# Bio-inspired Polymers as Organic Electrodes for Batteries


**Hanane Chakhtouna, Brahim El Allaoui, Nadia Zari, Rachid Bouhfid, and Abou el kacem Qaiss**

**Abstract** With the ever-increasing demand for energy sources, worldwide attention has been given to the development of advanced materials for energy storage applications, specifically for batteries. The use of abundant natural resources in such applications seems to be a simple and useful solution since they meet the 3E requirements of (i) excellent performance, (ii) environmental friendliness, and (iii) ease of handling. Indeed, although most academic research demonstrates the superior energy performance of electrode materials proposed in the literature for different types of batteries, they also suffer from early deterioration during charge and discharge cycles, leading to their short lifespan. Bio-inspired polymers such as polysaccharides, natural cellulosic fibers, quinones, flavins, and others represent the most bio-renewable resources suggested for developing and designing highly efficient materials as organic electrodes for batteries. These bio-inspired materials present a great diversity of structures and properties, adapted to the constraints of the environment and the type of electrode envisaged, and even participate in the improvement of their performances for long-term applications. This book chapter aims to provide an overview of recent advances in bio-inspired polymers for energy storage applications, especially as organic electrodes for batteries. Thus, before introducing the different categories of bio-inspired polymers used as electrodes for different types of batteries and the basic principle of their use, it was first found necessary to start with a general state of the art survey on batteries through the presentation of the fundamental principle of their working, their principal components and characteristics.

**Keywords** Battery · Energy storage · Bio-inspired polymers · Organic electrode · High performances · Long-term applications

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## 1 Introduction

Over the past few years, the world's energy consumption has increased significantly, leading to a growing awareness of the need for evolving towards new alternatives more economical to fossil fuels as well as reducing the $CO_2$ emissions, while meeting the needs of daily consumption [1]. Besides, storage solutions are required to offset the gap between supply and demand. Storage systems can be classified into 5 categories, including, mechanical energy storage (pumped storage), electrical storage (supercapacitors), electrochemical storage (batteries), chemical storage (hydrogen), and thermal storage (sensible and latent heat storage) [2]. The appropriate storage system is chosen based on the application and the required performance. It depends on several parameters, namely technical–economic performance, environmental impact, and social acceptability. Therefore, no storage technology can meet all the criteria imposed. To date, batteries remain the most traditional means of storing electricity in the form of chemical energy because they democratize cost and their advantageous performances [3]. Thus, in terms of energy density, high performance, and low costs, lithium-based batteries are the most promising. Nevertheless, working with liquid electrolytes, which are inflammable and harmful, poses some safety problems, limiting their more widespread and future applications [4]. Thus, the challenge of rechargeable batteries now is to develop battery systems that simultaneously meet both economic and environmental requirements. Therefore, it is to reduce the use of dangerous materials that the bio-inspired polymers as organic electrodes for batteries have been developed [5]. In fact, bio-inspired materials are mainly made of naturally abundant elements such as carbon, oxygen, sulfur, azote, and so on with the real potential to be derived from sustainable and renewable resources. Moreover, most bio-organic electrode materials are compatible with sodium, lithium, nickel, lead, etc. with the possibility of use as an electrode, separator binder per the purposes of the batteries, making them more suitable for a broad range of electrochemical storage arrangements. This book chapter aims to provide an overview of recent studies based on the use of bio-inspired polymers as organic electrodes for batteries, through the presentation of the main categories of these materials, namely, biomass and its derivatives, quinone, and its derivatives and flavin and its derivatives, even the few numbers of available scientific papers relative to this new search field, since these electrodes constitute the novel generation of batteries due to their environmental nature, low-cost, availability and electrochemical performances.

## 2 Generalities on Batteries

A battery, also known as an accumulator, can be generally defined as an energy storage system capable of converting electrical energy into a reversible chemical process. The functioning of the batteries consists in converting the chemical energy into electrical energy by electrochemical reactions. They are composed of one or

cells connected in series and/or parallel to obtain the desired voltage and capacity. Each cell contains a positive electrode known as cathode, a negative electrode called anode physically separated by a porous membrane and an electrolyte (which can be solid, liquid, or a combination of these two states, such as gelled electrolytes), ensuring the transport of ionic species (anions and cations) from one electrode to the other and the electroneutrality of the system. Batteries are manufactured in several sizes with capacities varying from less than 100 W to several megawatts and in various types with different chemical compositions depending on their application [6, 7]. The positive electrode is a host structure, usually composed of a transition metal oxide with high electrochemical potential, while the negative electrode, which has a lower electrochemical potential, can be an intercalation material. Indeed, the higher the potential difference between the electrodes, the higher the energy density. Besides, batteries can be divided into two main categories: primary and secondary. This section aims to give an overview of batteries by presenting the different types, their fundamental principle, and their characteristics.

## *2.1 Components of Batteries*

All types of batteries are usually made up of four main components, two electrodes (anode and cathode), an electrolyte to move charges between the electrodes, and a separator to prevent shorting as displayed in Fig. 1. The materials used as positive electrodes are chosen for their ability to release electrons. generally, they are metals

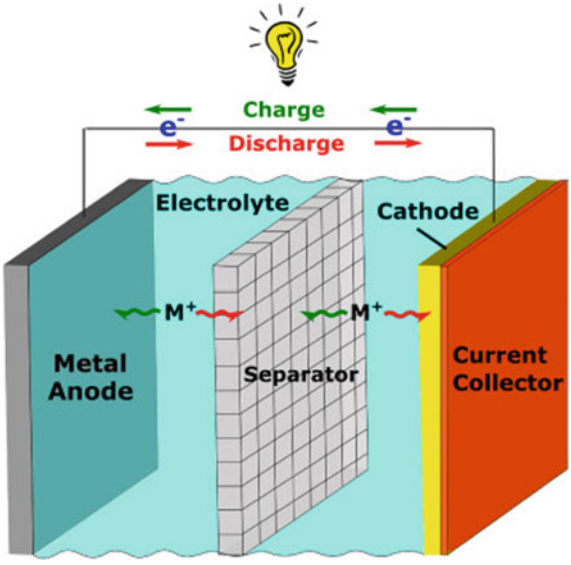


**Fig. 1** Schematic diagram of battery components. Adapted with permission from [8]

**Table 1** Desirable characteristics for battery components

| | Characteristics |
|---|---|
| Cathode | • Strong oxidizing compound<br>• Stable upon contact with the electrolyte<br>• Working voltage is useful<br>• Simple manufacturing process<br>• Low cost |
| Anode | • Highly effective reducing agent<br>• Excellent coulombic performance<br>• High conductivity<br>• Strong stability<br>• Facility of manufacturing<br>• Low cost |
| Electrolyte | • Strong ionic conductivity<br>• No electrical conductivity<br>• No reactivity with electrode materials<br>• Resistant to temperature changes<br>• Safety of handling |

with high reducing power such as lead, cadmium, lithium, etc. Conversely, the materials of the negative electrode must be strong oxidizers, i.e. capable of fixing the electrons. For this purpose, compounds of oxygen, sulfur, or halogens with other multivalent elements, such as transition elements, are used more frequently. Some batteries use positive electrodes known as insertion electrodes: the material used in this case is a chemical compound whose crystalline structure makes it possible to insert and disinsert charge carriers according to the charge and discharge. It happens that the negative electrode is itself an insertion compound, usually graphite. The electrolyte, which must be a good ionic conductor, is usually composed of a salt dissolved in a solvent that is stable to the electrodes, at least kinetically, and whose properties are chosen to solubilize and ionize this salt. It can be liquid, solid (polymer), or even in a mixed form (gel). Finally, the separator is a membrane made of one or more layers of polymers that separates the active materials. It is through this separation of charge the battery can generate electricity. During the charge or discharge cycle, the ions flow from one electrode to the other through the separator, while electrons migrate from the negative electrode to the positive electrode and through the outside circuit. The main characteristic of the separator is its porosity. Desirable characteristics for the anode, cathode and electrolyte materials are given in Table 1.

## *2.2 Batteries Fundamental Working Principle*

The conversion of chemical energy into electrical energy is carried out through redox or electrochemical reactions, hence the term “electrochemical generators”. Each half-reaction of oxidation and reduction takes place on each of the two electrodes, separated by an electrolyte that ensures ionic conductivity and electronic insulation

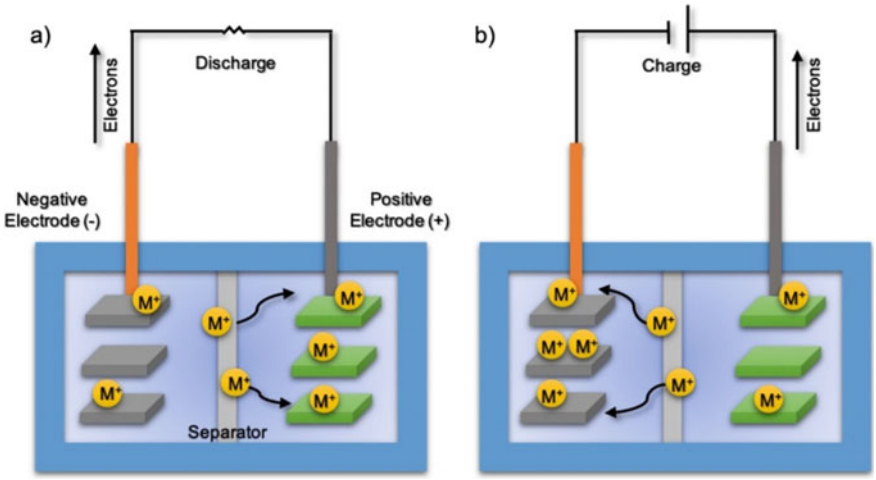


**Fig. 2** Example of battery, **a** discharge, **b** recharge. Adapted with permission from [9]

between them. We can also underline here that this conversion is reversible in the case of some batteries (secondary batteries), which distinguishes them from the second type of electrochemical generators, the primary batteries for which the transformation of energy is irreversible. The reversibility of the processes in the case of batteries thus implies two modes of operation. During discharge, the negative electrode is the seat of an oxidation reaction (i.e. a release of electrons) carried by the intermediary of a collector and then the external circuit to the positive electrode, the seat of a reduction reaction or gain of electrons. In charging, the opposite reactions occur: the negative electrode becomes the seat of a reduction reaction, and the positive electrode becomes the seat of an oxidation reaction (Fig. 2).

## *2.3 Types of Batteries*

Depending on the possibility of reuse after one period of use, batteries are classified into two main classes, namely, primary and secondary batteries. Primary batteries may be described as non-rechargeable batteries, in contrast to secondary batteries, which can be reused after discharge [10]. This section aims to highlight the difference between the most used types of batteries for high-energy applications.

### 2.3.1 Primary Batteries

A primary battery is a type of battery designated for a single use before discarding, meaning that it cannot be recharged with electricity and reused, whereby the inner

reaction happens in only one direction and the lifetime of the battery expires after a single cycle. Indeed, due to their low price, they are particularly appropriate for applications with low energy requirements and simply need a constant voltage. Primary batteries have been around for more than 200 years. The Italian scientist Alessandro Volta built the first practical battery in 1800 [11]. It is composed of a stack of small electrochemical cells each consisting of silver and zinc plates separated by a sheet of cardboard soaked in saltwater. Each cell generated a small amount of electrical energy, and then by connecting all the cells in the stack in series, Volta was able to generate a useful voltage for his experiments. The benefits of this kind of battery are their high energy density, high capacity, ease to use, low-cost, and slow discharge. Carbon-zinc and alkaline batteries are the most popular cell types [12].

### 2.3.2 Secondary Batteries

Secondary batteries are rechargeable batteries, they can be used during many cycles because the chemical internal reaction can be reversed by applying to it an electric current. Indeed, there are various subcategories of electrochemical storage technologies, which include mainly, lead-based batteries, nickel-based batteries, and lithium-based batteries. Thus, the principle of their work remains the same; the electricity is generated by chemical reactions involving the anode, cathode, and electrolyte, but the difference lies in the chemical composition of electrodes as well as the charge carrier element. Lead acid batteries (LABs), lithium-based, and nickel-based batteries are dominant with a total contribution of 94.8% of the global battery market according to some studies [13]. Table 2 summarizes the characteristics of different types of secondary batteries presented above.

**Table 2** Characteristics of different rechargeable batteries available in the market

| Features | Pb-acid battery | Ni-Cd battery | Ni-MH battery | Li-ion battery |
|---|---|---|---|---|
| In use since | Late 1800s | 1950 | 1990 | 1990 |
| Battery voltage (V) | 2.1 | 1.2 | 1.2 | 3.6 |
| Power density (W/kg) | 180 | 140–180 | 250–1000 | 1800 |
| Energy density (kW/kg) | 30–50 | 40–60 | 60–120 | 150–250 |
| Charging time (h) | 8–16 | 1 | 1–4 | <1 |
| Operating temperature (°C) | Ambient | −40 to +80 | Ambient | Ambient |
| Internal resistance | Low | High | Medium | Low |
| Cycle life | 300–800 | 1500 | 1000 | 500–2000 |
| Memory | No | Yes | No | No |
| Cost | Medium | Low | High | High |
| Toxicity | High | High | Low | Low |
| Maintenance | No | Low | Low | No |

# 3 Bio-inspired Polymers as Organic Electrodes for Batteries

In addition to inorganic materials, a rapidly developing area of research is the use of organic redox materials, especially as positive electrode materials. The materials initially used were p-conjugated polymers, good electronic conductors, such as polyheterocycles, etc. More recently, bio-inspired polymers from biomass and its derivatives, molecules such as quinones and nitroxides have been the subject of many very promising studies [14]. The interest in such materials is related to their natural abundance, their low cost, their very low toxicity, and their intrinsic properties [15]. Indeed, the interest in using bio-inspired electrode materials resides in the many advantages conferred by their structure, their higher specific capacity to inorganic materials, and the possibility of introducing different functional groups for raising or lowering the redox potential, depending on the application. The working principle of batteries based on bio-inspired polymers as organic electrodes is very similar to conventional batteries already mentioned before. The selection of the ideal electrode material, either for the cathode or the anode, is mostly driven by the reversibility of the electrochemical reaction (redox) of the active material. This section provides a comprehensive view of different bio-inspired polymers as organic electrodes for batteries.

## *3.1 Biomass and Its Derivatives*

Since prehistory, biomass has been the first source of energy to be discovered by humans. Biomass resources are very diverse and they are generally classified according to their origins and their physical nature. Lignocellulosic biomass is composed of carbon, hydrogen, oxygen, nitrogen, sulfur in minor proportions, and mineral matters such as Ca, Mg, K, P, Na, Si, etc. It contains also alkaline and alkaline earth minerals as well as metals. Moreover, it is mainly made from three compounds, namely, cellulose, hemicellulose, and lignin (Fig. 3). Cellulose microfibrils, embedded in a complex matrix of hemicellulose, pectin, and proteins, form the external skeleton of plant cells, while lignin is the rigid part of the plant wall and is linked to the hemicelluloses by covalent bonds [16, 17]. Recently, more interest has been shown in the use of biomass wastes for the preparation of different materials for various applications, including energy storage devices due to their low-cost, abundance, non-toxicity, and so on [5]. Biomass wastes can be valorized into cellulose and its derivatives, lignin, or others or might be carbonized through thermal processes with reduced environmental footprint and used in electrodes for batteries (e.g., sodium-ion, lithium-ion, metal–oxygen batteries, etc.) to improve their performances and environmental impacts as well as reduce their costs.

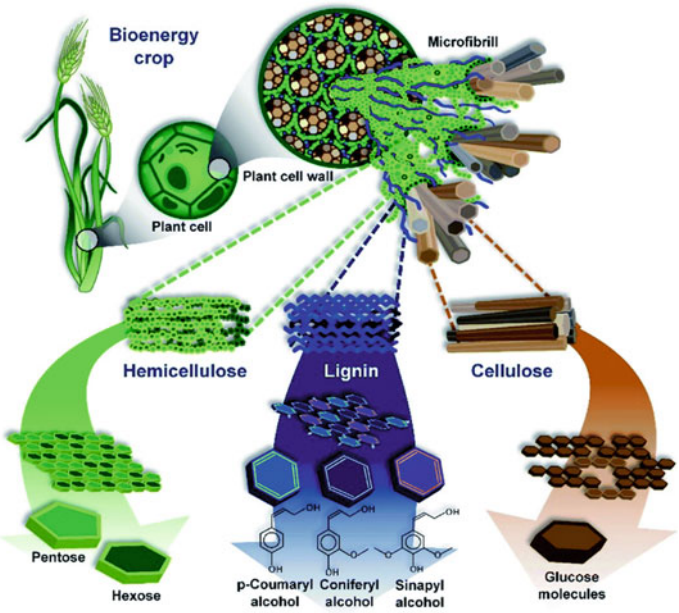


**Fig. 3** The structure of the main components of lignocellulosic biomass. Adapted with permission from [18]

(a) *Cellulose*

Cellulose is known as the most abundant renewable polymer on earth. It is a linear polysaccharide consisting of f β-1,4-linked D-glucose units, comprising macro- and microfibrils to create 3D hierarchical structures. Its amorphous phase possesses a large number of hydroxyl groups susceptible to forming hydrogen bonds with other molecules and is also responsible for its high hydrophilicity. Depending on the dimension and size of the individual cellulose fibrils, there is a variety of cellulosic materials, namely cellulose microfibrils (CMF), cellulose nanofibers (CNF), and cellulose nanocrystals (CNC) [19]. Moreover, due to its outstanding physico-chemical and mechanical properties (the tensile strength and modulus of nanocrystalline cellulose are approximatively equal to 140 and 7.5 GPa), cellulose and its derivatives such as nanocrystalline cellulose has been investigated for the design of bio-inspired polymer as organic electrodes, separators, binders, etc. for batteries [20, 21]. Indeed, cellulose-based batteries are contingent upon the structural, physicochemical, and mechanical properties of the materials of the electrode and the separator nature. The preparation of such batteries involves the immobilization of high conductive materials such as carbon nanotubes, graphite, graphene, metals, onto cellulose fibrils. Thus, cellulose and its derivatives, with abundant functional groups on their surfaces, are capable of forming high strong bonds with other materials through several chemical reactions, resulting therefore in a variety of straightforwardly electrode forms [22]. In this context, Cámer et al. developed a nano-Si/Cellulose composite as anode using

a simple and low-cost technique for improving the deficient features of lithium-ion cells [23]. The resulting composite electrode with high homogeneity, dispersion, and no-agglomeration exhibited outstanding electrochemical performances compared to neat Si electrode, indicating the role of cellulosefibers as green and eco-friendly materials in enhancing the battery features by maintaining interconnectivity between particles, thereby promoting the mobility of charge carriers in the bulk electrode and at the electrode–electrolyte interfaces. Indeed, the electrode with cellulose fibers showed a high specific capacity of about 1400 mAh/g after 50 cycles, versus only 400 mAh/g for the pristine Si electrode. Wang et al. fabricated a novel flexible bio-inspired polymer organic electrode with outstanding electrochemical performances for wearable electronicbased on cellulose, reduced graphene and ternary metal alloy [24]. Cellulose from cotton embedded with reduced graphene was firstly prepared through a dipping-drying method followed by the chemical reduction of amorphous Co–Fe–B alloy at ambient temperature. The structural characterization technique revealed the homogenous distribution of reduced graphene and metal alloy through the cellulose-based electrode. Besides, electrochemical features show that the elaborated electrode displays a high specific capacity of a maximum of 302.6 F/g compared to electrodes without cellulose, which can be attributed according to the authors to the synergistic effect of high conductivity, more accessible electroactive sites, and rapid electron collection efficiency. Thus, the cellulose bio-inspired electrode exhibited also high flexibility without any loss after 3000 charge and discharge cycles or being flexed 300 times, suggesting the excellent electrochemical properties of the elaborated electrode. A novel flexible electrode based on polyaniline and graphene as active material and bacterial cellulose as the material responsible for the flexibility of the electrode have been successfully fabricated using a facile in-situ polymerization followed by vacuum filtration [25]. Indeed, due to the abundance of functional groups on the bacterial cellulose, strong hydrogen bonds, and electrostatic interactions have been trained between the polymer/graphene composite and the cellulose. SEM and TEM images of the resulting electrode show the homogeneity of the prepared electrode over a larger surface and its porous structure, while electrochemical characteristics reveal that the combination of such materials leads to obtaining a highly efficient electrode in terms of specific capacity, areal capacitance, energy density, and conductivity. The electrode displays a high areal capacitance of 4.16 F/cm at a current density of 1 mA/cm, which remains a high value compared to other materials [26]. Li et al. investigated the preparation of cellulose-based cathode for lithium-ion batteries through aqueous slurry mixing and coating processes to improve their electrochemical performances and reduce their environmental risks [27]. In parallel, the authors fabricated a PVDF-based electrode as a reference to compare the performances of both electrodes. Results show that the electrode constituting from carboxymethyl cellulose provided an initial discharging capacity of 255.4 mAh/g at 0.2 C against 266.8 mAh/g in the case of PVDF-based electrodes, indicating the role of cellulose in improving the battery performances (Fig. 4). Recently, Jo et al. prepared cellulose–polyaniline–$Al_2O_3$ composites as separators for sodium-ion batteries. With the addition of alumina, the cellulose/PAN separator's electrochemical, thermal and mechanical performances have been tremendously upgraded. Compared to other

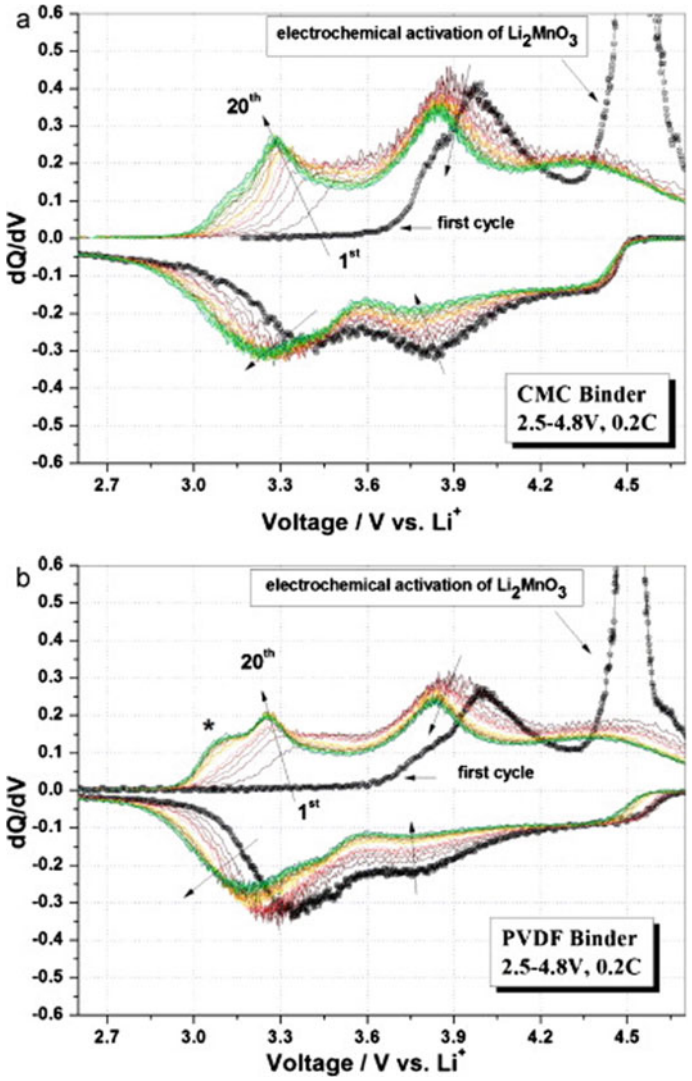


**Fig. 4** A derivative plot of the voltage profile for lithium-based battery with CMC (**a**) and PVDF (**b**) binder. Adapted with permission from [27]

separators, the elaborated composite showed high specific capacity with a maximum of 107 mAh/g at a rate of 1 C and high cycling stability of 88% for 300 cycles.

(b) *Lignin*

Lignin is the second most abundant organic biopolymer in plants after cellulose. This three-dimensional amorphous polymer has been extensively used in many applications, in particular in battery applications as electrodes. Milczarek and his co-author

first reported the possibility of using the quinone group of lignin as a cathode, since then a lot of studies investigated the application of lignin polymer as a green and inexpensive organic electrode for batteries [28]. In this context, Gnedenkov et al. investigated the use of Klason lignin derived from different types of biomass feedstocks, namely, buckwheat, husks of rice, rice straw, and sunflower as an organic electrode for lithium-based batteries [29]. Structural characterization demonstrated that all lignin exhibited amorphous structures whatever the type of biomass. In contrast to the results of the thermal analysis which showed that the thermal stability of the different types of lignin varies with varying the feedstock nature. Moreover, in terms of electrochemical properties, the lignin-derived from buckwheat exhibited a high specific capacity compared with other lignin electrodes, with a maximum of 425 mAh/g. The proposed electrochemical reaction at electrodes upon discharge is given by the following equations:

$$-\underset{|}{\mathrm{C}}=\mathrm{O}+\mathrm{Li}^{+}+\mathrm{e}^{-}\rightarrow-\underset{|}{\mathrm{C}}-\mathrm{O}-\mathrm{Li} \tag{1}$$

$$2\mathrm{C}_6-\mathrm{C}_3-\mathrm{OH}+2\mathrm{Li}^{+}+2\mathrm{e}^{-}\rightarrow 2\mathrm{C}_6-\mathrm{C}_3-\mathrm{O}-\mathrm{Li}+\mathrm{H}_2 \tag{2}$$

$$\mathrm{C}_6-\mathrm{C}_3-\mathrm{O}-\mathrm{R}^{*}+2\mathrm{Li}^{+}+2\mathrm{e}^{-}\rightarrow \mathrm{C}_6-\mathrm{C}_3-\mathrm{O}-\mathrm{Li}+\mathrm{R}^{*}-\mathrm{Li}_2 \tag{3}$$

where, ($C_6$–$C_3$) is a phenylpropane structural unit of lignin, R* is ($C_6$–$C_3$) or $CH_3$.

Pyrolysis of lignin has been also investigated to be utilized in electrode batterie. The pyrolysis of lignin involves complex reactions of cyclization, polymerization, condensation, and cracking. The products obtained are CO, $CO_2$, $CH_4$, and other gaseous hydrocarbons. Lignin is at the origin of most solid products especially in the case of slow pyrolysis. In this context, Tian et al. fabricated a hierarchical S-doped porous carbon using an easy template approach for high-performance electrode supercapacitors [30]. Indeed, doping heteroatoms such as sulfur into carbon materials is considered an attractive approach for enhancing the intrinsic chemical and electrical features. The resulting carbon layer with an interconnecting open structure and high surface area of 1054 $m^2$/g exhibited excellent specific capacity (328 F/g), outstanding rate performances, and high cycling stability, with 97% of capacity after 10,000 cycles.

(c) *Biochar*

To enhance the electrochemical features of batteries, especially their conductivity, carbonaceous materials ranging from graphene to carbon with hierarchical porosity and structure have been investigated [31]. Despite having demonstrated reasonable performances, the complex and costly manufacturing process precludes their mass production. Biomass feedstocks such as agricultural and crops wastes, wood, and plant residues are rich in carbon and can be easily burned through thermal conversion and used therefore to produce carbon-based materials such as biochar for energy storage applications. According to the International Biochar Initiative (IBI), biochar

can be described as a porous solid material produced by the thermochemical process of biomass in an environment with limited oxygen [32]. Nowadays, due to its fascinating properties, it is applied to develop new materials in numerous fields including environmental remediation, wastewater treatment, catalysis for fuel cells, and energy storage technologies as an electrode in batteries and supercapacitors [33, 34]. A nitrogen-rich, porous hierarchical carbon from wheat straw has been successfully prepared as anode for Lithium-ion batteries (Fig. 5) [35]. The anode was prepared through an easy and inexpensive technique consisting of treating firstly the raw wheat straw fibers with HCl and KOH to remove impurities and also to improve the surface

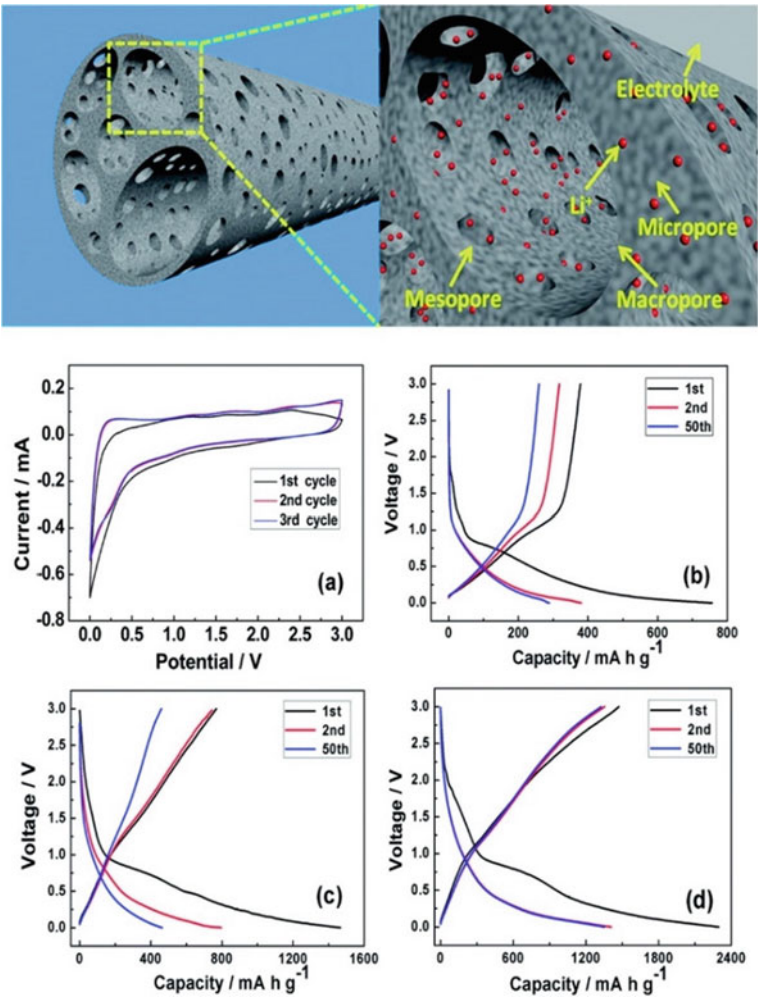


**Fig. 5** Hierarchically porous nitrogen-rich carbon morphology and electrochemical performances. Adapted with permission from [35]

properties (porosity and functional groups), and then pyrolyzed under nitrogen flux at high temperature (700 °C) for 1 h. The resulting biochar with a high interconnected structure exhibited a high specific surface area compared to nonactivated wheat straw biochar. The surface area was increased from 24.9 to 916 $m^2$/g, indicating the role of acid and alkaline treatments in improving the physicochemical features of biochar to be used later as anode for lithium-ion battery. XRD analysis confirmed the amorphous nature of the biochar, which is more beneficial for the intercalation and deintercalation of lithium ions during charge and discharges cycles. Moreover, electrochemical results displayed that the resulting anode exhibits high-rate capability, excellent specific capacity, high current density, and large reversible capacity. In fact, during the first charge–discharge cycle, the anode with activated biochar shows a highly specific capacity of about 1470 mAh/g at a current density of 37 A/g, which is much higher compared to the nonactivated anode. The reversible capacity of the anode is maintained at 1327 mAh/g after 50 cycles, indicating the stability of the elaborated anode. The slight decrease may be attributed to the conversion of the carbon electrode from its virgin form to an active lithium storage host. Li et al. fabricated carbon nanosheets from bacterial cellulose pyrolyzed at high temperature (800 °C) for use as cathode for lithium-sulfur batteries to resolve the problems of Li/S batteries related to the dissolution of polysulfide species, causing their self-discharge and bringing about their rapid capacity depletion [36]. Indeed, cathodes were made by coating $Li_2S_6$ catholyte on carbon a nanofiber aerogel to obtain a sulfur loading of 2.74 mg/$cm^2$ and 80% of sulfur across the overall electrode. The resulting cathode exhibited excellent electrochemical performances. The cells demonstrated an initial capacity of 1360 mAh/g at 0.2 C and present outstanding cycle stability in which 76% of the initial specific capacity was maintained after 200 cycles, which might be related to the ultra-strong absorption ability of CNFA for catholyte. Similarly, carbon nanosheets derived also from bacterial cellulose have been prepared to be used as bio-inspired organic anode for sodium-ion batteries [37]. Different carbon nanosheets-based anodes under different pyrolysis temperatures have been prepared to study the role of the temperature of pyrolysis on the electrochemical features of the resulting electrodes. Carbon pyrolyzed at high temperature was found to be the best anode, with a high specific capacity, excellent rate capacity, and cycling stability. The authors attributed this enhancement to its porous structure, an abundance of functional groups, in particular, oxygen functional groups, and excellent surface area. Microporous alkaline activated biochar with high surface area and excellent electronic conductivity was derived from bamboo fibers for use as cathode for Li–S batteries [38]. The electrode with 50 wt% sulfur content exhibits a high initial capacitance of 1295 mAh/g and good capacitance retention of 550 mAh/g after 150 cycles with excellent Coulombic efficiency.

### 3.2 *Quinone/Flavine and Their Derivatives*

Quinone and its derivatives are among the most investigated organic electrode materials derived from bio-resources [39]. According to the literature, quinones can be defined as a class of molecules obtained from aromatic substances such as naphthalene, benzene, and so on, through the conversion of –CH= groups into –C(=O)– groups, resulting, therefore, to fully conjugated cyclic diketone structure [40, 41]. They are the main redox-active moieties amongst the natural organic compounds playing a real role in the electron-transport processes. The reversibility of quinone compounds has been known for a few years, in particular through the work of Armand et al. on the reduction of lithium rhodizonate acid which showed a very good capacity of 515 mAh/g in the 1.5–3.5 V potential range [42]. Moreover, the redox characteristics of quinones such as p-benzoquinone or o-benzoquinone have been extensively applied in electrochemical energy storage systems either in the reduced or oxidized state. In this context, Song et al. synthesized a poly (anthraquinone sulfide) with an excellent cyclability, reversibility, and a capacity of 198 mAh/g at the first cycle with a loss of only 7% after 40 cycles. Triptycene-based quinone molecules were used as organic cathode materials in Li-ion batteries to improve their electrochemical features, delivering a specific capacity of 387 mAh/g, an energy density of 1032 Wh/kg 0.1 C rate, and a high capacity stability of 80% after 100 cycles [43]. Notwithstanding the high energy density expected, quinone derivatives are suffering from the dissolution of active materials in conventional organic-based electrolyte systems. Two Cross-conjugated oligomeric quinones have been proposed for use as a bio-inspired organic electrode for lithium-based batteries [44]. Both quinones-based electrodes provided a comparable capacity of over 200 mAh/g with a capacity stability retention of 96% over 250 cycles. The mechanism of the electrochemical reaction at the cathode is given in Fig. 6. Poly(5-amino-1,4-dyhydroxy anthraquinone) were also investigated for use as cathode material of lithium batteries [45]. The cathode was easily prepared through an oxidation approach. At the cutoff voltage of 1.5–3.7 V, the cathode displays an initial discharge capacity of about 101 mAh/g at the current density of 400 mAh/g. Moreover, the elaborated cathode was efficient to prevent the problems related to the dissolution and crystallization of its 5-amino-1,4-dyhydroxy anthraquinone monomer. Besides, the most attractive part of this study, is that the capacity of the cathode increased after 14 cycles reaching a value of 143 mAh/g and then decreased to 129 mAh/g after 50 cycles. Thus, the quinone based electrode shows high-rate capacity even at high current density, indicating the high electrochemical performances of this material. Shimizu et al. were also investigated the impact of introducing of two lithiooxycarbonyl groups into the organiccathode of lithium battery in enhancing their cyclability as well as resolving the problems of the solubility of quinone molecules in electrolyte. Electrochemical results show that the cathode exhibited an initial capacity of 217 mAh/g at 0.2 C rate, which is 73% of the theoretical capacity [46].

The versatility in designing redox flow batteries makes them suitable for efficient low-cost energy storage in large-scale applications. The discovery of inexpensive

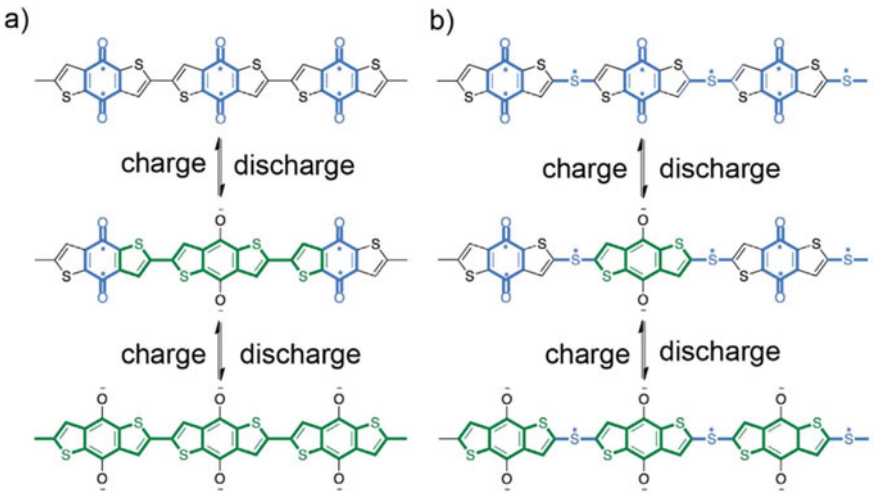


**Fig. 6** The electrochemical mechanism of the quinone-based electrode. Adapted with permission from [44]

organic electroactive materials for use in aqueous flow battery electrolytes is therefore a very attractive approach. Flavins are highly versatile electroactive molecules, catalyzing a multitude of redox reactions in biological systems. A redox flow battery using flavin mononucleotide negative and ferrocyanide positive electrolytes in a strong base exhibit stable cycling performance, with a retention capacity greater than 99% over 100 cycles. Sánchez-Díez et al. [47] investigated the role of using flavin redox cycling in mitochondria to lithium rechargeable batteries. The redox reaction of flavin takes place generally during battery function at the diazabutadiene nitrogen atoms in the flavin molecules via two sequential steps namely, single-electron and Li+ transfer steps.

## 4 Conclusion

In recent years, to overcome the drawbacks of conventional inorganic cathode materials, including their low specific capacity and poor removal system, organic compounds have emerged as promising candidates for use in the next generation of energy storage systems, in particular as electrodes for batteries. Indeed, the present research orientations in this field consist of to

1. use of eco-friendly materials with high electrochemical performance and stability after several cycles.
2. favor less energy-intensive synthesis methods “soft chemistry”.
3. develop electrodes based on organic materials (with multiple redox centers) renewable and from biomass and

4. develop new batteries beyond lithium.

In the face of this, biopolymers, such as cellulose or lignin, can be applied in binders, separators, and solid or gel electrolytes, and thus can be used industrially since their production from biogenic precursors is feasible. On the other hand, biopolymers, such as cellulose or lignin, can be applied in binders, separators, and solid or gel electrolytes, and thus can be used industrially since their production from biogenic precursors is feasible. Furthermore, several quinones, mainly explored as cathodic materials, have been obtained from bioresources. Even ionic liquid electrolytes have been synthesized using chemicals purely derived from biomass. Finally, carbonaceous materials are a key component of all types of batteries, not only as host materials for metal ions in the anodes but also, for example, as conductive additives. Using all kinds of biowaste or biogenic chemicals, carbons have been synthesized with the possibility to adjust properties such as porosity or conductivity. As a result, almost all the biomass on Earth could be used in battery applications in the future, either in the form of special biomass-based materials or as precursors for fine chemicals or carbons. While inorganic materials are often preferable when it comes to high voltage or high energy density applications, the disadvantages in terms of sustainability can be completely circumvented by switching to fully bio-derived energy storage devices in the future.

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