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Promising nature-based nitrogen-doped porous carbon nanomaterial derived from borassus flabellifer male inflorescence as superior metal-free electrocatalyst for oxygen reduction reaction

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Highlights

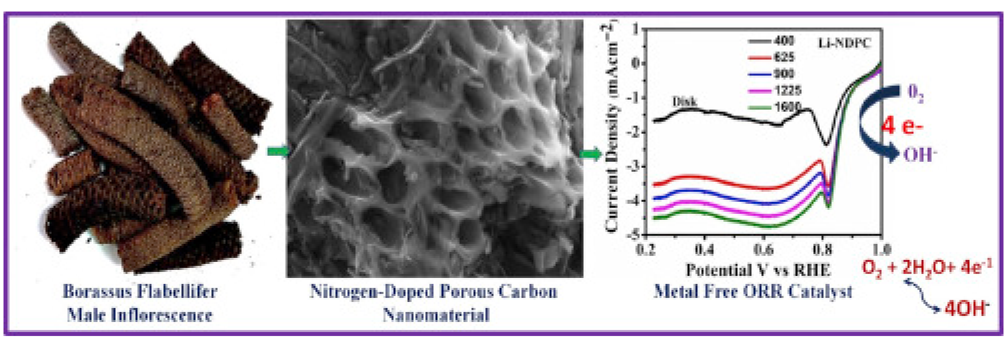
- Nitrogen-doped porous carbon derived from Borassus Flabellifer using novel activation.
- High surface area and surface energy were achieved using Li(OH) activation.
- The number of electrons in reduction of oxygen was calculated to be 3.7 for LHPC.

- LHPC electrode shows significant ORR catalytic activity when compared to Pt/C.

Abstract

In this present study, novel hierarchical nitrogen-doped porous carbon for use as a metal-free oxygen reduction reaction (ORR) electrocatalyst is derived from borassus flabellifer male inflorescences by calcining at 1000 °C in an inert atmosphere using metal hydroxides as activating agent and melamine as nitrogen doping agent. The BET surface areas of the lithium-ion (Li-ion), potassium-ion (K-ion) and calcium-ion (Ca-ion) activated carbon are observed to be 824.02, 810.88 and 602.88 $m^2 g^{-1}$ respectively. Another interesting fact is that the total surface energy calculated by wicking method (73.2 mJ/m^2), is found to be higher for Li-ion activated carbons. Among the prepared nitrogen-doped porous carbon, Li-ion activated system, showed an outstanding performance in ORR reaction in alkaline medium, thanks to its high surface area and notable surface activity. An incontrovertible of note that ORR half-wave potential of Li-ion activated nitrogen-doped carbon (0.90 V) is relatively higher in comparison to the commercial 20 wt % Pt/C catalyst (0.86 V). Inspite of overwhelming performance, the ORR reaction followed the preferred 4- electron transfer mechanism involving in the direct reduction pathway in all activated carbons. The ORR performance is also noticeably better and comparable to the best results in the literature based on biomass derived carbon catalysts.

Graphical abstract



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Introduction

ORR, the most significant cathodic reactions in energy storage and conversion technologies received wide attention among researchers and has been extensively studied over the decades [1], [2]. Platinum (Pt) and its carbon based catalysts (Pt/C) are widely explored as electrocatalysts for the ORR process which has four electron transfer path with over-potential limited and response of the current higher [3], [4]. However, commercial application aspects of Pt based electrocatalysts for ORR reaction are restricted due to the scarcity, weak stability, high price, weak durability, poor selectivity and instability of platinum metal [5], [6]. To overcome the demerits of commercial Pt based catalyst, other metal, metal alloys and metal doped carbon based electrocatalyst have been developed for ORR applications [7], [8], [9], [10], [11], [12], [13], [14], [15], [16]. In this context, cost effective metal-free porous carbon based electrocatalysts has received significant research interest for ORR reaction.

The carbon based catalysts were the maximum studied due to the low-cost, easy availability, inherent satisfactory electrical conductivity and cycling stability [17], [18]. Numerous types of the carbon based catalysts have been explored, for examples carbon nanotube–graphene [19], carbon derived partially graphene [20], carbon nanotube–carbon nanoparticle [21], carbon fiber–graphene [22], carbon nanosheet–carbon nanotube [23], carbon nanosphere–carbon and nanotube–graphene [24], nitrogen-doped carbon materials [25], [26] and interesting that nitrogen-doped carbon nanotubes [27], [28], [29], [30]. Newly, considered as an effective approach to improvement ORR catalyst activity beyond the use of individual constituent carbon materials. In recent years, the biomass derived nitrogen-doped carbon materials has attracted sufficient consideration in various energy-related applications [31], [32]. Doping with heteroatoms like nitrogen can be an effective alternative to enhance the potential for the conductivity of electrons and can improves the performance, due to the shifting of the Fermi level to valence band in carbon by the nitrogen-doping which makes the electron transfer as simple as it can.

Activation agents such as carbon dioxide, calcium chloride, $ZnCl_2$, KOH and H_3PO_4 are widely employed in preparing the porous carbon materials [33], [34]. Doping of nitrogen was carried out with the aid of melamine which is rich in nitrogen content and has higher reactivity rates with amino group, which is the main component for nitrogen compounds. This doping can eventually boost up the capacity, wettability of the surface and improve the conductivity of electrons in the carbon [35]. The nitrogen doped porous nanostructured carbon prepared by pyrolysis of different kind of biomass is been usually engaged as the electrode material for energy storage materials such as fuel cells, metal-air batteries, rechargeable batteries and supercapacitors [36], [37], [38]. There are many advantages for selecting the biomass, which are helpful in sustainable development of carbon, environmental-friendliness, low cost, and easy availability [39], [40].

Borassus flabellifer is a tall palm found in warmer portions of India. The male inflorescences of B. flabellifer were investigated for anti-inflammatory activity, hematological and biochemical parameters [41], immunosuppressant property [42], analgesic and antipyretic effects [43]. Previous report, Phosphoric acid as activating agent used this biomass and maximum surface area of 633.43 m^2/g was reached [44]. But here, for the first-time, hierarchical nitrogen-doped carbon nanomaterial is prepared from biomass of borassus flabellifer male inflorescences using physico-chemical activation method with different hydroxide salts (LiOH, KOH, $Ca(OH)_2$) were activating agents and it is used for oxygen reduction reaction (ORR) applications for the first time.

Section snippets

Materials

The precursor biomass materials viz., Borassus flabellifer male inflorescences (BFMI) was picked from Mukkur village, Thiruvannamalai district, Tamilnadu, India. The analytical grade hydroxide salt of lithium, potassium, and calcium, melamine were purchased from (Sigma Aldrich India Ltd) Recon in Chennai.

Synthesis of nitrogen-doped porous carbon (PC) using various activation agents

The borassus flabellifer male inflorescence (BFMI) sample was washed thoroughly using water to remove any impurities prior to drying in sunlight. The dried samples (BFMI) were cut into small

Morphology and structure of samples

Morphological features of the representative activated carbon samples (Ca-NDPC, K-NDPC and Li-NDPC) are shown in Fig. 1. As shown in Fig. 1(a), Ca-NDPC consists of relatively smooth surface with uniformly distributed pores (~5 μm). Alternatively, bimodal distribution of pores with varying pore sizes can be seen in KHPC samples (Fig. 1(b)). In contrast, Li- NDPC activated carbon consists of 3D honeycomb type network structure with multi-modal distribution of pores (Fig. 1(c)). While, the high

Conclusion

In the present study, hierarchal nitrogen doped porous carbon with excellent electrocatalytic activity was derived from Borassus flabellife male inflorescence by simple heat treatment combined with a chemical activation. Morphological study using FE-SEM studies revealed the formation of 3D honeycomb structure with multi-model distribution of randomized pores in lithium-ion activated carbon samples (Li-NDPC), whereas relatively smooth surface with well-ordered pore structures were formed in

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> …To ensure efficient sodium-ion intercalation in the hard carbon structures the pyrolysis procedure is conducted under high temperatures (1000–1800 °C) and inert atmosphere [41]. The male inflorescences obtained from Borassus flabellifer, a tall palm is one among the most abundant biomass material originating from the warm tropical portions of India and worldwide [42,43]. Owing to the presence of various polyaromatic groups, this biomass could render a classic hard carbon, when processed under stipulated experimental conditions.…

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…For instance, Cao et al. used ZIF-7 as template and glucose as carbon feedstock to produce N-doped porous carbon [17], which exhibits excellent electrocatalytic activity for ORR. Subashchandrabose's group fabricated hierarchical N–C with excellent electrocatalytic activity toward ORR, by using Borassus Flabellifer combined with a metal hydroxide activating agent [15]. However, for the template route, the cost was higher and more reaction steps were required to synthesize the template, use it, and remove it.…

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