

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/341049388>

Biochar for Electrochemical Applications

Article · April 2020

DOI: 10.1016/j.cogsc.2020.04.007

CITATIONS

0

READS

32

3 authors, including:



Tomas Edvinsson
Uppsala University

113 PUBLICATIONS 3,726 CITATIONS

[SEE PROFILE](#)



Philip CW Kwong
University of Adelaide

43 PUBLICATIONS 942 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Monte Carlo calculations and measures of polymer conformations [View project](#)



Semiconductor nano-materials for energy applications [View project](#)



Biochar for electrochemical applications

Mohammad Z. Rahman^{1,2}, Tomas Edvinsson² and Philip Kwong¹

Carbon-rich biochar can be produced by pyrolysis of biomass. Depending on the precise production pathway, the surface chemistry and porosity can be tuned and made compatible for a defined application. This shear benefit has persuaded researcher to explore its suitability in various electrochemical applications related to energy storage and conversion. In this article, we succinctly discuss the potentials of biochar in electrocatalysis, fuel cell, supercapacitors, and rechargeable batteries. We have concluded this article with recommendations for future research.

Addresses

¹ School of Chemical Engineering and Advanced Materials, The University of Adelaide, Australia

² Department of Engineering Sciences, Angstrom Laboratory, Uppsala University, Sweden

Corresponding author: Kwong, Philip (philip.kwong@adelaide.edu.au)

Current Opinion in Green and Sustainable Chemistry 2020, 23:25–30

This review comes from a themed issue on **Green processes and technologies**

Edited by Xiangping Zhang

<https://doi.org/10.1016/j.cogsc.2020.04.007>

2452-2236/© 2020 Elsevier B.V. All rights reserved.

Introduction

The energy produced in an environmentally friendly way is a key and inevitable ingredient for sustainable development of any nation. Currently, fossil fuels are predominant sources of primary energy production. Burning of fossil fuels, however, results in a net contribution of carbon dioxide in the atmosphere, and in many cases, additional soot particles and toxic effluents that have serious consequences for every sphere of life on earth. The recently signed Paris agreement therefore calls for renewable and sustainable energy production toward net-zero carbon emission [1]. Harnessing sunlight, wind, water, and biomass are considered the most promising and viable options for renewable and sustainable energy production [2,3].

For example, sunlight is converted to electricity using photovoltaic cells, also known as solar cells, at a price level that now is comparable to fossil fuel produced electricity in many parts of the world [4]. Pumped water, batteries, or photovoltaic electrolysis with electrodes for

producing hydrogen fuel via water splitting are options to mediate diurnal or seasonal variation in solar and wind power and store the energy for later use [5,6]. Rechargeable batteries and supercapacitors provide facilities for direct storage of electrical energy from renewable energy sources, whereas carbon free fuels like hydrogen instead can be used for longer time storage and provide heat from combustion or converted back into electricity via gas turbines or fuel cells for mobile or stationary applications [7–12].

There is a long list of inorganic and organic materials that meet the requirements to be used for electrochemical applications [8,13]. Evidently, carbon-based materials have been one of the preferred material of choice over any other genre of materials, and arguably the most flexible materials for electrocatalytic/photocatalytic water splitting into hydrogen and oxygen, oxygen electrocatalyst for fuel cells, and electrodes in supercapacitors and lithium-ion batteries (LIBs) [11,14–16].

Conventional high throughput synthesis of the functional carbon-based materials requires energy-intensive and complicated synthetic processes. For example, activated carbon is conventionally derived from coal, whereas carbon nanofibers/tubes and graphene may produce through the chemical vapor deposition or electric-arc discharge techniques using gaseous petrochemical products, such as methane, acetylene, ethylene, and hydrogen, at high temperatures (>800°C) [17]. These high-temperature and resource-intensive processes can be suitable for large-scale production in industrial settings, but are not compliant with a fully sustainable solution or production in smaller installations. It is therefore of high interest to develop alternative low-energy synthesis techniques to produce high-performing carbon materials from renewable resources or more effectively use the already produced carbon materials.

Biochar is derived from biomass resources [18], in this regard, has emerged as a viable alternative material for photoelectrochemical energy conversion and storage. In this article, therefore, we will succinctly discuss the progress and challenges associated with biochar for various electrochemical applications. As such, we will limit our discussion exclusive to water-splitting, rechargeable batteries, supercapacitors, and fuel cells.

Merit of biochar

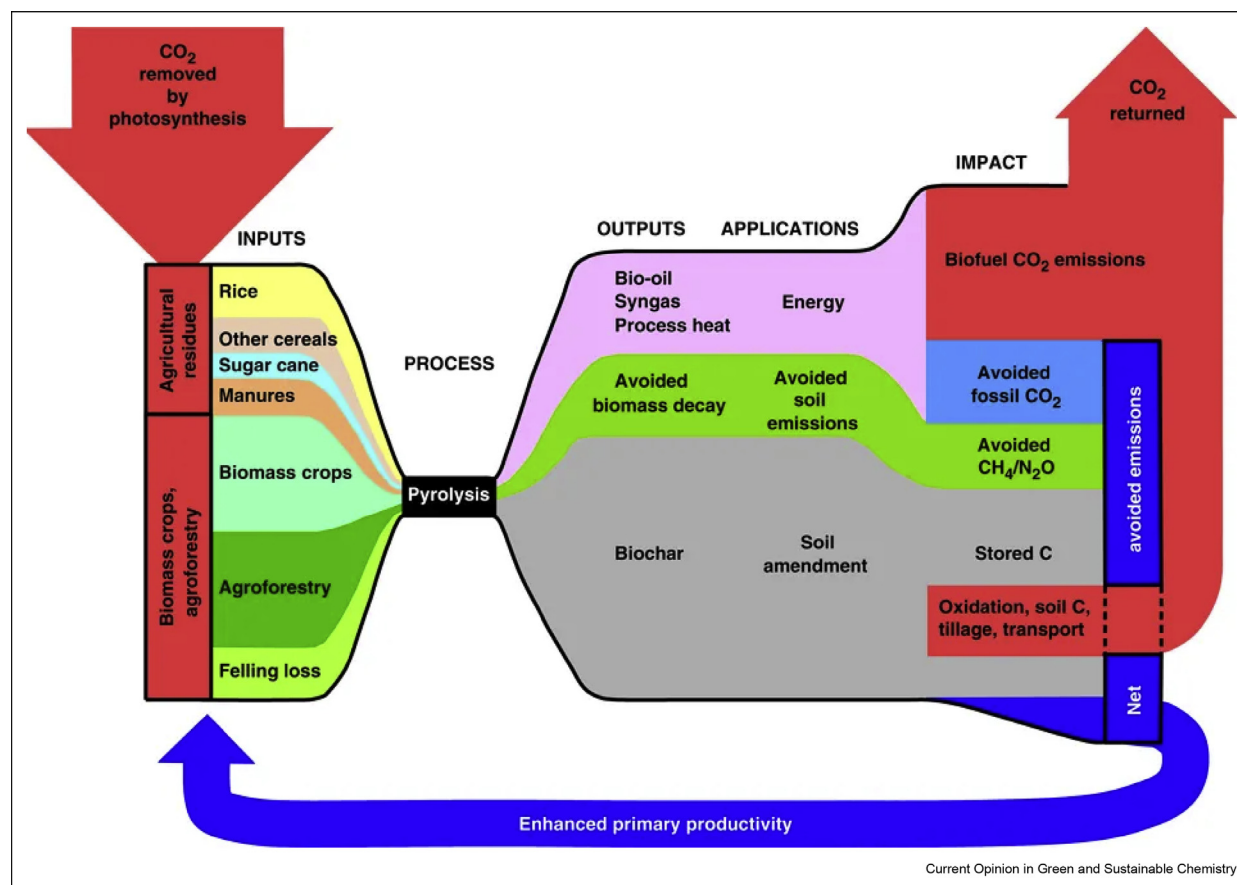
Biochar is a solid product of thermally decomposed biomass at temperatures between 350°C and 600°C [18]. Structurally, biochar has an amorphous atomic structure, naturally forming a porous matrix that results in a large number of pores and exposed surface [19]. In contrast to activated carbon and carbon black, biochar is produced from renewable sources and its surface is endowed with different functional groups. However, if activated carbon is produced through biomass decomposition, it could essentially then be regarded as biochar.

Because the conventional synthesis of activated carbon and carbon black involved using fossil fuels, their production also significantly contributed in anthropogenic CO₂ emissions. On the other hand, biochar is solely produced from renewable and green source biomass (Figure 1). Biochar production is then a carbon neutral process and can be regarded as one of the candidates to contribute to a sustainable energy system. Most importantly, the processes of biochar production lead CO₂ to be bound to the carbon matrix of biochar, and thus induces a carbon fixation strategy for efficient

removal of CO₂ from the carbon cycle. It ultimately could help abate the global warming through carbon sequestration. Exploiting biochar for application of carbon storage, it is possible to remove a considerable amount of CO₂ (0.1–0.3 billion tons) from the carbon cycle. Therefore, biochar is often termed as biocarbon [19].

The salient features of biochar are their tunability in porosity and surface chemistry. It has widely been studied as low-cost adsorbent [20,21], soil conditioner [22,23], and catalyst [24] for various environmental applications because of its versatility. Furthermore, its tunable porosity and surface functional groups are beneficial for controlling the interfacial chemical reactions and make the biochar attractive for electrochemical energy conversion and storage applications. For example, the surface functional groups may alter the thermodynamics of surface energy to influence the chemical reactions at the interface, whereas the surface porosity substantially influence the kinetics and reaction rates. Therefore, biochar and biochar-based nanostructures are deemed promising materials for electrochemical energy conversion and storage.

Figure 1



Conceptual overview of the sustainable synthesis of biochar. Reproduced with permission from Ref. [18]. Copyright 2010, Nature Publishing Group.

Applications of biochar

Electrochemical water-splitting

Biochar is being used as an electrocatalyst and photocatalyst for hydrogen and oxygen production via water-splitting [25–27]. Doping heteroatom creates active sites in biochar for enhanced hydrogen evolution reaction (HER). For example, S-doped and N-doped biochars derived from peanut root nodule have been reported to be efficient electrocatalyst for the HER. The doped biochar, because of its abundant porosity and a high electrochemical area of 27.4 mF cm^{-2} , exhibited an exceptional onset potential of 27 mV vs reversible hydrogen electrode (RHE) for HER, which is comparable to a commercial Pt/C catalyst with 20 wt% loading [28] (Figure 2a).

Another example includes nanostructure catalyst constructed from biochar derived from sunflower seed shells and Mo_2C nanoparticles. This integrated electrocatalyst demonstrated a current density of 10 mA cm^{-2} for HER at an over potential of only 60 mV. Most importantly, this catalyst endured outstanding durability and a near unity faradaic efficiency [29]. Other example includes growth of MoSe_2 nanosheets on a carbon fiber aerogel. The carbon aerogel was derived from cotton wool biomass. This MoSe_2 /carbon fiber aerogel electrocatalysts showed a HER at an onset potential of 104 mV vs RHE [30] (Figure 2b).

Needless to say that current state-of-the-art performance of biochar catalyst is way behind the most efficient water-splitting catalysts (e.g. overpotential of 13 and 17 mV at a current density of 10 mA cm^{-2}) [31]. However, it has a potential to be used as an abundant alternative catalyst material for hydrogen and oxygen productions.

Rechargeable batteries

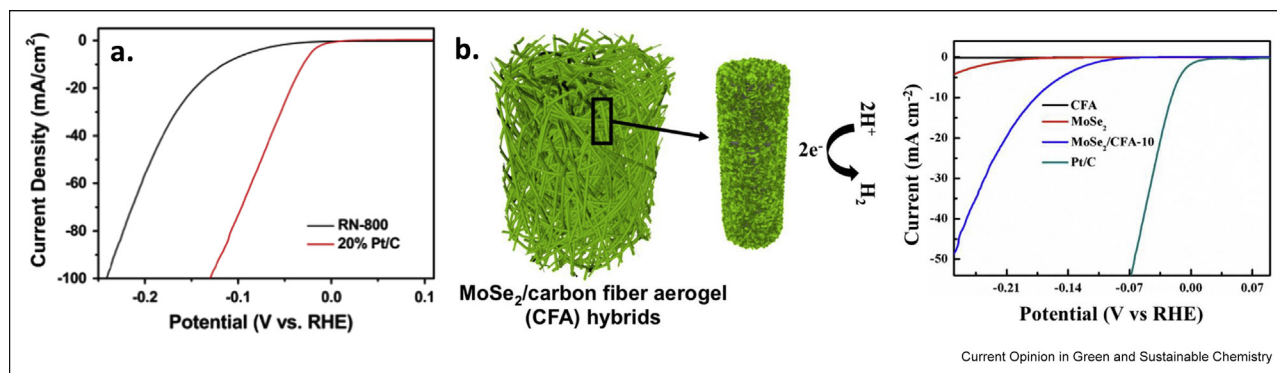
Cost-effective and sustainable synthesis of biochar and its high specific charge storing capacity compared to conventional graphite materials, make it desirable for various kinds of rechargeable batteries [32]. Biochar derived from wheat stalks, as an anode material in LIBs, was shown to provide multiple Li^+ storage sites, facilitating rapid electron and Li^+ ion transport, low and flat voltage profile and reduced voltage hysteresis [33]. Biochar-based LiB demonstrated a reversible capacity of 502 mA h g^{-1} (which is 1.35 times higher than the theoretical capacity of graphite) with excellent rate and cycling capabilities (Figure 3a) [33]. Bamboo-based biochar carbon fibers was shown to retain a reversible capacity of 710 mA h g^{-1} up to 300 cycles with a Coulombic efficiency of $\sim 100\%$ (Figure 3b) [34]. Biochar-based material were also been used in lithium–sulfur and sodium-ion batteries [35–37].

It is imperative to mention that further research is deemed necessary to increase the specific capacity through design of high-voltage cathode, and possibly low-potential anodes out of biochar [38,39].

Supercapacitors

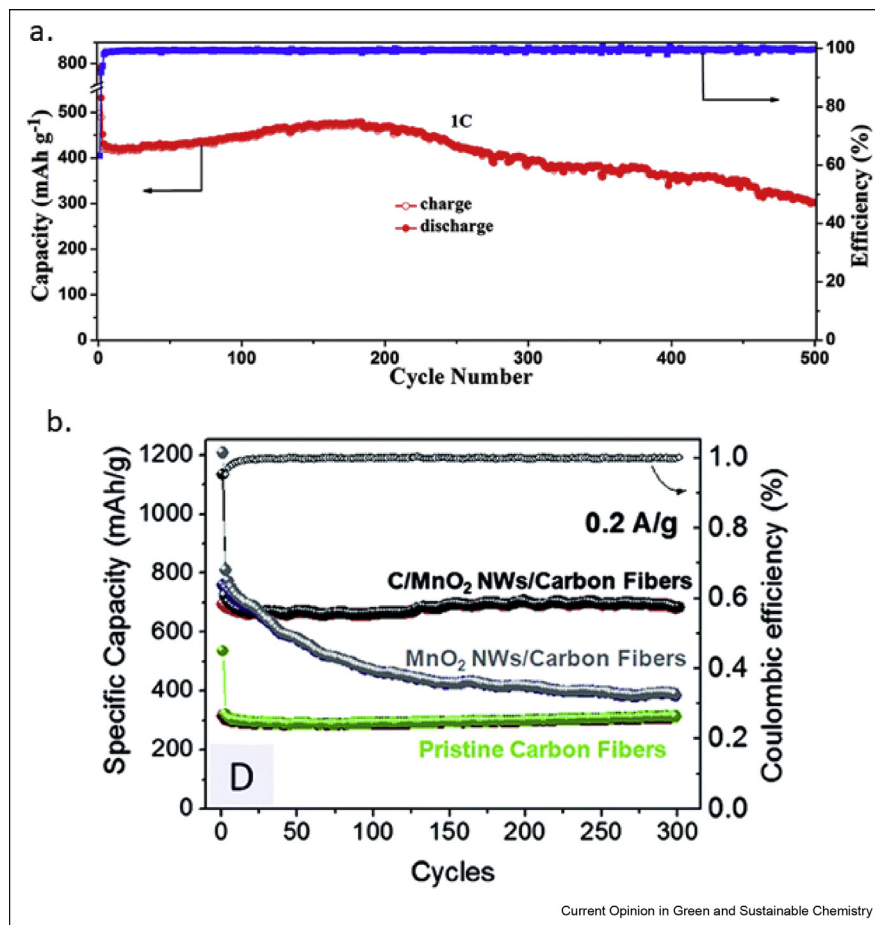
Modern supercapacitors are endowed with excellent reliability, high power density, and fast charging–discharging characteristics [40,41]. Supercapacitors are therefore used in a wide range of applications, particularly in electrical vehicles. Carbon with high specific surface area ($>2000 \text{ m}^2 \text{ g}^{-1}$), for example, activated carbon, are preferentially used to fabricate electrodes for supercapacitors' applications. These capacitors have shown a specific capacitance between 250 and 350 F g^{-1} [17,42]. However, synthesis of low-cost functional carbons with better specific capacitance is highly desirable.

Figure 2



HER performance of (a) peanut root–derived carbon and (b) cotton wool–derived carbon fiber aerogel. Adapted with permission from Refs. [28,30]. Copyright 2015 and 2017, Elsevier and American Chemical Society, respectively.

Figure 3



Cycling performance of (a) wheat stalks-derived biochar electrode at 1 C and (b) bamboo-based biochar electrode. Adapted with permission from Refs. [33,34]. Copyright 2016 and 2014, Royal Society of Chemistry.

Recent studies, in this regard, showed that biochar-based materials have excellent potential to substitute the conventional activated carbon [43]. Indeed, highly conductivity and microporous biochar are demonstrated as candidate materials for high specific capacitance supercapacitors. For example, biochar-based supercapacitors were reported to exhibit an excellent specific capacitance of 400 F g^{-1} with an energy density of 55 W h kg^{-1} [44]. Another example includes supercapacitors from heteroatom-doped biochars. A supercapacitor based on nitrogen-doped biochar achieved specific capacitances of 297 F g^{-1} in basic electrolytes, whereas 284 F g^{-1} in acidic electrolytes [45]. Importantly, these biochar-based supercapacitors have superior performance compared to supercapacitors based on activated carbon (203 F g^{-1} ; Figure 4).

Regardless of those promising results, research is performed to enhance the capacitance further, which could be achieved through the synthesis of geometric

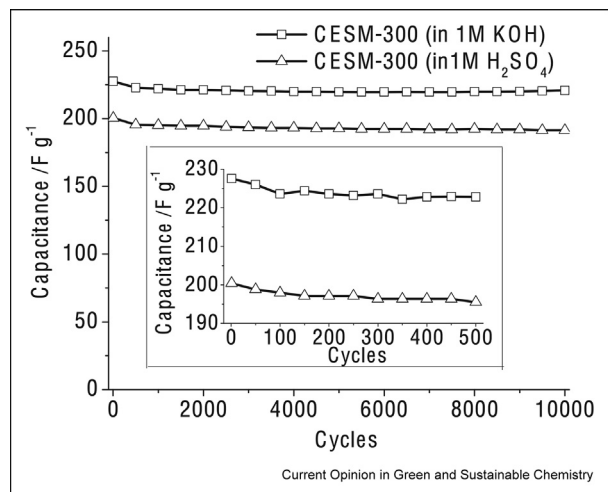
composite with other materials, and to understand the structure-property relationship [46,47].

Fuel cells

Biochar has prominent application as an oxygen reduction reaction catalyst in the proton exchange membrane fuel cell with the potential to be used in direct carbon fuel cells and microbial fuel cells (MFCs) [48–50]. In direct carbon fuel cells, oxidation of carbon into CO_2 and CO on the anode liberates electrons, and subsequently, contributes in electricity production at the cathode [51]. Therefore, high carbon content in biochar is presumably beneficial for high power density provided that the ash content is controlled at an acceptable level. Ash is a matter of concern because it impedes the ionic conductivity, and therefore, reduce the output power [52].

With a peak power output of $532 \pm 18 \text{ mW m}^{-2}$, biochar-based MFC systems are more cost-effective than conventionally MFC that use granular activated carbon

Figure 4



The evaluation of specific capacitance of eggshell membrane-derived carbons. Adapted with permission from Ref. [45]. Copyright 2012, Wiley-VCH.

and granular graphite. For example, per watt production cost in biochar-based MFC is only 17 US\$ per W, whereas it is 402 US\$ per W for granular activated carbon and 392 US\$ per W for granular graphite [53].

Care should be taken to prevent biofouling on biochar cathodes, however, as biofouling is the major cause for deterioration of MFC performance in these systems.

Conclusion and future perspective

It is evident that biochar is a potent material of interest for electrochemical energy storage and conversion. To further progress, research needs to be carried out in resolving a few outstanding issues. For large-scale and cost-effective deployment, the conversion efficiency and quality of biomass into biochar are required to be maintained without additional steps for treatments, whereas biochar functionalization (i.e. surface oxidation, amination, sulfonation etc.) should avoid intricate operations and toxic chemicals to retain a green solution. Regardless of the pretreatments and post-treatments, there can always remain residual impurities into biochar that may adversely affect the performance of the devices. Here, the development of strategies to reduce the impurity contents to acceptable minimum are necessary.

The electrocatalytic performance of biochar has been yet moderate. The performance may be enhanced through an in depth understanding of the surface chemistry and molecular interactions that demands combined theoretical and experimental studies. Owing to the unknown atomic surface structure of these highly amorphous materials, in many cases, precise

theoretical models are largely absent to date. We believe that further research endeavor in this area may open a new window of opportunities with new facets of science followed by its practical applications in diverse field.

Conflict of interest statement

Nothing declared.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

1. Davis SJ, *et al.*: **Net-zero emissions energy systems.** *Science* 2018, **360**.
2. Rahman MZ, *et al.*: **2D phosphorene as a water splitting photocatalyst: fundamentals to applications.** *Energy Environ Sci* 2016, **9**:709–728.
3. Chu S, Cui Y, Liu N: **The path towards sustainable energy.** *Nat Mater* 2016, **16**:16–22.
4. Green MA: **How did solar cells get so cheap?** *Joule* 2019, **3**: 631–633.
5. Walter MG, *et al.*: **Solar water splitting cells.** *Chem Rev* 2010, **110**:6446–6473.
6. Jacobsson TJ, *et al.*: **Sustainable solar hydrogen production: from photoelectrochemical cells to PV-electrolyzers and back again.** *Energy Environ Sci* 2014, **7**:2056–2070.
7. Liu Y, Zhu Y, Cui Y: **Challenges and opportunities towards fast-charging battery materials.** *Nature Energy* 2019, **4**: 540–550.
8. Liu K, *et al.*: **Materials for lithium-ion battery safety.** *Sci Adv* 2018, **4**, eaas9820.
9. Rahman MZ, Edvinsson T: **What is limiting pyrite solar cell performance?** *Joule* 2019, **3**:2290–2293.
10. Rahman MZ, Edvinsson T: **How to make a most stable Perovskite solar cell.** *Matter* 2019, **3**:562–564.
11. Pender JP, *et al.*: **Carbon nitride transforms into a high lithium-storage capacity nitrogen-rich carbon.** *ACS Nano* 2019, **13**:9279–9291.
12. Ardo S, *et al.*: **Pathways to electrochemical solar-hydrogen technologies.** *Energy Environ Sci* 2018, **11**:2768–2783.
13. Warren SC, *et al.*: **Identifying champion nanostructures for solar water-splitting.** *Nat Mater* 2013, **12**:842–849.
14. Rahman MZ, Moffatt J, Spooner N: **Topological carbon nitride: localized photon absorption and delocalized charge carrier separation at intertwined photocatalyst interfaces.** *Mater Horiz* 2018, **5**:553–559.
15. Rahman MZ, Davey K, Qiao S-Z: **Carbon, nitrogen and phosphorus containing metal-free photocatalysts for hydrogen production: progress and challenges.** *J Mater Chem A* 2018, **6**: 1305–1322.
16. Rahman MZ, *et al.*: **A benchmark quantum yield for water photoreduction on amorphous carbon nitride.** *Adv Funct Mater* 2017, **27**:1702384.
17. Najib S, Erdem E: **Current progress achieved in novel materials for supercapacitor electrodes: mini review.** *Nanoscale Adv* 2019, **1**:2817–2827.
18. Woolf D, *et al.*: **Sustainable biochar to mitigate global climate change.** *Nat Commun* 2010, **1**:56.
19. Liu W-J, Jiang H, Yu H-Q: **Emerging applications of biochar-based materials for energy storage and conversion.** *Energy Environ Sci* 2019, **12**:1751–1779.

20. Marshall JA, *et al.*: **Recovery of phosphate from calcium-containing aqueous solution resulting from biochar-induced calcium phosphate precipitation.** *J Clean Prod* 2017, **165**: 27–35.
 21. Dai YJ, *et al.*: **The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: a review.** *Chemosphere* 2019, **223**:12–27.
 22. Marshall J, *et al.*: **Pyrolysis temperature effects on biochar-water interactions and application for improved water holding capacity in vineyard soils.** *Soil Systems* 2019, **3**.
 23. Hagemann N, *et al.*: **Organic coating on biochar explains its nutrient retention and stimulation of soil fertility.** *Nat Commun* 2017, **8**.
 24. Lee J, Kim KH, Kwon EE: **Biochar as a catalyst.** *Renew Sustain Energy Rev* 2017, **77**:70–79.
 25. Lin Y, Pan Y, Zhang J: **CoP nanorods decorated biomass derived N, P co-doped carbon flakes as an efficient hybrid catalyst for electrochemical hydrogen evolution.** *Electrochim Acta* 2017, **232**:561–569.
- The authors have produced a novel N, P co-doped carbon flakes as an efficient electrochemical
26. Cui W, *et al.*: **MoP nanosheets supported on biomass-derived carbon flake: one-step facile preparation and application as a novel high-active electrocatalyst toward hydrogen evolution reaction.** *Appl Catal B Environ* 2015, **164**:144–150.
 27. Chen W-F, *et al.*: **Biomass-derived electrocatalytic composites for hydrogen evolution.** *Energy Environ Sci* 2013, **6**: 1818–1826.
 28. Zhou Y, *et al.*: **Sulfur and nitrogen self-doped carbon nanosheets derived from peanut root nodules as high-efficiency non-metal electrocatalyst for hydrogen evolution reaction.** *Nano Energy* 2015, **16**:357–366.
 29. An K, Xu X, Liu X: **Mo2C-Based electrocatalyst with biomass-derived sulfur and nitrogen Co-doped carbon as a matrix for hydrogen evolution and organic pollutant removal.** *ACS Sustain Chem Eng* 2017, **6**:1446–1455.
- The authors have synthesized a novel carbon base electrocatalyst derived from the pyrolysis of the shells of sunflower seeds. Sulfur and nitrogen were co-doped in the catalyst and demonstrated an excellent electrocatalytic activity for hydrogen evolution reaction (HER).
30. Zhang Y, *et al.*: **Cotton wool derived carbon fiber aerogel supported few-layered MoSe2 nanosheets as efficient electrocatalysts for hydrogen evolution.** *ACS Appl Mater Interfaces* 2016, **8**:7077–7085.
 31. Kweon DH, *et al.*: **Ruthenium anchored on carbon nanotube electrocatalyst for hydrogen production with enhanced Faradaic efficiency.** *Nat Commun* 2020, **11**:1278.
 32. Cheng F, *et al.*: **Functional materials for rechargeable batteries.** *Adv Mater* 2011, **23**:1695–1715.
 33. Zhou X, *et al.*: **Interconnected highly graphitic carbon nanosheets derived from wheat stalk as high performance anode materials for lithium ion batteries.** *Green Chem* 2016, **18**: 2078–2088.
 34. Jiang J, *et al.*: **Evolution of disposable bamboo chopsticks into uniform carbon fibers: a smart strategy to fabricate sustainable anodes for Li-ion batteries.** *Energy Environ Sci* 2014, **7**:2670–2679.
 35. Qu Y, *et al.*: **Highly ordered nitrogen-rich mesoporous carbon derived from biomass waste for high-performance lithium-sulfur batteries.** *Carbon* 2015, **84**:399–408.
 36. Li W, *et al.*: **Controlled synthesis of macroscopic three-dimensional hollow reticulate hard carbon as long-life anode materials for Na-ion batteries.** *J Alloys Compd* 2017, **716**: 210–219.
- Using rape pollen grain with hydrothermal pretreatment and low temperature pyrolysis, the authors synthesized a novel macroscopic 3D hollow reticulate hard carbon as the anode materials for sodium-ion batteries. The carbon material demonstrated excellent capacity retention of 90% after 1000 cycles.
37. Rios CDS, *et al.*: **Biochars from various biomass types as precursors for hard carbon anodes in sodium-ion batteries.** *Biomass Bioenergy* 2018, **117**:32–37.
- The authors have synthesized various biochar based hard carbon anode from woody and agricultural biomass. Their performance in sodium-ion batteries were correlated with the lignin, hemicellulose and inorganic contents of the source biomass.
38. Wu F, Maier J, Yu Y: **Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries.** *Chem Soc Rev* 2020.
 39. Liu J, *et al.*: **Pathways for practical high-energy long-cycling lithium metal batteries.** *Nature Energy* 2019, **4**:180–186.
 40. Wang G, Zhang L, Zhang J: **A review of electrode materials for electrochemical supercapacitors.** *Chem Soc Rev* 2012, **41**: 797–828.
 41. Poonam, *et al.*: **Review of supercapacitors: materials and devices.** *Journal of Energy Storage* 2019, **21**:801–825.
 42. Yang Z, *et al.*: **Carbon nanotube- and graphene-based nanomaterials and applications in high-voltage supercapacitor: a review.** *Carbon* 2019, **141**:467–480.
 43. Thangavel R, *et al.*: **Engineering the pores of biomass-derived carbon: insights for achieving ultrahigh stability at high power in high-energy supercapacitors.** *Chemsuschem* 2017, **10**:2805–2815.
- The authors have investigated the effect of structural, textural, and functional properties of the engineered porous carbon derived from cinnamon sticks on the performance of an electrical double-layer capacitor. Results indicated the porous carbon with poor textural properties could deliver high capacitance with outstanding stability when compared to the porous carbon with good textural properties.
44. Biswal M, *et al.*: **From dead leaves to high energy density supercapacitors.** *Energy Environ Sci* 2013, **6**.
 45. Li Z, *et al.*: **Carbonized chicken eggshell membranes with 3D architectures as high-performance electrode materials for supercapacitors.** *Advanced Energy Materials* 2012, **2**: 431–437.
 46. Pacchioni G: **Superelectrodes for supercapacitors.** *Nature Reviews Materials* 2019, **4**: 625–625.
 47. Pomerantseva E, *et al.*: **Energy storage: the future enabled by nanomaterials.** *Science* 2019, **366**, eaa8285.
 48. Shao M, *et al.*: **Recent advances in electrocatalysts for oxygen reduction reaction.** *Chem Rev* 2016, **116**:3594–3657.
 49. Yonoff RE, *et al.*: **Research trends in proton exchange membrane fuel cells during 2008–2018: a bibliometric analysis.** *Heliyon* 2019, **5**, e01724.
 50. Greenman J, Gajda I, Ieropoulos I: **Microbial fuel cells (MFC) and microalgae; photo microbial fuel cell (PMFC) as complete recycling machines.** *Sustain Energy Fuels* 2019, **3**:2546–2560.
 51. Jiang C, *et al.*: **Challenges in developing direct carbon fuel cells.** *Chem Soc Rev* 2017, **46**:2889–2912.
 52. Cao D, Sun Y, Wang G: **Direct carbon fuel cell: fundamentals and recent developments.** *J Power Sources* 2007, **167**: 250–257.
 53. Huggins T, *et al.*: **Biochar as a sustainable electrode material for electricity production in microbial fuel cells.** *Bioresour Technol* 2014, **157**:114–119.