold and the total pore volume 5.4-fold relative to PSC.

3.2. Electrochemical performance

The oxygen reduction reaction activity of the synthesized catalyst was evaluated using linear sweep voltammetry (LSV) measurements in oxygen-saturated 0.1 M KOH electrolyte. In the comparative LSV measurements (Fig. S2), NPAC-0.25 exhibited a more positive onset and half-wave potential than the other N-doped carbons derived from pecan shells.

As shown in Fig. 4a, the optimized NPAC-0.25 catalyst displayed a positive shift in onset potential and half-wave potential ($E_0 = 0.94 \text{ V}$, $E_{1/2} = 0.83 \text{ V}$ vs. RHE) than PAC ($E_0 = 0.87 \text{ V}$, $E_{1/2} = 0.73 \text{ V}$ vs. RHE) and PSC ($E_0 = 0.77 \text{ V}$, $E_{1/2} = 0.70 \text{ V}$ vs. RHE). However, its ORR activity remained lower than commercial Pt/C ($E_0 = 0.95 \text{ V}$, $E_{1/2} = 0.86 \text{ V}$ vs. RHE). These results suggest that this optimization improves the ORR performance of pecan shell-derived carbon, and further optimization is needed to replace Pt/C based electrode. A series of LSV curves of NPAC-0.25 (Fig. 4b), measured at different rpm, shows an increase in diffusion current density with elevated rpm. Based on the LSC curves of NPAC-0.25, the K-L plot (Fig. 4c) was analyzed in the potential range of 0.2 – 0.6 V , which shows a linear relationship at various potentials.

The methanol tolerance test analyzed the practical application of the synthesized catalyst, NPAC-0.25. This experiment was performed by adding 1 M methanol during the chronometric test. In Fig. 4d, a normal spike was seen upon the addition of methanol in the case of the NPAC-0.25 catalyst, whereas Pt/C shows a decrease in the current density and

cannot maintain its initial value. The long-term stability of NPAC-0.25 was evaluated by chronoamperometry at 1600 rpm in an O_2 -saturated 0.1 M KOH electrolyte. As shown in Fig. S3, the NPAC-0.25 retained approximately 87% of its initial current after 5000 s . The current decreased gradually during the measurement, without any sudden loss of activity. This behavior indicates that the catalyst remained electrochemically stable during prolonged operation in an alkaline electrolyte.

The ORR activity can be attributed to the combined effects of increased porosity, defect-rich carbon structure, and nitrogen-containing active sites. The porous structure generated through ZnCl_2 activation facilitated oxygen diffusion and electrolyte transport. Nitrogen doping improved charge redistribution and oxygen adsorption capability. Similar ORR enhancement mechanisms have been reported in biomass-derived porous carbon electrocatalysts containing heteroatom functionalities [31]. These findings are consistent with previously reported results for ZnCl_2 -activated and nitrogen-doped biomass-derived carbon electrocatalysts in alkaline media [13,32,33]. Comparable ORR activity trends have also been reported for nitrogen-doped carbon electrocatalysts derived from coffee grounds [32], nori seaweed-based precursors [33], and water hyacinth [34] in alkaline media. Comparisons with peat-derived carbon electrocatalysts [35] and evaluations using gas diffusion electrode setups [36] would provide better insight for analyzing the realistic fuel cell performance of the synthesized pecan shell-derived catalyst (Table 1).

3.3. Structure-Performance relationship

The porous structure and the nitrogen doping contribute to the catalyst's improved ORR performance. ZnCl_2 activation produced a highly porous carbon framework, exposing more active sites and improving mass transport through the pore network. Melamine-assisted doping

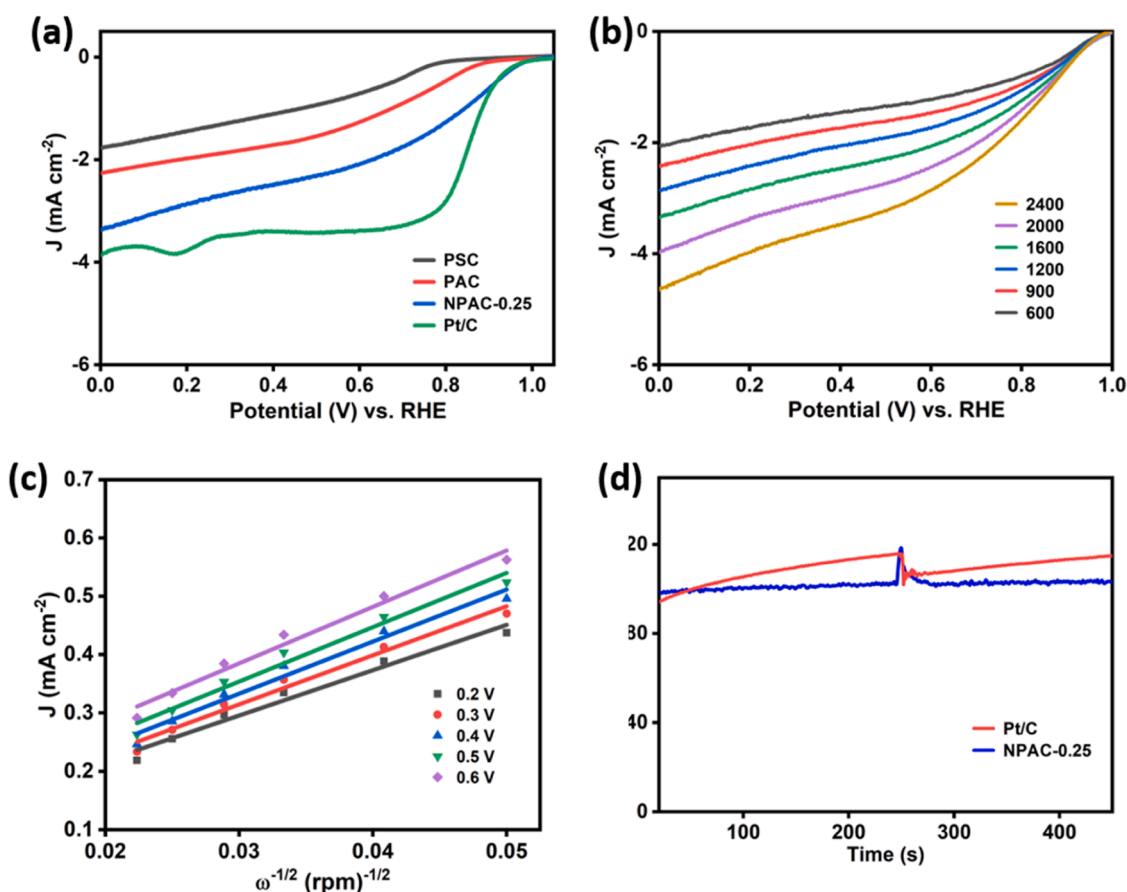


Fig. 4. (a) Comparative LSV curves at a rotation rate of 1600 rpm , (b) LSV curves of NPAC-0.25 at different rpm, (c) K-L Plot, and methanol tolerance test.

Table 1

Comparison of ORR electrochemical performance of different biomass-derived carbon electrocatalysts in 0.1 M KOH alkaline electrolyte. All potentials are referenced to the reversible hydrogen electrode (RHE).

Biomass Source	Catalyst Type	E_O (V)	$E_{1/2}$ (V)s	References
Pine needles	N-doped porous carbon	~0.96	0.72	[11]
Microalgae	N-enriching nanoporous carbon	~0.97	0.87	[12]
Tea leaves	Fe–N/C	0.93	0.84	[15]
Rice husk	N-doped porous carbon	0.99	0.89	[26]
N, P co-doped biomass	N, P co-doped carbon	0.94	0.84	[29]
Nori seaweed	N-doped porous carbon	0.92	0.85	[33]
Pecan shell	N-doped porous carbon	0.94	0.83	This work

added nitrogen functionalities favorable to catalysis throughout the carbon matrix. Raman analysis confirmed the presence of abundant structural defects, while XPS analysis showed pyridinic and graphitic nitrogen species in the carbon framework. These structural and surface modifications collectively improved oxygen adsorption, charge transfer, and catalytic reaction kinetics during ORR [29,37].

Overall, the results demonstrate that agricultural waste biomass such as pecan shell can be effectively converted into sustainable and functional ORR electrocatalysts through ZnCl_2 activation and heteroatom doping strategies. The synthesized catalyst therefore shows promising potential for future energy conversion and electrochemical applications. Other biomass-derived carbon systems, synthesized from different feedstocks, show the same activation-doping relationship [38]. Computationally guided catalyst design [39] and structural engineering of biomass-derived carbons from diverse feedstocks [40] further corroborate the structure-performance relationships established in this work.

The pecan shell-derived carbon electrocatalysts have limitations that should be considered alongside their ORR performance. The synthesis requires two separate pyrolysis steps at 800 °C, causing a higher thermal energy cost. ZnCl_2 used in the activation step should be recovered and recycled after washing to prevent zinc contamination of wastewater. Microalgae-derived nitrogen-enriched carbon [12] and nori seaweed-derived porous carbon [33] use single-step pyrolysis; the two-step activation and doping approach used in this work consumes more energy per gram of catalyst produced. Unlike metal-containing low-carbon catalysts, the pecan shell-derived carbon avoids transition metal precursor costs and the associated mining emissions. Because pecan shell is agricultural waste, no dedicated land cultivation is required. This lowers the carbon cost relative to catalysts made from commercially sourced precursors.

4. Conclusion

In this study, nitrogen-doped porous activated carbon derived from pecan shell biomass was prepared through ZnCl_2 -assisted activation followed by melamine doping, then tested as an ORR electrocatalyst in alkaline medium. Chemical activation created a rougher, more defect-rich carbon surface, and heteroatom doping added nitrogen-containing active sites to that framework. Structural characterization confirmed a porous carbon structure containing pyridinic and graphitic nitrogen species. Raman analysis indicated the presence of considerable structural disorder and graphitic domains, while XPS confirmed successful nitrogen incorporation and surface chemical modification. NPAC-0.25 showed higher ORR activity than PSC and PAC, with a more positive onset potential and higher limiting current density in 0.1 M KOH. The improved catalytic behavior results from the combined effects of porosity, defect density and nitrogen doping. Pecan shell agricultural waste can therefore serve as an effective precursor for sustainable, low-cost ORR electrocatalysts. The metal-free, nitrogen-doped porous

carbon material shows promising potential for further development as an alternative to platinum-group metal (PGM) catalysts in fuel cells and metal–air batteries.

CRediT authorship contribution statement

Mohammad Anisuzzaman: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ganesh Dhakal:** Writing – review & editing, Visualization, Validation, Supervision, Software, Conceptualization. **Basanta Dangal:** Data curation, Software, Writing – review & editing. **Anthony Stewart:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cartre.2026.100694](https://doi.org/10.1016/j.cartre.2026.100694).

Data availability

Data will be made available on request.

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