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High Performance Electrochemical Double Layer Capacitor (EDLC) Electrodes from Biomass Derived Carbon Materials †

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Abstract

Insecurity and scarcity of resources lead to war and conflict as seen in Ukraine and Gaza. To prevent the dangerous effects of resource crises, especially, energy, it is imperative to invent energy sources at a war footing. The present review article is a serious attempt in that path. Super capacitors, especially, the electrochemical double layer capacitors (EDLCs) are potential energy storage devices that could be a substitute to fossil fuels. Yet, the challenges are the sustainability, economic viability and environmental friendliness apart from the far far higher expectations pertaining to the electrochemical performance (volumetric capacitance value as high as 600 F/cm^3). The afore mentioned challenges can be surmounted by using the electrodes for super capcitors based on peculiar carbon materials derived from renewable sources like biomass with high spin concentration (a parameter indicative of electrical conductivity), rich in hetero atom (nitrogen, oxygen and sulphur) functionality and favourable textural properties. Based on the existing challenges in the field, it is proposed to exploit waste land weeds, native of India, namely, Calotropis gigantea, Ipomoea carnea as well as agricultural wastes from Borassus flabellifera and Limonea ascidissima for the production of exotic carbon materials with high spin concentrations for EDLC electrode applications.

Keywords: EDLCs, Supercapacitors, Electrodes, Activated carbon materials, Spin density, Free electron concentration

INTRODUCTION

Carbon materials from biomass owing to their sustainability, tunability of structure (graphitic or turbostratic) [1, 2], texture (specific surface area, and porosity), morphology, spin concentration (structural defects like an unpaired electron localized in a carbon dangling bond or persistent free radicals) [3-5] as well as the economic viability constitute promising candidates for electrochemical double layer capacitor (EDLC) electrode materials [6, 12]. It should be noted that the electrical conductivity of the carbon materials is closely related to the spin concentration, the key attribute, that was neglected in chemical literature related to electrochemical energy sources and this has been the focus of this review article [13]. With growing concerns on the fast depletion of the existing and easily extractable mineral energy sources, alternate and green energy sources, namely, fuel cells, batteries and super capacitors are widely investigated for enhancing their performance. Among various electrochemical energy conversion and energy storage devices, the super capacitors,

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stand out owing to the high values of energy density as well as the power density that could be possible in principle. So the emphasis of the review article is on the super capacitor electrodes, and that to on the unique class of super capacitors, namely, the electrochemical double layer super capacitors (EDLCs).

Recent Advances in the Development of Electrodes Based on Porous Carbon Materials Derived From Biomass

A web of science search with the keywords, namely, carbon materials and biomass and super capacitors, showed 2809 results. There is a steady growth in this field of research as evident from the number of publications per year during the past decade (Figure 1).

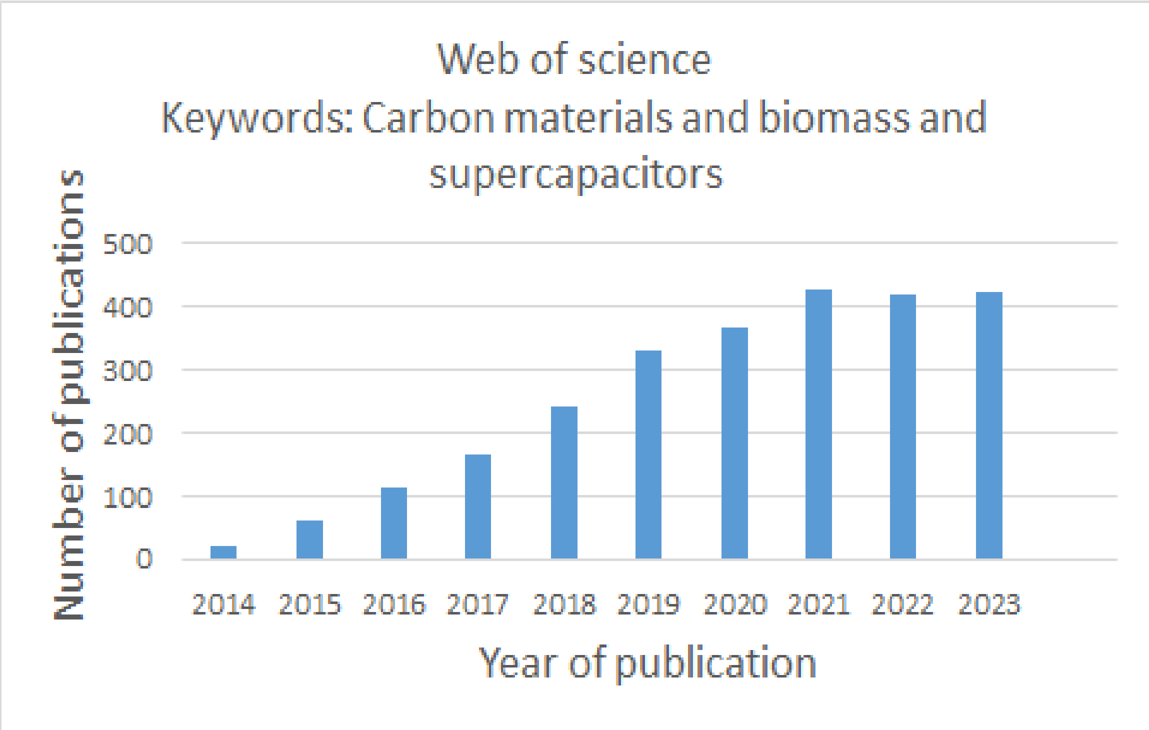

Fig. 1. Growth of the research activity in the field of super capacitors based on carbon materials from biomass [Source: Web of Science]

There have already been 201 papers (as on 8th July 2024) published during the past six months of 2024 on super capacitor electrodes made of carbon materials from biomass and the field is making an impact among scientific community across the globe [14, 20].

Hetero atom Containing Porous Carbon Materials for EDLC Electrode Application

Mingjiang Xie's group made remarkable contribution to the development of porous carbon materials containing high amounts of hetero atom content (oxygen and nitrogen) with high specific surface area using unconventional synthetic strategies [6, 11]. Such carbon materials showed satisfactory electrochemical performance when used as electrodes for EDLCs as shown in Table 1. However, the carbon feedstock is not based on renewable biomass but was rather based on conventional sources like hydroquilinoine-Zn complex, phenol-formaldehyde and the like [6, 11].

Table 1. Electrochemical performance of EDLCs using carbon materials rich in hetero atom produced from Mingjiang Xie's group [6, 11]

	Electrochemical performance	Reference

Hetero atom rich porous Carbon material	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (kW/kg)	
Nitrogen (4.4 atom %) and oxygen (17 atom %) codoped mesoporous carbon	220	30.6	2.0	6
Hierarchical porous carbon with high nitrogen content (21.7 atom %)	265	36.8	2.0	7
Nitrogen doped carbon material with enhanced mesoporosity via reduction in microporosity (from 66.5 to 12.9 %)	382	29.8	-	8
Oxygen enriched (8.8 atom %) carbon material with improved hydrophilicity	305	27.1	1.0	9
Highly graphitized carbon deoxygenated at high temperature	278	70.3	1.35	10
Nitrogen (20.7 atom %) enriched carbon material	285.2	34.5	1.37 kW/L	11

Spin Concentration of Activated Carbon Materials – A Game Changer of Electrode Performance

Judicious use of the spin concentration of activated carbon material is surprisingly an avenue that has not yet been explored by chemists. In the words of the famous poet Robert Lee Frost borrowed from his work, namely, stopping by the woods on a snowy evening, the Chemists, have to miles go before they sleep; miles to go before they sleep, miles to go before they sleep, the woods are dark and deep, miles to go before they sleep. A comparison of the magnitude of the spin concentration in various carbon materials (commercial vs biomass derived) is shown in Table 2 [3].

Table 2. Free electron concentration in activated carbon materials (Biomass derived vs Commercial) [3]:

Carbon material	**Free electron concentration (spins/g)**
Activated carbon from *Ipomoea carnea*	0.983×10^{20}
Activated carbon from *Limonea acidissima*	0.13×10^{19}
Activated carbon from *Calotropis gigantea*	0.15×10^{16}
Acetylene black	0.38×10^{20}
Graphon black	0.11×10^{20}
Graphite	0.14×10^{18}
Calgon	0.23×10^{19}
Vulcan XC72R	0.16×10^{19}
Nuchar	0.53×10^{18}
DPPH*	0.153×10^{22}

*DPPH, Diphenyl picryl hydrazyl radical, is standardly used in the EPR analysis for the quantification of free electron concentration in various commercial and biomass based carbon materials.

As can be observed from the data in Table 2, the biomass derived activated carbon materials, especially, from *Ipomoea carnea* and *Limonea acidissima* showed spin concentration values on a par with the celebrated commercial activated carbon materials, usually, produced from fossil based resources. In the words of the head devil, the senior diplomat, in the Screw tape letters by Professor C S Lewis, why murder when cards can do? So, biomass-based carbon material serves as a viable feedstock for carbon materials with high spin concentration. Typical examples of the biomass native to India that could be a potential feedstock for spin concentration rich porous carbon materials were shown in Figure 2 [21]. Microporous activated carbon (MAC) produced from *Calotropis gigantea* using chemical activation with K_2CO_3 as activating agent possessed a BET specific surface area value of 1296 m^2/g with a pore volume (Vp) value of 0.73 cm^3/g. Likewise, MAC produced from *Borassus flabellifera* using K_2CO_3 activation resulted in a material with S_{BET} value of 1070 m^2/g and Vp of 0.35 cm^3/g [3]. It should be noted that there is large scope for tuning as well as enhancing the spin concentration of carbon materials with advances in synthetic strategies. Adolfsson and coworkers succeeded in producing carbon nanoparticles from glucose under microwave irradiation using different solvents like water and ionic liquids and the spin concentration value of such carbon micro-nanoparticles from glucose is nearly three orders of magnitude higher ($4\text{-}12 \times 10^{22}$ spins/g) than the values of activated carbon materials shown in Table 2 [22]. This shows the fertility of the research field of carbon materials with high spin concentration for electrochemical device applications.

Landmark papers appeared in chemical literature on the use of biomass derived porous carbon materials which will be the subject of discussion in the next few paragraphs. However, a structure property

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relation with a correlation between free electron concentration and the electrochemical device performance has never been brought out explicitly and this issue has to be taken up by researchers in near future.

Fig. 2. Stems of *Calotropis gigantea* (a) and *Ipomoea carnea* (b); flower spikes of *Borassus flabellifera* (c) and shells of *Limonea acidissima* (d) [21].

Future Directions

One of the key challenges, in the use of porous carbon material based electrodes for (EDLC) application is to understand the molecular level details of the mechanism of electrochemical processes at the interface as well as the structure and dynamics of the electric double layer (EDL). One of the ways of overcoming this problem is to use model carbon material with less complexity in the porous architecture, like graphene, the famous 2D layered carbon material with atomic layer thickness, as the EDLC electrode material [23]. The success stories of world-renowned research groups in the field of carbon-based electrodes for super capacitors are highlighted in the next few lines. Zheng's group reported volumetric capacitance of 412 Fcm^{-3} using carbon nanosheets [24]. Gao's group reported volumetric capacitance of 573 Fcm^{-3} using nitrogen doped porous carbon microspheres [25]. Microporous activated carbon (MAC) produced by activation with a KOH/nitrogen doped carbon precursor, CP-N of 0.5 yielded carbon with 5.78 wt. % N (MAC-N-0.5) and this material showed outstanding performance. This imply that there is an optimum amount of the hetero atom content that leads to an outstanding volumetric capacitance, gravimetric capacitance, rate capability, capacitance retention, energy density and power density values [25]. Wei's group reported a volumetric capacitance of 507 Fcm^{-3} with nitrogen doped low surface area carbon materials [26]. Yang's group reported a volumetric capacitance of 521 Fcm^{-3} with F and N co-doped carbon microspheres [27]. However, none of these breakthroughs are with biomass based carbon materials. Thus, exploitation of biomass-based carbon materials with high spin concentration and with hetero atom functionalization (oxygen, nitrogen and sulphur) should be pursued actively as these materials hold a promising with enhanced performance of the super capacitors. Attaining a volumetric capacitance of 600 Fcm^{-3} from biomass derived carbon materials as highlighted above has been a challenge as well as a far far higher expectation.

CONCLUSION

Production of activated carbon materials with high spin concentration from renewable resources like biomass is an innovative strategy for sustainability in the realms of energy and environment. Effective use of the potential of carbon materials with high spin concentration (as high as 10^{20} spins/g) in addition to remarkable textural and functional properties derived from biomass is a viable strategy for fabricating electrodes for electrochemical double layer capacitors (EDLCs). The far far higher target of achieving a volumetric capacitance value as high as 600 F/cm^3 which is nowhere seen, for carbon materials from biomass, in literature could be realized by adopting such a key. One of the remarkable features of these carbon materials derived from biological sources is that they are rich in free electron concentration (spin concentration). Such high spin concentration values (0.15×10^{16} – 0.983×10^{20} spins/g) should form the basis for designing promising electrodes for electrochemical energy conversion (fuel cells) and energy storage (battery and super capacitor) devices. Based on the new insights provided herewith, it is recommended to evaluate the electrochemical performance of carbon materials derived from biomass possessing high spin concentration, high specific surface area and rich hetero atom content, for electrochemical energy conversion and storage applications in general and for EDLC application in particular.

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† Dedicated to the legendary chemical engineer Professor Tae Hyun Kim on his birthday on 1st October 2024

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