



## Biomass-derived materials for electrochemical energy storages



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### ABSTRACT

During the past decade humans have witnessed dramatic expansion of fundamental research as well as the commercialization in the area of electrochemical energy storage, which is driven by the urgent demand by portable electronic devices, electric vehicles, transportation and storage of renewable energy for the power grid in the clean energy economy. Li-secondary batteries and electrochemical capacitors can efficiently convert stored chemical energy into electrical energy, and are currently the rapid-growing rechargeable devices. However, the characteristic (including energy density, cost, and safety issues, etc.) reported for these current rechargeable devices still cannot meet the requirements for electric vehicles and grid energy storage, which are mainly caused by the limited properties of the key materials (e.g. anode, cathode, electrolyte, separator, and binder) employed by these devices. Moreover, these key materials are normally far from renewable and sustainable. Therefore great challenges and opportunities remain to be realized are to search green and low-cost materials with high performances. A large number of the properties of biomass materials—such as renewable, low-cost, earth-abundant, specific structures, mechanical property and many others—are very attractive. These properties endow that biomass could replace some key materials in electrochemical energy storage systems. In this review, we focus on the fundamentals and applications of biomass-derived materials in electrochemical energy storage techniques. Specifically, we summarize the recent advances of the utilization of various biomasses as separators, binders and electrode materials. Finally, several perspectives related to the biomass-derived materials for electrochemical energy storages are proposed based on the reported progress and our own evaluation, aiming to provide some possible research directions in this field.

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## 1. Introduction

In the 21st century, with the rapid demand of electric vehicles and portable electric devices, a new energy economy is emerging, which is critically based on the cheap and sustainable energy supply. Undoubtedly, to exploit clean, sustainable and secure energy supplies is one of the most important scientific and technical challenges for humans [1–3]. State-of-the-art electrochemical energy storage devices, typically including Li-ion batteries (LIBs) and electrochemical capacitors [4–7], provide a potential and promising solution since they can efficiently store energy from sustainable sources such as the wind and solar power and then work as power sources. These energy storage devices are typically composed of a negative electrode (anode), a positive electrode (cathode), an electrolyte that allows ions transport, a separator that separates the two electrodes, and current collectors that allow current to flow out of the cell to perform work. The overall performance of these energy devices depends intimately on the properties of the materials used. Hence, material science and technology hold the key to new generations of energy storage devices. Numerous materials, including various anodes, cathodes, separators, binders, and electrolytes, are designed and fabricated to improve the performances of LIBs and electrochemical capacitors [4–10].

The principal remaining challenges for the future development and widespread of energy storage, other than performance and safety enhancements, are the reduction of both production and overall device costs, the realization of flexible devices, the identification of environmentally friendly materials and production processes and the development of easily recyclable and up-scalable systems [1–3]. Presently, these electrochemical energy devices mainly depend on the substantive use of components that are far from renewable and sustainable, for instance, inorganic compounds that often require rare metals as electrode materials, expensive polymers as separators

and binders, and organic solutions as electrolytes, and so forth [4–7]. Broad applications of electrochemical energy devices require more abundant and inexpensive materials than those currently available. As Armand and Tarascon wrote in 2008, “Researchers must find a sustainable way of providing the power our modern lifestyles demand” [1], a consensus forms across the world that it is highly urgent and desired to decrease the consumption of non-sustainable electrochemical energy device resources by developing materials from easily accessible and renewable sources. Among numerous candidates, biomass-derived materials have gained increasing attention as attractive components of various electrochemical energy devices.

Biomass is biological material derived from living, or recently living organisms. As earth-abundant renewable energy source, biomass is typically used directly via combustion to produce heat, or used indirectly after converting it to various forms of biofuel [11,12]. However, the more intriguing and promising utilization of biomass in energy storage is to replace non-sustainable components in electrochemical energy devices, such as separators, binders, and electroactive electrode materials [13–15]. In the recent years, many significant efforts have been put into developing sustainable and high-performance biomass and/or biomass-derived materials for energy storage, and several significant review articles related to these research fields have been presented. Nyholm et al. reported the progress toward flexible polymer and paper-based energy storage devices [13]. Cui et al. reviewed the state-of-the-art flexible energy and electronic devices based on nanostructured papers [14]. Jabbour et al. summarized the progress of cellulose-based LIBs [15]. However, there is no a systemic review related to the applications of diverse biomasses and their polymer derivatives in electrochemical energy storages yet. In this review, we will give a short introduction of biomass materials, and then focus on recent progresses of biomass-derived materials as advanced separators, binders, and electrode materials in electrochemical

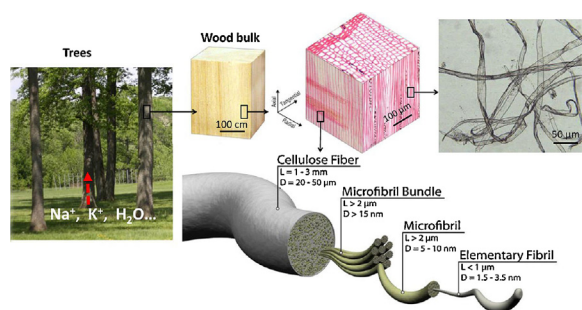


Fig. 1. Hierarchical structure of wood fiber [19].

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energy storages, and finally provide an overview and outlook about these fascinating research fields.

## 2. Overview of biomass material

Biomass is all biologically-produced matter based on carbon, hydrogen and oxygen. The estimated biomass production in the world is 146 billion tons a year, consisting of mostly wild plant growth [16]. Biomass most often refers to plants or plant-derived materials, specifically called lignocellulosic biomass. In addition to lignocellulosic biomass, marine organisms also constitute a large part of biomass materials. It is well known that biomass has been widely applied in many fields, and the application of a particular type of biomass depends on the chemical and physical properties of the macromolecules [17]. In this review, several biomass-derivatives materials that have been widely used for energy storage devices, including cellulose, alginate, and some others, are mainly mentioned. The basic information of cellulose and alginate, including manufacture methods, molecular structures and properties, is summarized in Table 1.

As the most important skeletal component in plants, the polysaccharide cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, linear stiff-chain homopolymer is characterized by its hydrophilicity, biodegradability, broad chemical modifying capacity, and its formation of versatile semicrystalline fiber morphologies [18]. The nature of cellulose fibers is affected by the source of the raw material stock, e.g. wood pulp versus cotton linters, and the chemistry and mechanics of the fibers forming process. Interestingly, cellulose exists in hierarchical structure from micrometric cellulose fibers to nanocelluloses and water/solvent soluble cellulose derivatives, which promises an expected porosity (Fig. 1) [19]. For instance, thousands of microfibrils cellulose assemblies one tracheid in wood fiber, which has a multichannel, mesoporous structure and allows for the intercellular transportation of water and mineral salts (Fig. 1) [19]. Over the last 10 years, celluloses, especially nanocellulose, have attracted an ever increasing attention for the production of cellulose based nanocomposite materials, due to their

high strength and stiffness combined with low weight, biodegradability and renewability [20].

Marine polysaccharides, including alginate, chitin, agar and carrageenan, can be easily obtained from diverse marine organisms such as fishery products, seaweeds, microalgae, microorganisms, and corals [21]. Since these organisms inhabit in a very diverse marine environments, marine polysaccharides exhibit some unique properties, which are useful in a variety of applications such as food technology, biotechnology, pharmacy, and chemical industries. For instance, alginate is a naturally occurring anionic polymer typically obtained from brown seaweed, and typically alginate is a linear copolymer with homopolymeric blocks of (1–4)-linked  $\beta$ -D-mannuronate and its C-5 epimer  $\alpha$ -L-guluronate residues. Due to its biocompatibility, low toxicity, relatively low cost, and mild gelation by addition of cations, alginate is widely used in food industry and pharmaceutical industry.

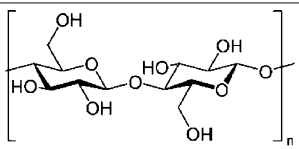
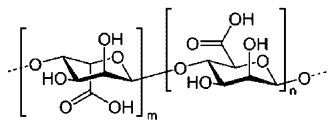
## 3. Biomass-derived separators

Battery separator, a porous membrane placed between electrodes of opposite polarity, serves to prevent contact between the positive electrode and the negative electrode and also plays a very important role in improving battery performance and enhancing its safety [22,23]. In the present battery production, the separator is impregnated typically into a mixture of supporting electrolyte (e.g. LiPF<sub>6</sub> salts) and organic solvents such as ethylene carbonate (EC), ethyl methyl carbonate, and diethyl carbonate. A number of factors must be considered in selecting the suitable separator for a practical battery, and the general characteristic and requirements of separators are well illustrated in the review by Aoroa and Zhang (as shown in Table 2) [24]. Actually the data summarized in Table 2 are mainly focus on the polyolefin separators, and these parameters for non-woven separators are somewhat depend on their specific materials and configurations.

Many researchers are interested in high-power LIBs due to their excellent properties, resulting in the expansion in the use of large-scale LIBs in the power market and power grid areas. These emerging markets have led to new demands on separators for LIBs [22,23,25]. The most widely used separators in LIBs are fabricated from polyolefins, predominantly polyethylene (PE), polypropylene (PP) and their copolymers. These polyolefin separators have many advantageous attributes in terms of practical application to commercialized LIBs, such as low cost, proper mechanical strength and pore structure, electrochemical stability, and thermal shutdown properties [22,26]. However, these separators suffered from a severe challenge in large shrinkage ratio at relatively high temperature of more than 100 °C. Moreover, their intrinsically hydrophobic character and low porosity raise serious concerns over insufficient electrolyte wettability, which could directly impair ionic transport through the separators and deteriorate cycle lives. Recently many approaches have been proposed to improve this insufficient heat resistance of microporous polyolefin separators including the ceramic coating on the surface of microporous membrane [27] and surface grafting modification using plasma treatments or electron beam

**Table 1**

The basic information of two typical biomass materials.

Biomass	Manufacture methods	Structures	Properties
Cellulose	Extract from plants; fibrillation and refining of cellulose pulp; bacterial synthesis		Abundant, high dielectric constant, heat resistance, and good chemical stability
Alginate	Extract from seaweeds		Hydrophilic, highly viscous, odorless and tasteless, and good stability

irradiation [28,29]. The most used fillers incorporated into the polymer hosts are inert oxide ceramics ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ) and molecular sieves (zeolites) with the main function of increasing wettability, mechanical stability and thermal dimensional stability of the separators [30,31]. Despite these advances, it is difficult to fully ensure electrical isolation between electrodes due to their inessential poor thermal shrinkage and weak transverse mechanical properties for intrinsic polyolefin materials at elevated temperature [32,33]. In addition, the high processing cost and exhaustible fossil derived materials of polyolefin separators remains a critical burden on manufacture boosting and environments. Hence, a more advanced separator that can overcome these stringent shortcomings of polyolefin separators is urgently needed for facilitating the successful development of high-energy density/high-power density cells.

Luckily, sustainable biomass-derived separators including cellulose, chitin and alginate, that exhibit superior wettability and thermal stability, are demonstrated as promising alternatives to conventional polyolefin separators for state-of-the-art electrochemical energy storage devices. These hydrophilic stiff-chain homopolymers endow super solvophilicity, wettability, recycling, accessible to electrolyte and better thermal stability (over  $230^\circ\text{C}$ ) than polyolefin. Actually, cellulose and cellulose composite separators were initially explored for using in alkaline batteries. In recent 30 years, cellulose nonwoven has been widely explored as separators for LIBs and electrochemical

capacitors. The common properties of biomass-based separators for alkaline batteries, electrochemical capacitors and LIBs include: (1) favorable separator surface and interface wettability by electrolyte, (2) high ion conductivity, and (3) large-scale production with low cost.

### 3.1. Cellulose materials for alkaline battery separators

About 70 years ago, the utility of regenerated cellulose membrane as a battery separator was recognized as a forward step which advanced the silver/zinc battery to a practical system. In 1941, Henri Andre, a pioneer of regenerated cellulose membrane, discovered that the short life of the silver/zinc battery system could be considerably improved by the introduction of a suitable cellulose semipermeable separator [34]. Then, for their excellent wettability, low processing cost, high porosity, good mechanical properties and light weight, paper sheets prepared using alkaline-resistant cellulose pulp or other cellulosic components were successfully used in a series of commercially available alkaline batteries including alkaline manganese cell, nickel/cadmium industrial batteries, zinc/air cells, silver/cadmium batteries, as well as in silver/zinc batteries [35]. Although the electrolytes are different from one to another, the similar fundamental properties and problems for separator films are commonly observed in these systems. Harlan Lewis studied the properties of cellulosic separator and their relationships with the cycle- and wet-life information from model

**Table 2**

General parameters for LIB separators.

Parameter	Goal	Test method (N.A. = not available)
Sale price ( $\$/\text{m}^2$ )	<1.00	The American Society for Testing and Materials (ASTM) test method D5947-96
Thickness ( $\mu\text{m}$ )	<25	
Permeability (MacMullin, dimensionless)	<11	
Wettability	Complete wet out in typical battery electrolytes	N.A.
Chemical stability	Stable in battery for 10 year	N.A.
Pore size ( $\mu\text{m}$ )	<1	ASTM test method E128-99
Puncture strength	>300 g/25.4 $\mu\text{m}$	ASTM F1306-90
Thermal stability	<5% shrinkage after 60 min at $90^\circ\text{C}$	ASTM D1204
Purity	<50 ppm $\text{H}_2\text{O}$	
Tensile strength (for spirally wound)	<2% offset at 100 psi	ASTM test method D882-00

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electrochemical cells as a functional of separator composition on an alkaline chemistry rechargeable cell set [36].

Alkaline battery accounts for 80% of manufactured batteries in the US and over 10 billion individual units produced worldwide, and the cellulose based separators for alkaline battery are still one of the intensive research focuses. Recently, some new progress related to cellulose materials for alkaline battery separator was achieved. Wang et al. fabricated alkaline Zn/MnO<sub>2</sub> separator with an ultra-fine fibrillated Lyocell fibers by wet-laid non-woven method, and the resulting separators manifested better properties than commercial separator especially in thickness and pore size [37]. Similarly, Toshimitsu Harada disclosed an alkaline battery composite separator including alkali-resistance synthetic fiber, fibrillated organic solvent-spun cellulose fiber and mercerized pulp, wherein the cellulose fiber intertwines with the mercerized pulp. This kind of composite separator exhibited excellent properties in denseness, electrolyte retention capability, and alkali resistance and great stiffness strength [38]. Most recently, Nippon Kodoshi Corporation developed an alkaline battery separator on the basis of cellulose. This separator is constructed by including 20–90 mass% cellulose fiber and having the remains being an alkali-resistant synthetic fiber, and can suppress reduction in the characteristics of the alkaline battery after storage [39].

### 3.2. Cellulose materials for electrochemical capacitor separators

Electrochemical capacitors store the energy at the electrode/electrolyte interface of high surface area materials, such as porous carbons or some metal oxides. Although their energy densities are somewhat low, electrochemical capacitors possess of many important benefits, such as high power density, long lifetime, low cost, good cycle performance and rate capability, etc. Electrochemical capacitors have been commercially available for more 30 years, and have been widely applied in consumer electronic products, (alternative) power source, and electric vehicles. [7,40].

In principle, electrochemical capacitor can work without a separator if a suitable distance between electrodes can be kept. However, practically, separators are necessary for the electrochemical capacitors to prevent from short circuits. Owing to the large market, the separator of electrochemical capacitors should be quite low in price and quite high in quality. Numerous studies have been demonstrated that cellulose-derived separators are very suitable for electrochemical capacitors applications, due to their low cost and high porosity (in the order of 45–90%) [7]. Currently, numerous cellulose based paper products are available for use as separator membranes in commercially available electrochemical capacitor systems. Such products include single-sheet cellulose fiber materials, multi-sheet cellulosic and composite materials with various densities which ostensibly yield the desirable properties, i.e., electrolyte absorption, electronic insulation, and physical strength [41]. Although such separator papers perform quite well in the intended physical compression type of electrochemical capacitors, the resistance between these papers and the desirable cell electrode compositions (particularly in

preferred thermal laminating procedures), restricts use of these papers in the fabrication of unitary laminated cell structures [42]. In addition, paper separators often suffer from performance deterioration at high voltage and water contamination in electrochemical capacitors, thus it is critical to overcome these obstacles for the development of paper separator-based capacitors.

### 3.3. Commercial paper-derived LIB separators

Some cellulose papers, which are manufactured using commercial cellulose papers, as advanced separators of lithium-based batteries have been reported. In 1996, Kuribayashi carried out a systematic investigation on the use of thin hybrid cellulose separators for LIBs. These paper separators, comprising fibrilliform cellulosic fibers embedded in a microporous cellulosic matrix soaked with an aprotic solvent, were supplied by Nippon Kodoshi Corporation and Tomiyama Pure Chemical Industry. The proposed separators showed fair-to-moderate physical strength, an apparent completely freedom from pinholes, and a comparable impedance to that of conventional polyolefin separators [43]. The commercial rice paper, a low cost and highly porous, flexible cellulose membrane, invented over a thousand years ago in China for traditional Chinese painting and calligraphy, was recently explored for the application as separator of LIBs, which exhibit fair cycling electrochemical stability at low current density [44].

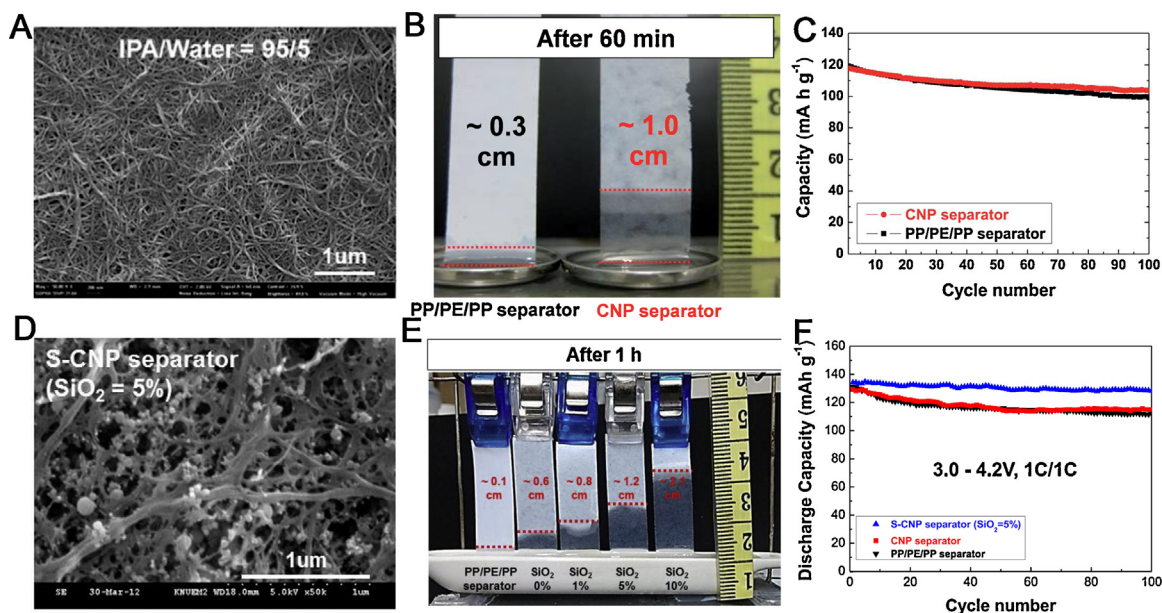
The cellulosic papers directly as separators suffer from moisture absorption owing to the hygroscopic nature. The moisture content of cellulose fibers can range between 2 and  $12 \times 10^4$  ppm [45], which severely exceeds the humidity requirement of a LIB electrolyte (not exceed ca. 20–50 ppm). A high humidity condition usually leads to the degradation of lithium salts, particularly LiPF<sub>6</sub> hydrolysis and HF formation [46]. Nevertheless, as demonstrated in recent works, this apparent limitation of moisture accessibility can be solved by prolonged thermal treatment over 120 °C owing to its superior thermal stability of cellulose which allows removing most of water adsorbed on cellulose [47].

Due to the high thermal stability and cost-effective of cellulose materials, the commercial cellulose papers can be used as separators for LIBs. However, the macro/microfiber-based cellulose papers face some stringent limitations in securing a satisfactory porous configuration (particularly, pore size and pore size distribution, and thermal shutdown effect), and mechanical strength and flammable characteristic, which in turn hamper their application as LIB separators. As a result, it seems not very suitable to directly use commercial papers as LIB separators.

### 3.4. Micro-/nano-fibrillated cellulose-derived LIB separators

Micro-/nano-fibrillated elluloses, consisted of highly crystalline domains and attractive nanoporous structure, possess excellent mechanical property and attractive porous structure. These fascinating characteristics would endow micro-/nano-cellulose membrane as a very





**Fig. 2.** CNFs paper (CNP)-derived separators by Lee group: (A) scanning electron microscopy (SEM) image of CNP separator. (B) Comparison of liquid electrolyte (1 M LiPF<sub>6</sub> in EC/DEC = 1/1, v/v) immersion-height between the PP/PE/PP separator and CNP separator [48]. Copyright 2012. Reproduced with permission from the Royal Society of Chemistry. (D) SEM image of SiO<sub>2</sub> decorated CNP (S-CNP) separator (SiO<sub>2</sub> = 5 wt.%). (E) Comparison of liquid electrolyte (1 M LiPF<sub>6</sub> in EC/DEC = 1/1, v/v) immersion-height between the PP/PE/PP separator, CNP separator, and S-CNP separators (SiO<sub>2</sub> = 1, 5, 10 wt.%). (F) Comparison of cycling performance of cells assembled with CNP separator, S-CNP separators, or PP/PE/PP separator [52]. Copyright 2013. Reproduced with permission from Elsevier Ltd.

promising separator for LIBs. In the most recent years, Lee and his colleagues devoted much contribution in the field of nanocellulose-based separators. They developed eco-friendly cellulose nanofibers (CNFs) paper-derived separators with a salient feature of electrolyte-philic, nanoscale labyrinth structure established between closely piled nanocelluloses. The unusual porous structure is fine-tuned by varying the composition ratio of the solvent mixture (isopropyl alcohol (IPA)/water) in the CNFs suspension, wherein IPA is introduced as a CNFs-disassembling agent while water promotes dense packing of CNFs. For example, when the IPA content is 95%, the CNFs separator provides a porous structure containing many nanopores formed between highly interconnected CNFs (Fig. 2A). Compared with the PP/PE/PP separator, the CNFs separator presents a much improved wettability of liquid electrolyte (Fig. 2B). Due to the nanoporous structure and strong affinity for liquid electrolyte, these CNFs paper-derived separator shows good cycling performance (Fig. 2C) and rate capability [48].

However, CNFs paper separators suffer from a limitation in providing highly-porous structure, which may stagger ionic transport via the liquid electrolyte-filled CNFs paper separator. This structural shortcoming may arise from the dense packing of CNFs for the strong hydrogen bonding between nanocellulose [49–51]. Lee et al. recently designed a colloidal SiO<sub>2</sub> nanoparticle-based strategy to tune the porous structure of CNFs paper separators, in which the SiO<sub>2</sub> nanoparticles are introduced as a CNFs-disassembling agent instead of IPA. The SiO<sub>2</sub> nanoparticles are dispersed between the CNFs and allow loose packing of CNFs, thereby facilitating the formation

of a more developed porous structure (Fig. 2D). With increasing the content of hydrophilic SiO<sub>2</sub> nanoparticles, the as-prepared SiO<sub>2</sub>-CNFs exhibit the greater and greater electrolyte immersion-height than the PP/PE/PP separator (Fig. 2E). With well-developed porous structure and optimized membrane properties, the SiO<sub>2</sub>-CNFs paper separator greatly improves the cycle performance and rate capability (Fig. 2F) [52].

Although the above developed CNFs paper-derived separators exhibited an enhanced cell performance, these separators still suffered from a poor mechanical strength and the fabrication process is somewhat complicated. It still remains a challenge to produce nanocellulose separator in a large-scale, low-cost and environmental friendly approach. To simplify the fabrication of CNFs-based separator, Lee et al. also developed a new method, which relies on simply mixing cellulose nanofibrils and a pore-forming resin. The pore-forming resin, consisting of polyethylene glycol, polypropylene alcohol, PP, and hydroxyl cellulose, was explored to form micropores [53].

### 3.5. Cellulose composite-derived LIB separators

In recent years, many efforts have been made to improve the porous structure, mechanical property and electrochemical performance of the cellulose based separators for LIBs. Among them, incorporating other polymer materials with the cellulose nonwoven to form composite separators seems a very promising approach. It can improve the mechanical property of cellulose separator, and at the same time, it might bring a synergetic effect for the composite separator. The principal features of battery separators

based on cellulose derived composite materials are summarized in Table 3.

In order to improve the separator performance with minimal water adsorption and enlarged voltage window for high energy battery, Cui et al., from Chinese Academy of Sciences, explored a cellulose-based composite nonwoven via an electrospinning technique for LIB separator. The nonwoven mat of cellulose was prepared by deacetylation, and then formed composite with poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) by dip coating, and followed by calendaring. Compared with cellulose nonwoven, the cellulose/PVDF-HFP composite nonwoven shows smaller pore sizes and uniform pore distribution (Fig. 3A and B), which might be in favor of mitigating self-discharge and achieving uniform current density at high rates. The cells using such composite separator displayed better rate capability (Fig. 3C) and enhanced cycling stability (Fig. 3D) when compared with the cell using commercialized PP separator under the same conditions. This attractive result owned to its superior interfacial stability and high ionic conductivity of cellulose/PVDF-HFP composite separator [54].

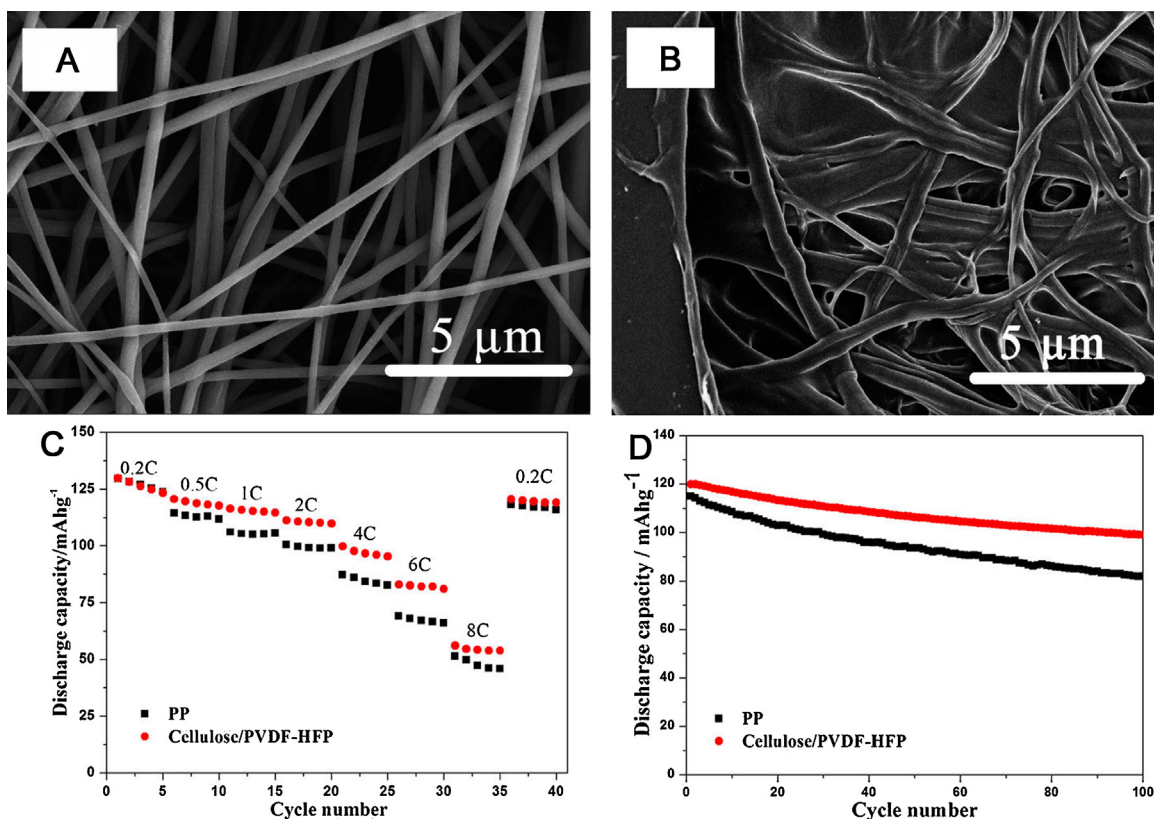
Polysulfonamide (PSA) is one kind of high performance synthetic polymers known for its excellent thermal, mechanical, dielectric properties and chemical resistance. To improve overall performance of cellulose-based separator, Cui et al. fabricated cellulose/PSA composite membrane from mixture of microfibrillar cellulose and PSA via a facile papermaking process (Fig. 4A). LiFePO<sub>4</sub>/lithium cell employing cellulose/PSA separator exhibited perfect charge-discharge capability even at 120 °C (Fig. 4B), indicating a superior thermal dimensional stability [55].

Very recently, Cui et al. successfully explored a sustainable, heat-resistant and flame-retardant cellulose-based composite nonwoven (FCCN) separator for LIBs [56]. This FCCN, which presented distributed pores with diameters ranging from 100 to 200 nm, was made from cellulose pulp, sodium alginate, flame retardant and silica by papermaking approach. It was demonstrated that this FCCN separator possessed superior heat tolerance (Fig. 5A), excellent flame retardancy (Fig. 5B) and satisfactory mechanical strength. Owing to the facile ion transport and excellent interfacial compatibility of FCCN, the LiCoO<sub>2</sub>/graphite cell using FCCN separator exhibited better rate capability (Fig. 5C) and cycling retention than that using PP separator. Furthermore, the LiFePO<sub>4</sub>/Li cell with FCCN separator delivered a stable cycling performance and thermal dimensional stability even at 120 °C (Fig. 5D) [56].

Mitsubishi Paper Mills Ltd also reported many natural cellulose/synthetic polymer fiber composite separators for LIBs [57–60]. Due to the good heat resistance of poly(ethylene terephthalate) (PET) fiber nonwoven and cellulosic materials, the cellulose/PET composite separator (NanoBase2) shows excellent heat resistance even at 220 °C, indicating a higher margin of safety. Meanwhile, the NanoBase2 composite shows improved mechanical strength and excellent protection against foreign particle because of the rich contents of ceramic particle. In addition to the inherent advantages of nonwoven kept after the ceramic coating, such as electrolyte wettability and ion conductivity, these composite separators displayed the

**Table 3**  
Principal features of cellulose-based composite separators.

Property	Thickness (μm)	Gurley (s/100 cc)	Porosity (%)	Pore size (μm)	TD shrinkage (%)	MD shrinkage (%)	TD strength (MPa)	MD strength (MPa)	Elongation (%)	Fabricating method	Remarks	Ref.
Cellulose/PVDF-HFP	27	36	65	0.7	0 (at 200 °C)	0 (at 200 °C)	–	–	3	Electrospin and coating	Good interfacial stability	[54]
Cellulose/polysulfonamide	40	60	66	~0.3	0 (at 200 °C)	0 (at 200 °C)	160	160	6	Paper making	Good flame retardancy and thermal stability	[55]
cellulose-based composite nonwoven (FCCN)	40	45	70	0.3	0 (at 200 °C)	0 (at 200 °C)	50	50	5	Paper making	Heat-resistant and flame-retardant	[56]
PET/cellulose, FPC 2515 (NanoBase2, Mitsubishi Paper Mills)	23	4.7	53	0.6	<0.3 (at 180 °C)	<0.3 (at 180 °C)	353	490	3	Paper making	High strength and heat resistance	[60]
PET/cellulose, FPC 3018 (NanoBase2, Mitsubishi Paper Mills)	30	7.0	59	0.5	<0.3 (at 180 °C)	<0.3 (at 180 °C)	490	700	3	Paper making	High strength	[60]
Micro-/nano-composite cellulose material (DWI)	30	110	55	0.5	0 (at 90 °C) 0 (at 160 °C)	0 (at 90 °C) 2 (at 160 °C)	90	180	4	Paper making	Even currents	[61]



**Fig. 3.** Typical SEM image of the cellulose nonwoven (A) and cellulose/PVDF-HFP composite nonwoven (B), and comparison of rate capability (C) and cycling performance (D) of LiCoO<sub>2</sub>/graphite cells assembled with PP separator and cellulose/PVDF-HFP composite separator [54]. Copyright 2013. Reproduced with permission from the American Chemical Society.

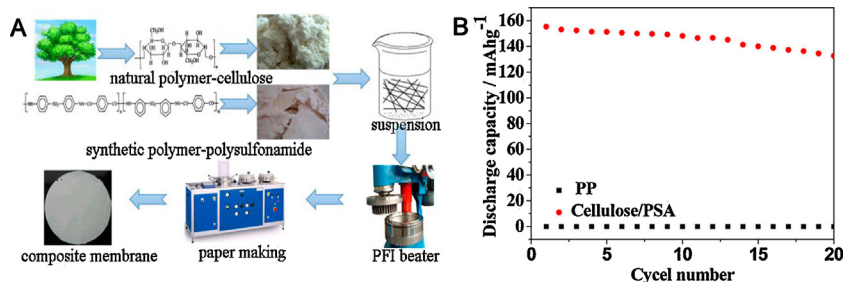
longer cycle life than that of commercial polyolefin micro-porous membrane separators.

Jim Schaeffer and Brian Morin, from Dreamweaver International (DWI), fabricated a high-performance separator for LIBs combination of CNFs and cellulose microfibrils. When the microfibrils and nanofibrils are combined, the cellulose composite material has the strength and openness of the microfiber scaffolding while the nanofibrils drape over the microfibrils strategically, closing down the pore size and maintaining a high permeability for ions. For safety testing including Nail penetration, over charge, short circuit, hot box and temperature cycling tests, this DWI separator of 30 μm in small 50 mAh pouch cells

showed identical performance with that of trilayer PP/PE separators of 25 μm. Moreover, the DWI separator delivered a higher energy at large discharge rates for all cell builds compared with several other film-based separators [61].

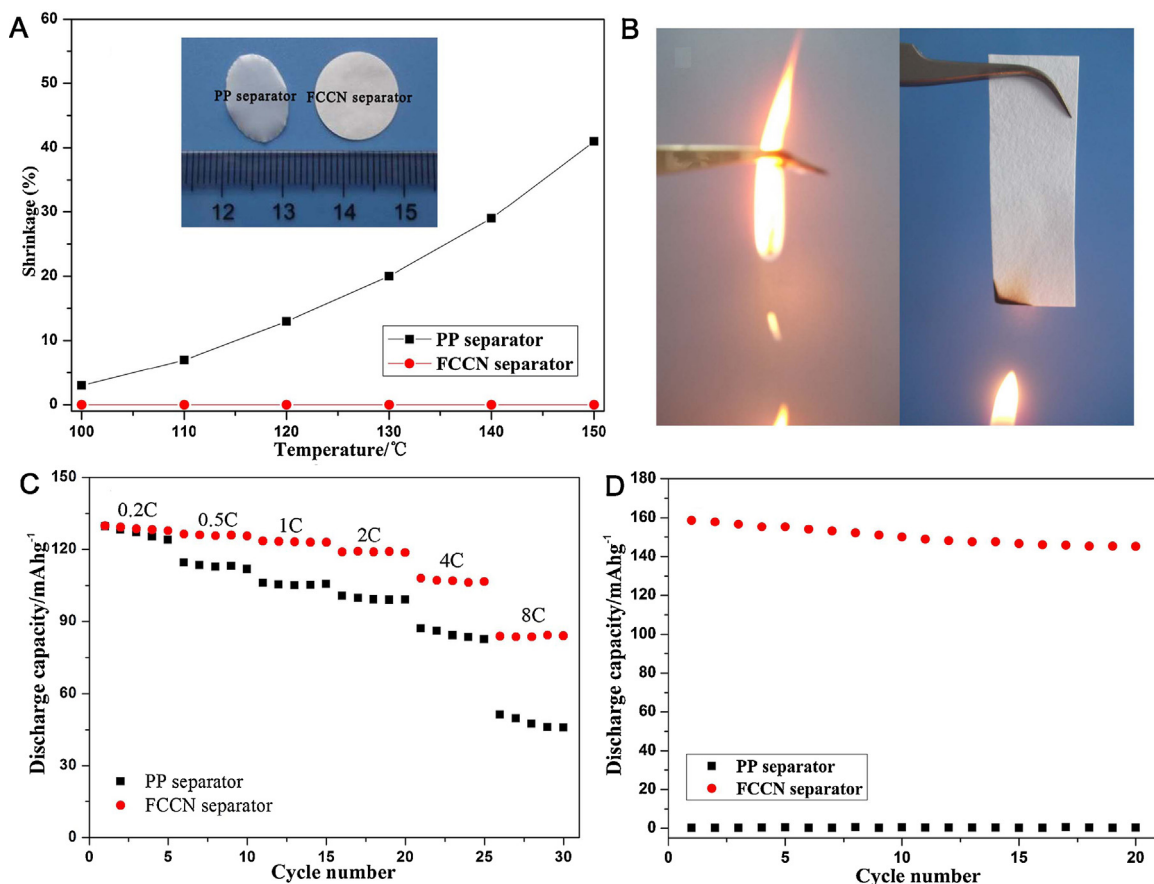
### 3.6. Bio-inspired materials for battery separators

In addition to the battery separators with biomass materials as the skeleton material, bio-inspired surface coating is another practical method to overcome the shortcomings of conventional polyolefin separators. Messersmith et al. noticed the mussel's strong adhesion

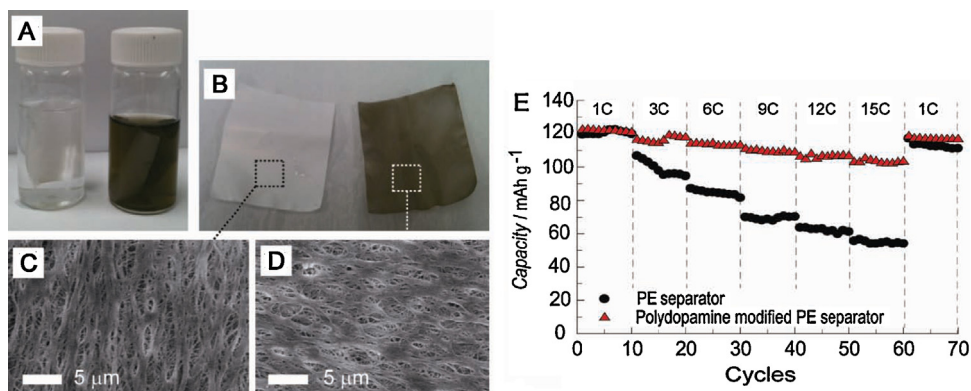


**Fig. 4.** (A) Schematic of the preparation of cellulose/PSA composite membrane for LIB separator, and (B) comparison of cycling performance of LiFePO<sub>4</sub>/Li cells assembled with PP separator and cellulose/PSA composite separator at 120 °C [55]. Copyright 2014. Reproduced with permission from the American Chemical Society.





**Fig. 5.** (A) Thermal shrinkage behavior of FCCN and PP separators with increasing the temperature, and the inset is the photograph of FCCN and PP separators after treating for 0.5 h at 150 °C. (B) Combustion behavior of FCCN and PP separators, showing the flame retardancy characterization of FCCN separator. (C) Comparison of rate capability of LiCoO<sub>2</sub>/graphite cells assembled with FCCN separator and PP separator. (D) Comparison of cycling performance of LiFePO<sub>4</sub>/Li cells assembled with FCCN separator and PP separator at 120 °C [56]. Copyright 2014. Reproduced with permission from the Nature Publishing Group.



**Fig. 6.** Preparation and application of the polydopamine-modified PE separator. (A) Photograph of PE separators immersed in dopamine solution without (left) and with (right) the buffer treatment at pH 8.5 after 24 h. (B) Photograph of PE separators without (left) and with (right) the polydopamine modification. (C) SEM image of PE separator and (D) SEM image of PE separator with the polydopamine treatment, indicating that the polydopamine film is thin enough and does not modify the original morphology of PE separator. (E) A comparison of discharging capacities between the pouch-type half-cell with polydopamine modified PE separator and the cell with PE separator. The measurements were performed between 3.0 and 4.5 V vs Li/Li<sup>+</sup> [65]. Copyright 2011. Reproduced with permission from WILEY-VCH Verlag GmbH & Co., KGaA.

ability onto virtually all types of surfaces and identified 3,4-dihydroxy-L-phenylalanine and lysine peptides in *Mytilus edulis* foot protein 5 of mussel's adhesive threads as the origins of the extraordinarily strong adhesion. Based on this interesting finding, they recognized that dopamine, a commercially available chemical, containing both catechol and amine groups, can function as a basis for the strong adhesion for various applications [62–64]. Inspired by the above-mentioned works, Pyou et al. developed a simple dipping process to generate polydopamine-coated PE separators. After treatment, the color of PE separator changes to black-brown, indicating the spontaneous deposition of thin polydopamine film on the surface of PE (Fig. 6A and B). SEM images show that there is no obvious structure change after the polydopamine coating (Fig. 6C and D). Meanwhile, after the polydopamine coating, the surfaces of the separators transfer hydrophilic from hydrophobic and the wetting ability of electrolyte solvents on the separators is greatly improved. Taking advantage of the hydrophilic surface character, the modified PE separators exhibit significantly improved power performance without sacrificing the original advantages of PE separators (Fig. 6E) [65]. Importantly, it was then demonstrated that lithium-metal anodes in LIBs with mussel-inspired polydopamine-coated separators exhibited excellent cycle life, which results from the suppression of Li-dendrite growth and the uniform Li ionic flux originating from the increased electrolyte uptake, as well as the strong mussel-inspired catecholic adhesion onto the Li surfaces [66].

In order to improve the mechanical strength of cellulose-based battery separator, especially in wet condition, Cui et al. explored the polydopamine treatment of cellulose membrane by a facile and low-cost papermaking process (Fig. 7A) [67]. It was found that the composite membrane possessed compact porous structure, superior mechanical strength and excellent thermal dimensional stability. Compared with those of commercial PP separator and pristine cellulose separator, the cells using the composite separator displayed a superior rate capability (Fig. 7B) and excellent capacity retention (Fig. 7C). The bio-inspired polydopamine treatment has been demonstrated to be a versatile approach, and thus may be applicable to other separators with similar surface properties, to improve the surface property and mechanical strength.

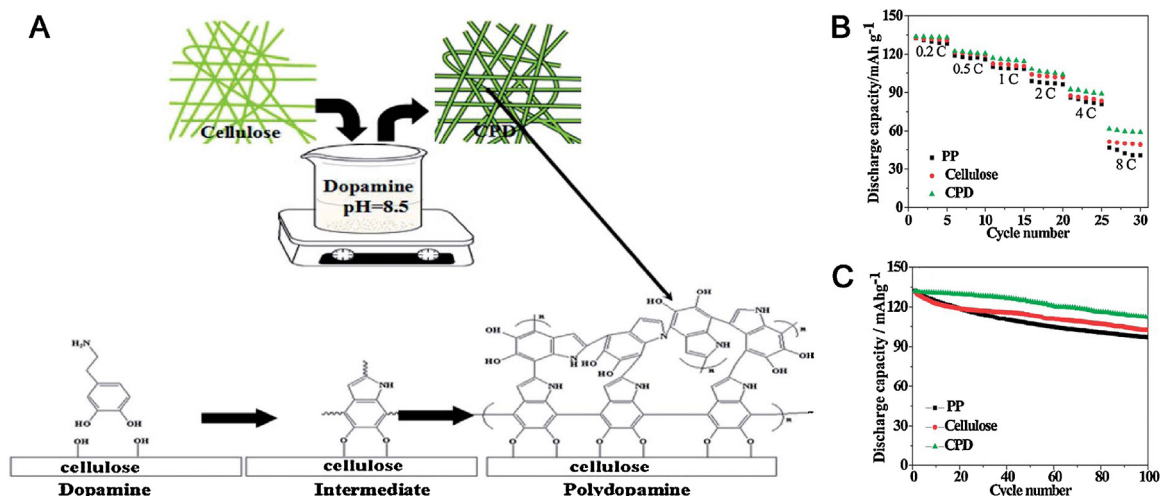
#### 4. Biomass-derived binders

As to LIBs, electrochemical capacitors and other energy storage devices, there have been extensive studies on electrode materials, separators, electrolytes and additives to achieve improvement of the device performance [68,69]. Compared with the significant progress in these components, however, binders have not yet attracted extensive interests till now due to its characteristic of inactive material [70–72]. Typically, the binder provides structural integrity at relatively low mass fractions, bringing together the active material, the carbon black and the current collector. Although a binder is electrochemically inactive, considerable researching indicates that it can have a significant influence on the electrode performance especially for the newly-developed Si-based electrodes.

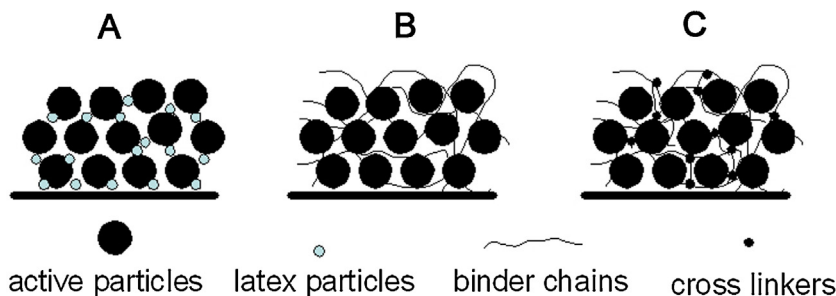
In lithium batteries, a suitable binder must meet the following prerequisites [73]. (i) The binder is usually characteristic of polar groups such as  $-\text{OH}$ ,  $(\text{C}=\text{O})-\text{OH}$ ,  $\text{O}-(\text{C}=\text{O})\text{R}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{CN}$  or other groups in the side chain, delivering strong adhesion and high tensile strength at the interfaces between the active material powders, conductive carbon black powders and the current collector foils. (ii) The binder should stay physically and chemically stable after being immersed in the electrolyte, such as EC, propylene carbonate and dimethyl carbonate, etc. (iii) The binder for cathode materials should possess wide electrochemical stability window up to 4.5 V (vs.  $\text{Li}^+/\text{Li}$ ) avoiding electrochemical oxidation when charged up to the cut-off voltage limit. Similarly, the binder for the anode materials should have enough electrochemical reduction stability at low potential around 0 V (vs.  $\text{Li}^+/\text{Li}$ ). (iv) The binder cannot cause adverse effect on the impedance of the electron and  $\text{Li}^+$  diffusion for the electrode reaction. (v) The binder should be well dissolved or dispersed in the slurry and result in uniform distribution of both active materials and conductive carbon black. (vi) The binder and its utilization should be cost-effective, environmental-friendly and safe.

According to the interaction between the binders and the active powders, the binders can be divided into three types, i.e. dot-to-surface contact, segment-to-surface contact and network-to-surface contact, which are illustrated in Fig. 8 [73]. The dot-to-surface contact binders comprise of the emulsion binders such as polytetrafluoroethylene (PTFE) latex, styrene-butadiene-rubber (SBR) latex and polyacrylates latex. After mixing, coating and drying, these latex particles stick to the surface of the active particles and bind them together by point connection, which usually leads to weak adherence. The segment-to-surface contact binders include most of the polymer solution binders such as PVDF, carboxymethyl cellulose (CMC), polyacrylic acid (PAA), polyvinyl alcohol, polyacrylate and polyacrylonitrile etc. After drying, the polymer chain segments adhere onto the surface of the active particles resulting in moderate adherence. The network-to-surface contact binders are characteristic of three-dimensional (3D) networks formed after coating via a thermal treatment or chemical reaction. Although 3D network causes strong adherence, the fabrication is complicated and the electrode sheets lack of flexibility. In regard to solvents, the binders can also be classified into two categories, organic solvent-based (nonaqueous) binders and water-based (aqueous) binders [74]. The non-aqueous binders are relatively expensive and harmful to environment because of using a large amount of organic solvent. Considering environmental benignity and cost-effectiveness, the aqueous binders have been attracted increasing attention [75,76].

Among all the synthetic binders originating from the fossil oil, PVDF (as shown in Fig. 9) possesses superior electrochemical stability and are commercially used as binder for LIB electrode fabrication [77–79]. However, there are still some drawbacks, which limit the extensive application of PVDF. Firstly, PVDF is high-priced due to complicated synthesis and expensive monomer. Secondly, the expensive and volatile N-methyl-2-pyrrolidone has to be used as solvent to dissolve PVDF, which further raise the cost of the battery and pollute the environment as well. Thirdly,



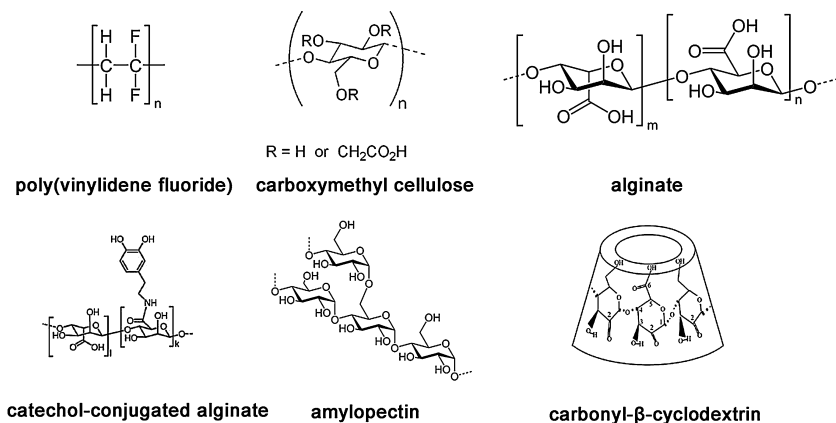
**Fig. 7.** A) Schematic illustration of the fabrication of cellulose/polydopamine (CPD) membrane, and the coating mechanism of polydopamine onto the surface of cellulose microfibers. (B) Comparison of rate capability of LiCoO<sub>2</sub>/graphite cells assembled with CPD separator, cellulose separator, and PP separator. (C) Comparison of cycling performance of LiCoO<sub>2</sub>/graphite cells assembled with CPD separator, cellulose separator, and PP separator [67]. Copyright 2014. Reproduced with permission from the Royal Society of Chemistry.



**Fig. 8.** Schematic illustration of the interactions between binders and active powders. (A) dot-to-surface contact, (B) segment-to-surface contact, and (C) network-to-surface contact.

PVDF solution is seriously sensitive to moisture in air which can deteriorate its viscosity. Finally, PVDF reacts with the lithium metal at elevated temperature which impairs the battery safety. Therefore, the development of greener, cheaper, and higher performance binders is of great importance today for battery technology.

The state-of-the-art LIBs composed of a transitional metal oxide cathode and a carbon-based anode can only deliver an energy density around 150 W h kg<sup>-1</sup>, which is far away from the requirement of EV for driving a distance of 200 km upon a single refuel. In order to meet the demand of 200 km, the higher energy density rechargeable batteries



**Fig. 9.** Chemical structures of PVDF and some biomass-derived binders.

**Table 4**

The comparison of typical synthetic binders and biomass-derived binders.

Binders	Applicable scope	Advantages	Disadvantages	Cost (\$ kg <sup>-1</sup> )	Ref.
PVDF	Cathode materials such as LiFePO <sub>4</sub> , LiCoO <sub>2</sub> , LiMn <sub>2</sub> O <sub>4</sub> , LiNi <sub>(1/3)</sub> Co <sub>(1/3)</sub> Mn <sub>(1/3)</sub> O <sub>2</sub> , etc.	Chemical synthesis; superior electrochemical stability	Expensive; using organic solvent; sensitive to moisture; high ionic impedance	20–30	[77–79]
SBR	Graphite anode	Chemical synthesis; sheap; excellent elasticity; environmental-friendly	Poor chemical stability; low electrochemical stability;	3–5	[80–84]
CMC-Na	Graphite anode Si, Sn or Ge based anodes LiFePO <sub>4</sub> cathode	Carboxylmethylation from cellulose; cheap; environmental-friendly; high viscous and less dosage; low ionic impedance; stiffness (good to Si based anode)	Stiff and poor flexibility; variable chemical structure; variable slurry viscosity	2–5	[85–91]
Alginate-Na	Si, Sn or Ge based anodes	Extracted from aquatic brown algae; moderate price; carboxyl group evenly distribution; lower ionic impedance; high stiffness in electrolyte	Variable M and G-blocks; variable slurry viscosity;	10–14	[93]
Alginate (catechol-conjugated)	Si based anodes	Catechol conjugated alginate; strong adherence; wetness-resistant adhesion	Complicated synthesis; low substitution	>10	[98]
β-CD	Sulfur based cathode, Si based anodes	Produced from starch by means of enzymatic conversion; cheap; environmental-friendly	Low viscosity	3–4	[99,100]
Amylopectin	Si, Sn and Ge based anodes	Obtained from starch; cheap; environmental-friendly	Easy to degrade; variable molecular weight; variable slurry viscosity; moderate adherence	5–7	[101]
Gelatin	Graphite anode, LiMn <sub>2</sub> O <sub>4</sub> cathode, sulfur based cathode	Obtained from various animal by-products; moderate price; SEI improvement	Electrochemical instability; Complicated Constituents; pH-dependent viscosity	7–10	[103–107]

(300 W h kg<sup>-1</sup>) are desirable and the silicon-based anode batteries and lithium sulfur (Li-S) batteries are expected to boost energy density even up to 300–500 W h kg<sup>-1</sup>. However, the cycle lives of Si electrodes are very short due to their significant volume expansion by up to 400% upon full lithiation and the sulfur cathode also suffers serious sulfur dissolution problem. Some natural polymers or their derivatives, such as CMC, alginate, amylopectin, carbonyl-β-cyclodextrin (C-β-CD) and gelatin have been recently explored to serve as robust and green binders to overcome the above mentioned defects of PVDF or huge volume expansion of the Si-based material or sulfur dissolution. The chemical structures of some typical biomass-derived binders are presented in Fig. 9, and the comparisons between the biomass-derived binders and PVDF as well as SBR are summarized in Table 4. The cells using these green binders typically exhibit high energy density, long cycle life, low cost, high safety, and environmental benignity compared to the conventional PVDF binder.

#### 4.1. Carboxymethyl cellulose-derived binder

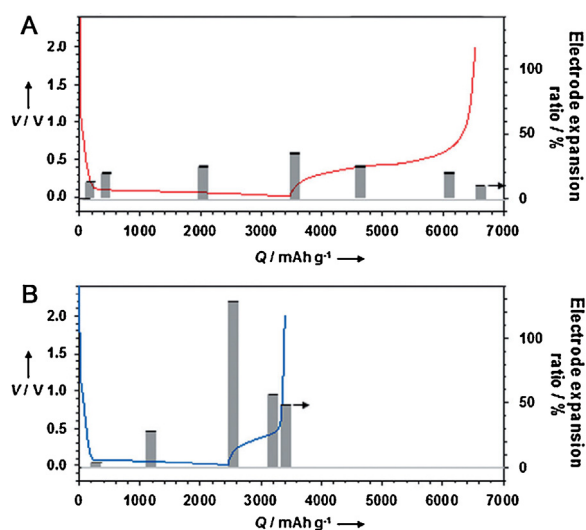
CMC is a cellulose derivative, and its backbone is made up by the coupling of carboxymethyl groups (–CH<sub>2</sub>–COOH) to some of the hydroxyl groups of the glucopyranose monomers. It is nontoxic, and is generally considered to be hypoallergenic. CMC membranes possess a good stiffness and a small elongation at break (5–8%). Its sodium salt, CMC-Na is well water-soluble and used as a viscosity modifier or thickener to stabilize emulsions in various products.

CMC-Na serves widely as the anode binders with lower fractions (usually 2–5 wt.%). However, CMC-Na molecules lack enough elasticity and always blend with elastic SBR to improve the flexibility of the electrode sheets in LIBs [80–84].

The Si or Sn based anodes suffer from poor cycling stability owing to huge volume changes during charge/discharge when using flexible PVDF as a binder. Owing to its stiffness nature, CMC-Na was proved to be an excellent binder for improving cycling stability of Si or Sn based anodes [85,86]. It was further demonstrated that a self-healing process of the strong Si-CMC hydrogen bonding is critical for superior performances during cycling. This understanding leads to the well designing of Si-based electrodes with capacity retention reaching 1000 mA h g<sup>-1</sup> of composite (i.e., full Si capacity) for at least 100 cycles and with a Coulombic efficiency close to 99.9% per cycle [87].

In order to improve CMC-Na binding performance, a noticeable work has been done by Choi et al. They presented a thermally cured interconnected network of PAA and CMC-Na as a novel binder for silicon-based electrodes with superior performance even at high temperature [88]. The cross-linked PAA-CMC binder presents excellent mechanical resistance to strain and even permanent deformation because of the 3D linked polymer chains. The adoption of cross-linked PAA-CMC binder can effectively mitigate the large volume expansion of silicon anodes upon lithium insertion compared to PVDF binder: the cross-linked PAA-CMC binder better accommodates the expansional strain of silicon and a volume expansion





**Fig. 10.** Discharge-charge profiles of silicon composite electrodes with (A) cross-linked PAA-CMC binder (red line), and (B) PVDF binder (blue line) at  $175 \text{ mA g}^{-1}$  between 0.005 and 2.0 V versus  $\text{Li}^+/\text{Li}^0$ . The black lines show the volume changes of electrodes during charging and discharging processes [88]. Copyright 2012. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.) Reproduced with permission from WILEY-VCH Verlag GmbH & Co., KGaA.

of 35% in the fully lithiated state can be obtained (Fig. 10A), whereas the use of the PVDF binder leads to a drastically increased volume expansion of about 130% (Fig. 10B). Nanosized silicon powder with a 3D network as binder exhibits a high reversible capacity of capacity of  $1600 \text{ mA h g}^{-1}$  for a very high current density of  $30 \text{ A g}^{-1}$  at  $60^\circ\text{C}$ , which is much higher than those using the CMC-Na binder.

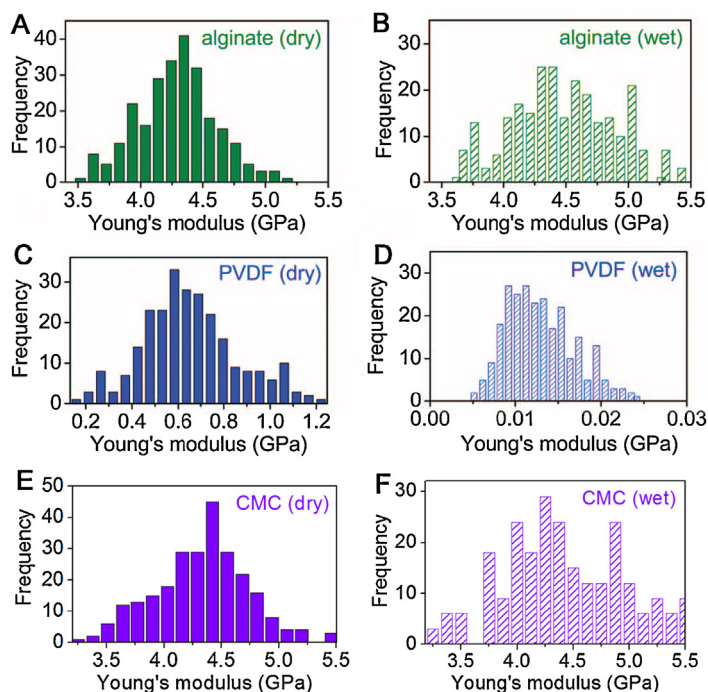
To date, only very limited investigations of the effects of CMC-Na on cathode materials have been carried out in comparison with different binders. Passerini recently reported that CMC-based  $\text{LiFePO}_4$  electrodes dried at  $170^\circ\text{C}$  were also able to display a capacity cycling retention of 75% for 1000 cycles [89], which corresponded to an overall capacity fading of only 0.025% per cycle. This is a support that CMC-Na might be electrochemically stable at positive potential over 3.6 V (vs.  $\text{Li}^+/\text{Li}$ ). It was also reported that the  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrode blended with CMC binder presented better cycling performance and rate capability than those with alginate and PVDF binders. Electrochemical impedance spectroscopy results indicated that the  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrode using CMC as binder had much lower charge transfer resistance and lower activation energy than the electrodes using alginate and PVDF as the binders [90,91]. Moreover, Li et al. studied the effects of the SBR/CMC blending ratio on the dispersion and the electrochemical properties of  $\text{LiCoO}_2$  electrodes. It was demonstrated that CMC-Na was highly efficient in dispersing  $\text{LiCoO}_2$ , and SBR contributed to uniform dispersion of the CMC-Na binder and the flexibility of the electrode sheets after drying. This study revealed that the binder distribution had a significant influence on the electrical and electrochemical properties of the aqueous  $\text{LiCoO}_2$

electrodes than the dispersion of cathode powders did [92]. On the basis of the above-mentioned reports, it can be drawn a conclusion that the introduction of CMC-Na binder for cathode appears to be a very viable and promising solution to improve the overall electrode performance in a greener process.

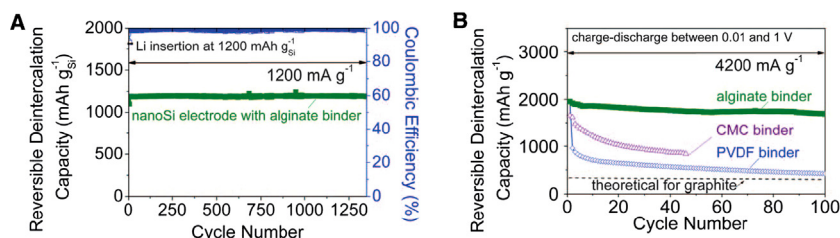
#### 4.2. Alginate-derived binder

Alginate contains a specific carboxylic group in each of the homopolymer's monomeric units (Fig. 9), which endows it a promising binder candidate especially for Si based anode. Recently, Yushin and his colleagues explored an alginate binder-based strategy to build Si anodes with improved performance characteristics for LIBs [93]. Compared with PVDF, the alginate binder, whatever in dry state or electrolyte solvent-impregnated wet state, shows much better mechanical properties. Importantly, when immersed into the electrolyte solvent, the stiffness of PVDF decays severely, whereas the stiffness of alginate does not change apparently (Fig. 11A–D). This strong stiffness of alginate is supposed to be of great benefit to the Si anode by alleviating the large changes in particle volume. Although CMC has a similar mechanical property with alginate (Fig. 11A, B, and E, F), there is a natural and much uniform distribution of carboxylic groups along the chain of alginate but not CMC, which is responsible for the better transport of  $\text{Li}^+$  in the vicinity of Si nanopowders via hopping of  $\text{Li}^+$  between the adjacent carboxylic sites, and the formation of a uniform and stable SEI layer on the Si surface, preventing degradation. Owing to the critical properties of alginate, the mixing Si nanopowder with alginate yielded a stable battery anode possessing a reversible capacity of  $1200 \text{ mA h g}^{-1}$  for more than 1300 cycles (Fig. 12A), which was eight times higher than that of graphitic anodes. The reversible capacity of the cell for 100th cycles was also much higher than those using the PVDF and CMC binders (Fig. 12B) [93].

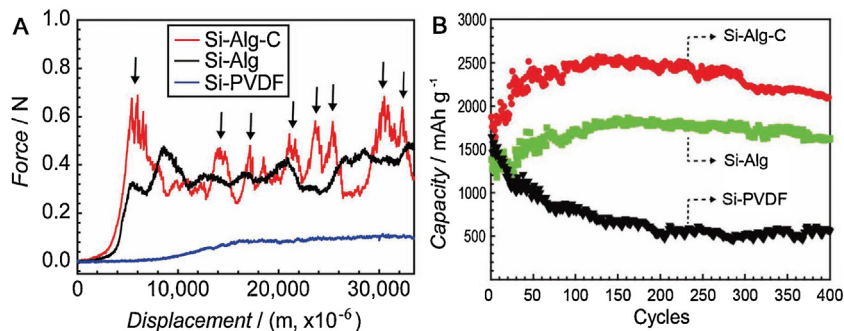
The investigations of mussel-inspired adhesive materials have revealed that the catechol group plays a decisive role in the exceptional wetness-resistant adhesion [62,94–97], which could be also very useful for improving binders' properties in battery because of the contact mode of each battery components in organic solvents. In 2013, Park et al. synthesized the catechol-conjugated alginate ( $3.4\% \pm 0.4\%$  substitution) (Fig. 9) and discovered that the interaction between the Si and catechol-conjugated alginate is double than that without catechol conjugation on a single-molecule level via atomic force microscopy pulling tests (Fig. 13A). The Si electrodes with catechol-conjugated alginate have good electrochemical stability and structural integrity, the enhanced film adhesion between Si and catechol-conjugated alginate can significantly improve the capacities and cycle performance of Si-based anodes (Fig. 13B). More importantly, since the wetness-resistant catecholic adhesion works availably with various substrates, this mussel-inspired catechol-conjugated alginate binder has potential applications in other LIB electrodes that suffer similar volume changes as Si during cycling [98].



**Fig. 11.** Atomic force microscopy indentation studies showing the Young's modulus comparison between the Na alginate (A, B), PVDF (C, D), and CMC (E, F) in both dry state and electrolyte solvent-impregnated wet state [93]. Copyright 2011. Reproduced with permission from the American Association for the Advancement of Science.



**Fig. 12.** (A) Reversible Li-extraction capacity and Coulombic efficiency of the alginate binder-based nano-Si electrodes versus cycle number for Li insertion level fixed to 1200 mA h g<sup>-1</sup> Si. (B) Reversible Li-extraction capacity of nano-Si electrodes with alginate, CMC, and PVDF binders versus cycle number at 4200 mA g<sup>-1</sup> between 0.01 and 1 V versus Li/Li<sup>+</sup> [93]. Copyright 2011. Reproduced with permission from the American Association for the Advancement of Science.



**Fig. 13.** (A) Atomic force microscopy force-distance curves and (B) the cycling performance at a C/2 rate (2100 mA g<sup>-1</sup>) of the Si electrodes with catechol-conjugated alginate (Alg-C), alginate (Alg), and PVDF binders, indicating that the better film adhesion caused by Alg-C leads to the better cycle performance [98]. Copyright 2013. Reproduced with permission from WILEY-VCH Verlag GmbH & Co., KGaA.

#### 4.3. $\beta$ -cyclodextrin-derived binder

$\beta$ -CD is a 7-membered sugar ring molecule incorporating D(+)-glucose monomeric units linked by  $\alpha(1 \rightarrow 4)$  linkages, and it can be easily obtained from ordinary starch by the well-established enzymatic hydrolysis method. The limited water solubility (1.85 g in 100 g H<sub>2</sub>O at 25 °C) of  $\beta$ -CD restricts its application as aqueous binder in batteries; however via simple chemical modification or polymerization one can realize the potential application of  $\beta$ -CD derivatives as binders in rechargeable Li batteries [99,100].

By the partial carbonylation of hydroxyl groups of  $\beta$ -CD with H<sub>2</sub>O<sub>2</sub>, Wang and his colleagues synthesized C- $\beta$ -CD, which has a much better water solubility than  $\beta$ -CD and exhibits a strong bonding capability and electrochemical stability. When C- $\beta$ -CD was utilized as a binder for sulfur-based cathodes, the high solubility and strong bonding make C- $\beta$ -CD forms a mechanically strong gel film around the surface of the sulfur composite, which can effectively suppress the aggregation of the sulfur composite and reduce the dissolution of soluble polysulfide. As a result, satisfied electrochemical performances, including a high reversible capacity of 694.2 mA h g<sub>(composite)</sub><sup>-1</sup> and 1542.7 mA h g<sub>(sulfur)</sub><sup>-1</sup>, a high sulfur utilization (92.2%) and a much improved cycle performance (Fig. 14A), were achieved for the sulfur-based composite using C- $\beta$ -CD as the binder [99]. Very recently, Choi and his colleagues reported a polymerized  $\beta$ -CD ( $\beta$ -CD<sub>p</sub>) as an effective multidimensional binder for Si nanoparticle anodes in lithium batteries to mitigate the severe capacity fading caused by unparalleled volume change of Si during cycling [100]. In this work, hyperbranched  $\beta$ -CD<sub>p</sub> network structure, which incorporated a series of hydroxyl and ether groups, was obtained from the reaction between  $\beta$ -CD and epichlorohydrin under strong basic conditions. Compared against other conventional linear binders, multidimensional non-covalent contacts between  $\beta$ -CD<sub>p</sub> and Si particles come into being, which can provide superior mechanical strength against the volume expansion of Si and also create a self-healing effect. Owing to the above advantages,  $\beta$ -CD<sub>p</sub>-based Si electrode presented significantly improved cycle performance (Fig. 14B), and the cycle performance can be further improved by the  $\beta$ -CD<sub>p</sub>/alginate hybrid binder in a synergistic effect [100]. Considering its low cost, environmental benignity and easy manipulation of modification (or polymerization),  $\beta$ -CD becomes a very attractive binder candidate for practical adoption in rechargeable lithium battery manufacturing processes.

#### 4.4. Amylopectin-derived binder

Amylopectin, one of the most common polysaccharides, is a major component of starch produced by plants. As a branched polymer of glucose, the linear chains of amylopectin are linked with  $\alpha(1 \rightarrow 4)$  glycosidic bonds, and branching occur every 24–30 glucose units with  $\alpha(1 \rightarrow 6)$  glycosidic linkages (Fig. 9). Recently, Komaba et al. explored amylopectin as binder for Si-based electrodes, which exhibited significantly higher capacity and better cycle performance (the capacity remains at ~800 mA h g<sup>-1</sup> over 150 cycles,) in LIBs compared with PVDF binder. The

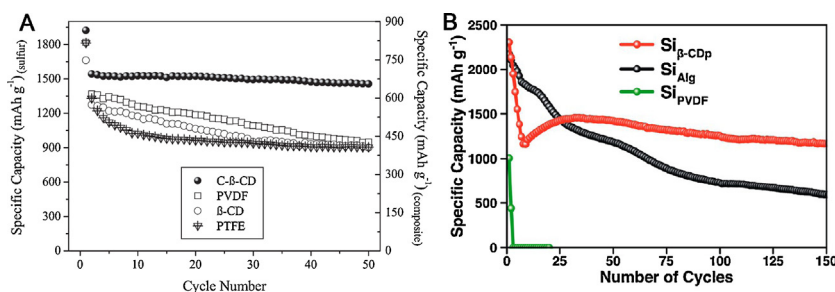
improved performance of amylopectin binder is probably related to the degree of branching [101]. However, the inferior adhesion ability resulting from the hydroxyl groups and the relatively higher price of amylopectin might hamper its extensive application as a sustainable binder.

#### 4.5. Gelatin-derived binder

Gelatin is a translucent, colorless and flavorless solid substance, produced by partial hydrolysis of collagen obtained from various animal by-products, and is usually classified as a foodstuff. As a mixture of peptides and proteins, gelatin possesses a plenty of amino and carboxyl groups, which might entail superior binder properties, e.g. good adhesion and fast ion diffusion. It was reported by Gaberšček et al. that, gelatin has been successfully applied as a green binder for the graphite anodes [102,103] and LiMn<sub>2</sub>O<sub>4</sub> cathodes [104,105]. The gelatin binder could mitigate the irreversible initial capacity loss of graphite anode because it could contribute to SEI formation. The gelatin binder could also be beneficial for the uniform distribution of conductive carbon black particles and improved the capacity and cycling stability of LiMn<sub>2</sub>O<sub>4</sub> cathode. Gelatin was also successfully used as a new binder of the sulfur cathode in Li-S batteries [106]. For the sulfur cathode, it is demonstrated that gelatin not only functions as an effective adhesive agent and dispersion agent, but also enhances the redox reversibility by slowing down the reducing reaction of elemental sulfur during the discharging process and reforming S<sub>8</sub> after the charging process [107]. The drawback of the gelatin binder is lower electrochemical stability originating from the complicated chemical constituents and chemically instable groups in gelatin, which hampers its real application in lithium batteries.

### 5. Biomass-derived electrode materials

Current electrochemical energy devices mainly depend on the substantive use of electrode materials that are far from renewable and sustainable, e.g. inorganic compounds, which often require rare metals [4–7]. To merit the requirements of a resource-conserving, environment-friendly society, it remains great challenges and significances to pursue renewable and sustainable electrode materials. Owing to their intrinsic properties and advantages, including the environment-friendly characteristics, the diverse structures, the intrinsic mechanical strength and flexibility, as well as the capability to efficiently accommodate other functional materials or liquid electrolyte, the renewable biomass and their derivatives have been spontaneously considered as the possible alternatives to replace the traditional non-sustainable electrode materials. In the past decade, some significant efforts have been put into developing sustainable and high-performance biomass-derived electrode materials: (1) The most broad research avenue is to apply biomass-derived nanostructures as renewable and favorable electrode materials in the advanced energy storage devices [13–15]. In order to be applied as electrode material, various electrochemically functional materials (e.g. conductive polymers, advanced carbon nanomaterials, etc.) have been integrated to endow cellulose composite



**Fig. 14.** (A) Cycle performance of sulfur-based cathodes with  $\beta$ -CD, C- $\beta$ -CD, PVDF, and PTFE binders at 0.2 C [99]. Copyright 2013. Reproduced with permission from WILEY-VCH Verlag GmbH & Co., KGaA. (B) Cycle performance of Si-based cathodes with  $\beta$ -CD<sub>p</sub>, alginate, and PVDF binders at 1C (4200 mA g<sup>-1</sup>) [100]. Copyright 2014. Reproduced with permission from the American Chemical Society.

with good electrical conductivity and electrochemical function. These conducting materials can be introduced into hierarchical biomass at different scales, from chemical modification of a biomass polymer at molecular scale to composite formation at nanofibrillated/microfibrillated fiber scale to surface coating onto biomass-based paper. (2) The other interesting and challenging research avenue is to facilely synthesize electroactive molecules from renewable natural biomass precursors via modern green chemistry concepts and then apply them as sustainable electrode materials [1].

In this section, we will present recent progress in the development of biomass derived electrode materials and their applications in energy storage. Although many works report the significant applications of pyrolyzed carbon, derived from diverse biomass, as electrode materials [108–115], considering the subversive transformation of biomass, the related progress is not involved in this review.

### 5.1. Conducting polymer/biomass composites as electrode materials

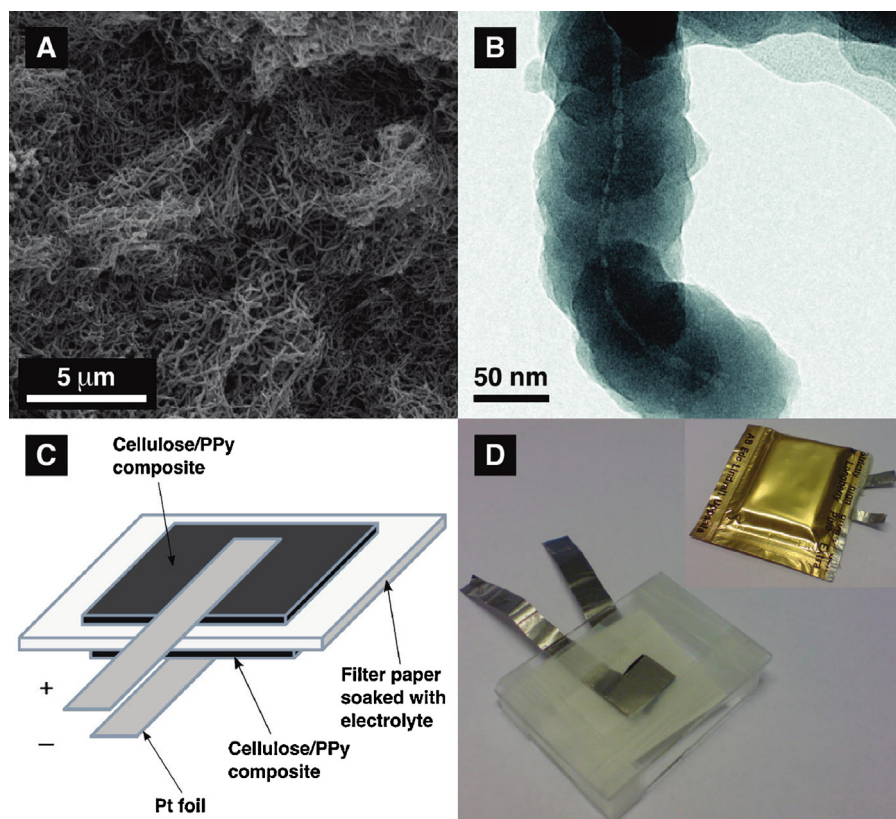
Conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), polythiophene and poly(ethylenedioxythiophene), are organic polymers that are able to conduct electrons and ions [116]. The characteristics of conducting polymers, including distinguished electrochemical and mechanical properties, low cost, ease of processability, convenient modification of the chemical structures, and relatively light weight, allow them (typically PPy and PANI) to be used as attractive electrodes in electrochemical capacitors and LIBs [117,118]. However, conducting polymers suffer from low capacity since redox processes usually only occur at the surface of conducting polymer films due to limited accessibility. Thus, conducting polymers are commonly deposited onto some substrates, in which the porous and less expensive substrates are desirable [119–123]. Interestingly, the distinguished characteristics of biomass endow them as great candidates to modify the electrochemical and mechanical properties of the brittle conducting polymers. Biomass/conducting polymer composites can be molded in different shapes to obtain conductive paper material which can be either directly used as a working electrode or function as an underlying conductive substrate material for deposition of various metals or metal oxides [13,124].

#### 5.1.1. Polypyrrole/biomass composites

PPy, one typical conductive polymer, shows promise but too inefficient for practical electrochemical energy storage applications, probably due to the inaccessibility and the thick and dense layers of the PPy material used [125]. Early in 1980s, the electrically conducting PPy/methylcellulose composite has been synthesized to improve the mechanical properties of PPy, which finally presented a maximum conductivity of 0.2 S cm<sup>-1</sup> [126]. In recent years, despite extensive efforts to develop new cellulose-based electrodes for battery applications, there is no satisfactory charging performance to be obtained until in 2009 by one group at Uppsala University [127]. Strømme and colleagues firstly developed a novel nanostructured high-surface area electrode material of *Cladophora* nanocellulose coated with a 50 nm layer of PPy (Fig. 15A and B), which exhibited an exceptionally high ion-exchange capacity [128], and then they explored the possibilities of utilizing these composite electrode materials for energy storage in paper-based batteries (Fig. 15C and D) [127]. *Cladophora* algae cellulose has a unique nanostructure, entirely different from that of terrestrial plants, and the possibility of energy-storage applications was raised in view of its large surface area (80 m<sup>2</sup> g<sup>-1</sup>). Batteries based on this prepared conductive paper composite material can be charged with currents up to 600 mA cm<sup>-2</sup>, with only a loss of 6% after 100 charging cycles. The aqueous-based batteries entirely based on cellulose and PPy, also exhibited high charge capacities (between 25 and 33 mAh g<sup>-1</sup>). It was demonstrated that the extreme thinness of the PPy layer coated on *Cladophora* algae cellulose played a critical role in obtaining a much higher charge capacity than the previous batteries based on advanced polymers.

After their original work, Strømme and colleagues continued to complete some substantial works in this area. They reinforced the composites of PPy/*Cladophora* nanocellulose with 8  $\mu$ m-thick chopped carbon filaments (Fig. 16). It suggests that the nonelectroactive carbon filaments can decrease the contact resistances and the resistance of the reduced cellulose/PPy composite. The obtained paper-based energy-storage devices by using the reinforced composites as electrode materials show enhanced capacitances and cycle performance (Table 5) [129]. Then, they detailedly investigated how different postsynthesis treatments (e.g. polymerization conditions, rinsing, and storage) affected both the short-term and the



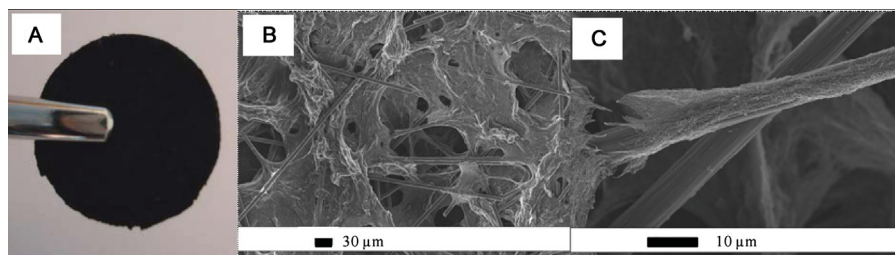


**Fig. 15.** SEM (A) and TEM (B) images of the PPy/*Cladophora* cellulose composite fiber. Schematic (C) and photograph (D) of the PPy/*Cladophora* cellulose composite paper-based battery cell [127]. Copyright 2009. Reproduced with permission from the American Chemical Society.

long-term properties (in terms of purity, chemical composition, conductivity, and electroactivity) of the *Cladophora* nanocellulose/PPy composite [130]. They also demonstrated that it was possible to coat the individual fibers of wood-based nanocellulose with PPy using in situ chemical polymerization. The obtained dry composite exhibits an even better capacity performance than that of *Cladophora* nanocellulose/PPy composite (Table 5) [131].

In addition to *Cladophora* cellulose and land plant cellulose, other kinds of cellulose, e.g. bacterial cellulose and cotton cellulose [132,133], can also be adopted to prepare high-performance cellulose/conducting polymer composites. The core/sheath structured conductive nanocomposites were prepared by wrapping a homogenous

layer of PPy around bacterial CNFs (produced by *Acetobacter xylinum*) via in situ polymerization. By optimizing reaction protocols, the ordered core/sheath bacterial CNFs/PPy nanostructure achieved an outstanding electrical conductivity as high as  $77 \text{ S cm}^{-1}$ , and demonstrated promising potential for supercapacitors, with a highest mass specific capacitance hitting  $316 \text{ F g}^{-1}$  at  $0.2 \text{ A g}^{-1}$  current density (Table 5) [132]. Porous nanocomposites consisting of cotton cellulose nanocrystals and PPy were fabricated using electrochemical co-deposition. The obtained nanocomposite presented a high capacitance of  $256 \text{ F g}^{-1}$  and a good stability, which were comparable to that of a PPy/carbon nanotubes (CNTs) composite deposited under the same conditions [133]. Significantly,



**Fig. 16.** Photograph (A) and SEM images (B, C) of PPy/*Cladophora* cellulose composite sample reinforced with 8 μm-thick chopped carbon filaments [129]. Copyright 2012. Reproduced with permission from WILEY-VCH Verlag GmbH & Co., KGaA.

**Table 5**

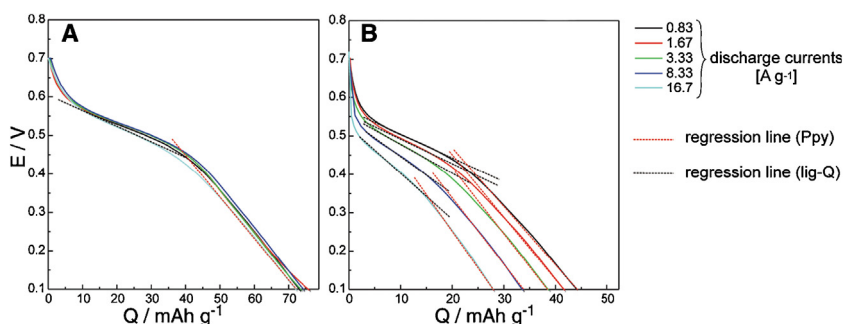
Literature data on biomass/conducting polymer composites-based electrodes for supercapacitor or battery applications.

Electrodes	Preparation	Conductivity ( $\text{S cm}^{-1}$ )	Device performance: capacity ( $\text{F g}^{-1}$ ) or capacitance ( $\text{mA h g}^{-1}$ ) or energy density ( $\text{W h kg}^{-1}$ ) or power density ( $\text{kW kg}^{-1}$ )	Remarks	Ref.
Nanocellulose/PPy conductive paper composite	In situ chemical polymerization	$>1 \text{ S cm}^{-1}$	25 $\text{mA h g}^{-1}$ at 10 mA 33 $\text{mA h g}^{-1}$ at 320 mA	PPy layer (50 nm in thickness) was coated on <i>Cladophora</i> algae cellulose	[127]
Nanocellulose/PPy/carbon filaments conducting composite	In situ chemical polymerization followed by acid-washed	/	77 $\text{mA h g}^{-1}$ $\sim 60\text{--}70 \text{ F g}^{-1}$ 1.75 $\text{W h kg}^{-1}$ 2.7 $\text{kW kg}^{-1}$	8 $\mu\text{m}$ -thick chopped carbon filament was used to strength the nanocellulose/PPy composite	[129]
Nanocellulose/PPy conducting composite	In situ chemical polymerization	$\sim 1.5 \text{ S cm}^{-1}$	80 $\text{mA h g}^{-1}$	Wood-based nanocellulose was used	[131]
Nanocellulose/PPy core/sheath structured conductive nanocomposite	In situ chemical polymerization of self-assembled pyrrole	77 $\text{S cm}^{-1}$	316 $\text{F g}^{-1}$ at 0.2 $\text{A g}^{-1}$	Bacterial cellulose produced by <i>Acetobacter xylinum</i> was used	[132]
Cellulose/PPy conductive nanocomposite	Electrochemical co-deposition	/	256 $\text{F g}^{-1}$	Cotton extracted cellulose nanocrystals were used	[133]
Printing paper/PPy composite	"Soak and polymerization" method	15 $\text{S cm}^{-1}$	0.42 $\text{F cm}^{-2}$ 1 $\text{mW h cm}^{-3}$ 0.27 $\text{W cm}^{-3}$	Common printing paper was used	[134]
Cellulose/PPy composites	Chemical polymerization followed by electropolymerization	/	250 $\text{C g}^{-1}$ (charge capacity)	PPy was doped with anthraquinone-2,6-disulfonic acid	[135]
Lignin/PPy interpenetrating networks	Electrochemical polymerization of pyrrole	$\sim 1 \text{ S cm}^{-1}$	70–75 $\text{mA h g}^{-1}$	Lignin derivatives from the brown liquor (a by-product from the manufacture of paper pulp) was used	[136]
CNFs/PANI nanocomposites	In situ polymerization of aniline onto bacterial CNFs	5.1 $\text{S cm}^{-1}$	273 $\text{F g}^{-1}$ at 0.2 $\text{A g}^{-1}$	Bacterial CNFs was used	[144]
CMC/PANI nanorods	Via one-step in situ oxidation polymerization	/	451.25 $\text{F g}^{-1}$	Commercial CMC was used	[145]
CNFs/Ag/PANI aerogel	Electrodeposition of PANI onto Ag/CNFs	1 $\Omega \text{ sq}^{-1}$ (for CNF/Ag aerogel)	176 $\text{mF cm}^{-2}$ at 10 $\text{mV s}^{-1}$	Bleached kraft softwood pulp-derived CNFs was used	[146]

not only CNFs directly derived from natural organisms have been used, some cellulose products, such as commercialized printing paper, have also been demonstrated to be very suitable materials to fabricate biomass/conjugated polymer composite electrodes for electrochemical devices. Very recently, Zhou and colleagues reported a highly conductive paper fabricated through PPy coating on common printing paper, which shows a high electrical conductivity and good electrochemical performance as electrode material [134]. To further enhance the charge storage capacity of cellulose/PPy composites, the chemical doping seems an alternative approach. The PPy/cellulose composites doped with anthraquinone-2,6-disulfonic acid via electropolymerization were prepared, which significantly increased the gravimetric charge capacity to 250  $\text{C g}^{-1}$  due to the redox activities of PPy and the dopant [135].

Lignin is another abundant biomass in nature, and it has also been demonstrated to be efficient electrode material by forming lignin/conjugated polymer interpenetrating networks. Inspired by the fact that quinones usually

play the role of soluble electron/proton transport agents in photosynthesis process and that lignin can be easily incorporated with large numbers of quinone sites from phenolic groups, Inganäs and colleagues created an inexpensive, electroactive conjugated polymer/biopolymer composite cathode by combining quinone electrochemistry and PPy conductivity [136]. The interpenetrating PPy/lignin composite film was electrochemically prepared from a mixture of pyrrole and lignin derivatives from the brown liquor, which is a by-product from the manufacture of paper pulp and is largely composed of lignosulfonate. The lignin-derived quinone group was used for electron and proton storage and exchange during redox cycling, thus the charge storages of lignin and PPy in the PPy/lignin composite were combined. It can be seen that in the galvanostatic discharge curves for the PPy/lignin composite films, two slopes were observed, which should be ascribed to electrochemical activities of PPy and lignin-derived quinones respectively (Fig. 17). Especially for the thinner PPy/lignin composite film, it was a favorable diffusion situation, and the



**Fig. 17.** Discharge curves under galvanostatic conditions in 0.1 M  $\text{HClO}_4$  for (A) thinner ( $0.5 \mu\text{m}$ ) and (B) thicker ( $1.9 \mu\text{m}$ ) PPy/lignin composite film, and the linear regression lines used for capacitance analysis [136]. Copyright 2012. Reproduced with permission from the American Association for the Advancement of Science.

capacities of lignin-derived quinones and PPy was calculated to be  $\sim 40$  and  $30\text{--}35 \text{ mA h g}^{-1}$ , respectively (Fig. 17A). Finally, reasonable charge densities between 70 and  $75 \text{ mA h g}^{-1}$  were realized for the prepared low-cost, green thin-film electrode [136].

### 5.1.2. Polyaniline/biomass composites

As another outstanding conducting polymer, PANI has a relatively high theoretical specific capacity ( $964 \text{ F g}^{-1}$ ). However, PANI has common weaknesses with PPy, i.e. the limited achieved capacitance and the poor potential cycling stability [125,137]. Recent studies showed that, the fabrication and application of highly porous PANI-inorganic nanomaterial (CNTs, graphene, and metal oxides) composites were very effective to improve the capacitance and stability by facilitating ion and solvent movements [125,137–140]. Recently, biomass materials especially cellulose have also been explored as very promising scaffold materials for fabrication of PANI-based composites for energy storage applications [141–143]. Tang et al. prepared the bacterial CNFs-supported PANI nanocomposites with flake-shaped morphology via in situ polymerization of aniline onto bacterial CNFs scaffold, which presented a good electrical conductivity of  $5.1 \text{ S cm}^{-1}$ , and a high mass-specific capacitance of  $273 \text{ F g}^{-1}$  at  $0.2 \text{ A g}^{-1}$  in supercapacitor application [144]. Lei et al. prepared CMC/PANI nanorods with uniform diameters about 100 nm, and obtained a specific capacitance as high as  $451.25 \text{ F g}^{-1}$  and a good cycle performance [145]. Very recently, Deng et al. showed that the incorporation of Ag nanoparticles into CNF/PANI composite can provide fast electron transportation channels to achieve high capacitance. The solid-state flexible supercapacitors based on the CNF/Ag/PANI aerogel can reach a high specific capacitance of  $176 \text{ mF cm}^{-2}$  at  $10 \text{ mV s}^{-1}$ , and can remain the same electrochemical properties even under severe bending [146].

### 5.2. Carbon nanomaterials/biomass composites as electrode materials

Carbon materials are always playing a critical role in energy conversion and storage [147]. Due to their novel size-/surface-dependent electronic, optical, mechanical and thermal properties as well as catalytic properties,

carbon nanomaterials, especially CNTs and graphenes, have been emerged as new class of electrode materials for the next generation electrochemical energy storages. Tremendous efforts have been made to develop carbon-based high-performance energy storage devices, and many great progresses have been achieved [9,148–150]. In the most recent development of flexible and versatile energy storage devices, various types of carbon nanomaterials/biomass composites have been explored as electrode materials, owing to the intrinsic characteristics of biomass materials. As systematically demonstrated, mesoporous cellulose fibers in these composite electrode not only functions as a substrate with large surface area but also acts as an interior electrolyte reservoir, where electrolyte can be absorbed much in the cellulose fibers and is ready to diffuse into an energy storage material [151].

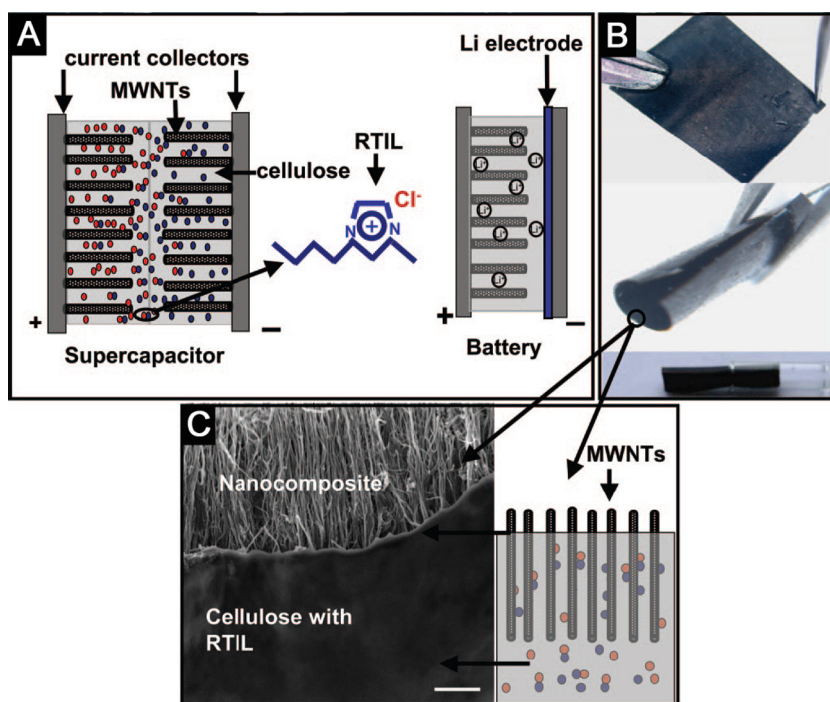
#### 5.2.1. Carbon nanotubes/biomass composites

CNTs are the most common carbon nanomaterials selected to form composite electrode with cellulose, due to their excellent properties, such as high conductivity, excellent electrochemical stability, low mass density, high mechanical strength, and high specific surface area. It is known that CNTs are particularly versatile in binding with cellulose. Ajayan and colleagues have developed a new nanocomposite paper energy storage technology which integrates the three basic components of an electrochemical storage device—electrode, separator and electrolyte—into single contiguous nanocomposite units that can serve as building blocks for thin, mechanically flexible electrochemical energy devices. Unmodified cellulose fibers were dissolved in a room-temperature ionic liquid (1-butyl-3-methylimidazolium chloride ( $[\text{bmIm}][\text{Cl}]$ ), and then the cellulose solution was then coated onto vertically grown multi-walled CNTs (MWCNTs) to form the conductive nanocomposite paper, in which MWCNTs were partially exposed from the cellulose- $[\text{bmIm}][\text{Cl}]$  thin films (Fig. 18) [152]. This single contiguous nanocomposite paper can avoid the use of a separate electrolyte and spacer and is versatile to various supercapacitors and LIBs with electrolytes including aqueous solvents, room temperature ionic liquids, and bioelectrolytes (Fig. 18). As a consequence, it was used as electrode for various flexible supercapacitor, battery, hybrid, and dual-storage battery-in-supercapacitor

**Table 6**  
Literature data on carbon nanomaterials/biomass composites-based electrodes for supercapacitor or battery applications.

Electrodes	Preparation	Conductivity	Device performance: capacity ( $\text{F g}^{-1}$ ) or capacitance ( $\text{mA h g}^{-1}$ ) or energy density ( $\text{W h kg}^{-1}$ ) or power density ( $\text{kW kg}^{-1}$ )	Remarks	Ref.
Cellulose fibers/[bmIm][Cl]/vertically grown CNTs conductive nanocomposite paper	Infiltrating cellulose/([bmIm][Cl]) solution into the MWNT film	/	36 $\text{F g}^{-1}$ (in KOH electrolyte) 22 $\text{F g}^{-1}$ (in RTIL electrolyte) 13 $\text{W h kg}^{-1}$ 1.5 $\text{kW kg}^{-1}$ 110 $\text{mA h g}^{-1}$ at 10 $\text{mA g}^{-1}$ 178 $\text{F g}^{-1}$ at 5 $\text{mV s}^{-1}$ 13.6 $\text{mW cm}^{-2}$ 20 $\text{mW h cm}^{-2}$	The nanocomposite paper contains MWNTs as the working electrode and the cellulose surrounding individual MWNTs, as well as the extra layer as the spacer and the RTIL in cellulose as the self-sustaining electrolyte	[152]
CNFs/MWCNT nanohybrid aerogel	Supercritical $\text{CO}_2$ drying	/	110 $\text{mA h g}^{-1}$ at 10 $\text{mA g}^{-1}$ 178 $\text{F g}^{-1}$ at 5 $\text{mV s}^{-1}$ 13.6 $\text{mW cm}^{-2}$ 20 $\text{mW h cm}^{-2}$	(1) All-solid-state flexible supercapacitors are fabricated using CNFs/MWCNTs film as electrode material and charge collector (2) The device remains at 99.9% of the initial capacitance after 1000 cycles	[153]
Microfibrillated cellulose/MWCNT composite	Buried-in method	$8.2 \times 10^{-4} \text{ S cm}^{-1}$	154.5 $\text{mF cm}^{-2}$ at 20 $\text{mV s}^{-1}$	Flexible all solid-state supercapacitors were fabricated for tests	[154]
SWCNTs or AgNWs/paper composite	The Meyer rod coating method	10 $\Omega \text{ sq}^{-1}$	200 $\text{F g}^{-1}$ 30–47 $\text{W h kg}^{-1}$ 200,000 $\text{W kg}^{-1}$	(1) Capacitor owns a stable cycling life over 40,000 cycles (2) Conductive paper can also been used as an excellent lightweight current collector in LIBs	[155]
CNFs/CNTs/silicon-conductive nanopaper	Paper-making technique, manual Meyer rod coating, plasma-enhanced chemical vapor deposition method	$\sim 80 \Omega \text{ sq}^{-1}$	1200 $\text{mA h g}^{-1}$ at 0.8 $\text{A g}^{-1}$	(1) The lightweight and flexible Si-conductive nanopaper structure performs as LIB anodes (2) After 100 cycles, the discharge capacity still remains 77% compared to the first cycle	[157]
Homemade cellulose paper/CNTs/ $\text{MnO}_2$ /CNTs	Solution-based coating of CNTs, electrodeposition of $\text{MnO}_2$	10.7 $\Omega$	327 $\text{F g}^{-1}$ at 10 $\text{mV s}^{-1}$ 201 $\text{F g}^{-1}$ at 200 $\text{mV s}^{-1}$	The capacitance retention was reached with 96, 93, 88, and 85% at the 20,000th, 30,000th, 40,000th, and 50,000th cycles, respectively	[151]
Natural wood fiber/CNTs/Sn film	Solution-based coating of CNTs, electrodeposition of Sn	$\sim 30 \Omega \text{ sq}^{-1}$	339 $\text{mA h g}^{-1}$ at 84 $\text{mA g}^{-1}$	Natural wood fiber/CNTs/Sn film composite electrode-based Na-ion batteries were developed	[19]
Graphene–cellulose paper membrane material	Filtering a GNS suspension through a filter paper	6 $\Omega \text{ cm}$	120 $\text{F g}^{-1}$	The supercapacitor retains >99% capacitance over 5000 cycles	[163]
Graphene/cellulose composite paper	Paper-making process	11.6 $\text{S m}^{-1}$	252 $\text{F g}^{-1}$ at 1 $\text{A g}^{-1}$ 257 $\text{mA h g}^{-1}$ at 200 $\text{mA g}^{-1}$	The flexible and mechanically tough composite works well in both supercapacitors and LIBs	[164]
Graphene sheets/cotton cloth nanocomposite	Brush-coating and drying	225 $\Omega \text{ cm}^{-1}$	326.8 $\text{F g}^{-1}$ at 10 $\text{mV s}^{-1}$ , 7.13 $\text{W h kg}^{-1}$ in 6 M KOH electrolyte 73.2 $\text{F g}^{-1}$ at 0.1 $\text{A g}^{-1}$ , 12.3 $\text{W h kg}^{-1}$ in 2 M EMIMBF <sub>4</sub> /acetonitrile electrolyte	The supercapacitors fabricated using the GNSs–CC composite have good cycle durability in both 6 M KOH and 2 M EMIMBF <sub>4</sub> /acetonitrile electrolytes (6–7% decay of capacitance after 1500 cycles)	[165]
CNFs-RGO hybrid aerogels	Supercritical $\text{CO}_2$ drying	100 $\text{S m}^{-1}$	207 $\text{F g}^{-1}$ at 5 $\text{mV s}^{-1}$ 15.5 $\text{mW cm}^{-2}$ 20 $\text{mW h cm}^{-2}$	The device capacitance still retains about 99.1% of the initial capacity after 5000 charge–discharge cycles	[166]
CNFs–[RGO] <sub>n</sub> hybrid paper	LbL self-assembly approach	2.4 $\text{k}\Omega \text{ m}^{-1}$ (20 layers of RGO)	1.73 $\text{mF cm}^{-2}$ at 5 $\text{mV s}^{-1}$	After 5000 cycles, the capacitance decay is $\sim 19\%$ The transmittances of T-SC-10 and T-SC-20 are about 56% and about 30% (at 550 nm) respectively	[167]
Carbon nanomaterials-cellulose paper composite	Drawing with a graphite rod on standard printing paper	223 $\Omega \text{ cm}^{-1}$	2.3 $\text{mF cm}^{-2}$ at 200 $\text{mA g}^{-1}$ 12 $\text{F g}^{-1}$	(1) Paper supercapacitors by a solvent-free drawing method were developed (2) The supercapacitor has excellent cycling performance with nearly 100% retention of capacity up to 3000 cycles	[159]





**Fig. 18.** Fabrication and application of the cellulose fibers/[bmIm][Cl]/vertically grown CNTs conductive nanocomposite paper units. (A) Schematic of the supercapacitor and LIB assembled by using nanocomposite paper units. (B) Photographs of the nanocomposite units demonstrating flexible property. (C) SEM image and corresponding schematic of the nanocomposite paper showing MWNTs protruding from the cellulose-[bmIm][Cl] thin films [152]. Copyright 2007. Reproduced with permission from the National Academy of Sciences.

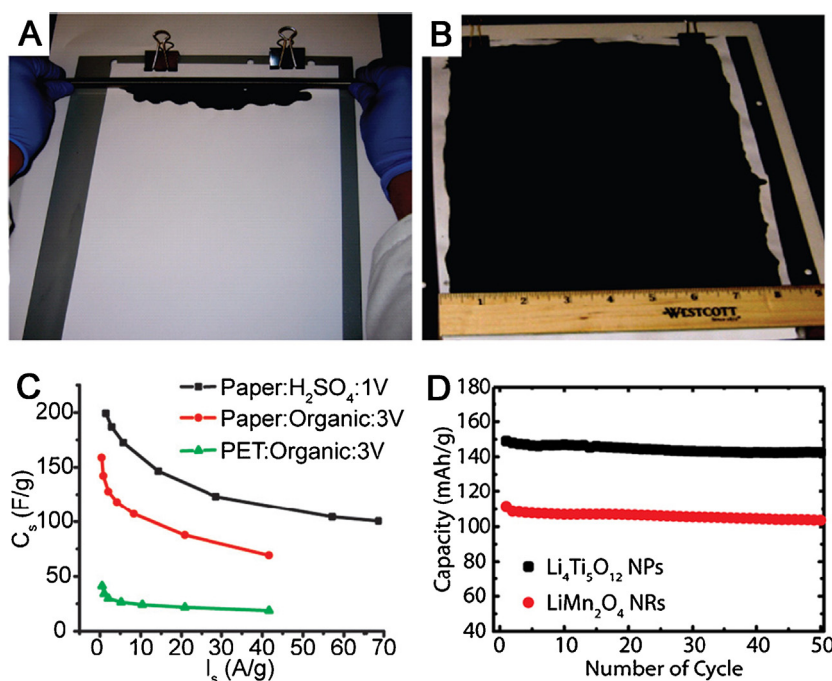
devices, and the assembled devices displayed excellent electrochemical performance (Table 6). Recently, CNFs/MWCNT composites have also been successfully used as electrode for constructing high-performance all-solid-state flexible supercapacitors (Table 6) [153,154].

It is worth noting that, in the most recent years, Cui, Hu and their colleagues have paid much attention on the development of nanostructured, highly conductive cellulose paper for flexible energy and electronic devices [14,19,151,155–160]. They demonstrated the generation of conductive electrodes on commercially available paper via forming conformal coating of single-walled carbon nanotubes (SWCNTs) or silver nanowire (AgNWs) films on the paper. The intrinsic properties of paper including high solvent absorption and strong binding with nanomaterials allow easy and scalable coating procedures by using simple solution processes (Fig. 19A and B). The prepared conductive paper has a sheet resistance as low as  $1\ \Omega\ \text{sq}^{-1}$ . Supercapacitors based on the CNT-conductive paper show excellent performance (on the basis of CNT mass): a specific capacitance of  $200\ \text{Fg}^{-1}$  (Fig. 19C), a specific energy of  $30\text{--}47\ \text{Wh kg}^{-1}$ , a specific power of  $200\ \text{kW kg}^{-1}$ , and a stable cycling life over 40,000 cycles. This conductive paper has also been used as an excellent lightweight current collector in LIBs to replace the existing metallic counterparts (Fig. 19D). These results indicate that the performance of the prepared conductive paper is competitive with conventional metal foils and its related electrodes in which similar chemistries are used [155].

Cui, Hu and their colleagues carried out the first study on the optical properties of nanopaper substrates,

and developed transparent and conductive composite materials including tin-doped indium oxide, CNTs and AgNWs have been achieved on nanopaper substrates, opening up wide applications in flexible optoelectronics and electrochemical devices [156]. They also reported a CNFs/CNTs/silicon-conductive nanopaper for LIBs, the thin-layer of silicon was deposited on the CNFs/CNTs substrate through a plasma-enhanced chemical vapor deposition method. Such lightweight and flexible Si-conductive nanopaper structure presents a stable capacity of  $1200\ \text{mAh g}^{-1}$  for 100 cycles in half Li-ion cells [157].

Though its energy density is somewhat lower than that of LIB, sodium (Na)-ion battery offers a fascinating alternative for low cost energy storage, because of the huge availability of sodium, its low price and the similarity of both Li and Na insertion chemistries [161]. Recently, Hu et al. demonstrated that the soft and mesoporous wood fiber substrate can be utilized as an attractive platform for low cost Na-ion battery electrode. A Sn thin film was deposited on a CNTs-precoating hierarchical wood fiber substrate, and the composite electrode thereby obtained was used as the anode for Na-ion battery, which can reach a stable cycling performance of 400 cycles with an initial capacity of  $339\ \text{mAh g}^{-1}$  at a current density of  $84\ \text{mA g}^{-1}$  (Fig. 20A). These exciting properties that come from the natural wood fiber-based Sn anode can simultaneously address the critical challenges associated with conventional Sn anodes. On the one hand, the soft nature of wood fibers can effectively accommodate the large volume expansion associated with the sodiation



**Fig. 19.** (A) Conformal coating of CNT or Ag NW ink on commercial Xerox paper via Meyer rod method. (B) The photograph of conductive Xerox paper after CNT coating. (C) Gravimetric capacitances of CNTs-conductive paper at various currents measured in aqueous and organic electrolytes, and data from CNTs on PET are presented for comparison. (D) Cycling performance of  $LiMn_2O_4$  nanorod and  $Li_4Ti_5O_{12}$  nanopowder half LIBs with CNTs-conductive paper as the current collectors [155]. Copyright 2009. Reproduced with permission from the National Academy of Sciences.

process (Fig. 20B). On the other hand, the hierarchical and mesoporous structure functions as an electrolyte reservoir that can enhance the ion transport kinetics (Fig. 20C) [19].

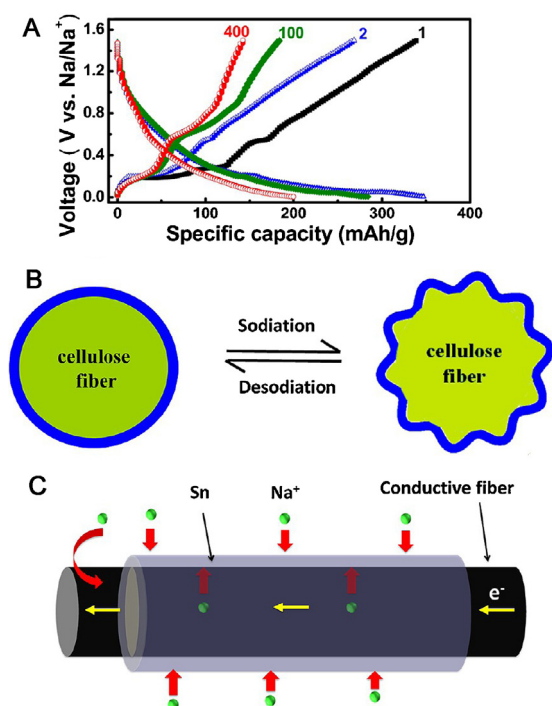
### 5.2.2. Graphenes/biomass composites

The combination of CNTs with cellulose paper has shown promising application as electrodes of flexible energy storage devices. However, the selection and functionalization of diverse carbon nanomaterials remains optimization to further improve the performance of carbon-cellulose composites. Graphene, a two-dimensional material consisting of a single layer of carbon atoms arranged in a honeycomb or chicken wire structure [162], has been extensively demonstrated as another outstanding candidate. Cheng and colleagues developed a graphene-cellulose paper membrane material as a flexible electrode via a simple filtering method (Fig. 21A). Via the strong electrostatic interaction, graphenes cover the cellulose fibers tightly (Fig. 21B), and are distributed through the macroporous texture of the filter paper to form a conductive interwoven network. Due to the large capacitance ( $120\text{ F g}^{-1}$ ), low electrical resistance, and high strength, when the graphene-cellulose paper electrode was used as freestanding and binder-free electrodes for flexible supercapacitors, satisfied performance was achieved (Fig. 21C and D) [163]. Various graphene/cellulose composites, such as graphene/cellulose pulp composite, graphene sheets/cotton cloth composite, CNFs-reduced graphene oxide (RGO) hybrid aerogels, and CNFs-[RGO] $_n$  hybrid paper, have been recently fabricated via diverse process,

and all these composites showed excellent performances as the electrode materials of supercapacitors (Table 6) [164–167].

Most of the previously reported electronically conductive polymers or flexible carbon nanomaterials-cellulose paper composite electrodes were fabricated by solution-based processes, which involve dispersing the active materials in a special solvent, followed by reforming the electrode on a substrate. The use of environmentally unfriendly chemicals and the requirements of post-treatment pose challenges for the wide applications of the techniques. More recently, Cui et al. developed a solvent-free approach to fabricate supercapacitor electrodes, i.e. by drawing with a graphite rod on standard printing paper. The supercapacitors thus fabricated show stable long cycling performance with 90% capacity retention after 15,000 cycles and a high areal capacitance of  $2.3\text{ mF cm}^{-2}$ . The drawing approach holds promising extension to fabricate other types of low cost energy storage device electrodes [159].

The above-mentioned composite electrodes typically derive high electronic conductivity from conducting materials (e.g. CNTs, graphene, conducting polymers), and fast ion transport from the hierarchical porosity of cellulose. Hu and colleagues clearly verified that mesopores within a cellulose fiber act as an electrolyte reservoir and provide extra paths for ion transport. The use of porous, electrochemically inert cellulose paper as a substrate may sacrifice some volume energy and power density; however it provides efficient utilization of active storage materials at high rates [160].



**Fig. 20.** (A) Discharge–charge profiles of the Na-ion battery based on the anode of 50 nm Sn on CNTs-precoating wood fiber (Sn@WF) at a rate of C/10. (B) Schematic of how the soft wood fibers release the sodiation generated stresses experienced by the Sn@WF electrode. (C) Schematic of the dual pathways for Na<sup>+</sup> transport that effectively enhance the kinetics of the Sn@WF anodes for Na-ion batteries [19]. Copyright 2013. Reproduced with permission from the American Chemical Society.

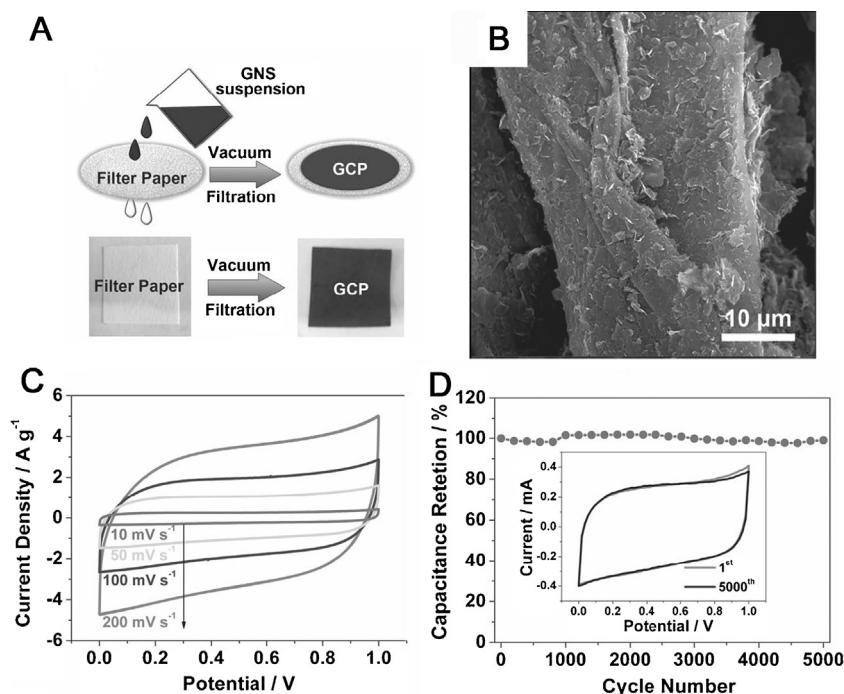
### 5.3. Biomass-derived small molecules as electrode materials

Organic compounds offer new possibilities for high energy/power density, cost-effective, environmentally friendly, and functional rechargeable lithium batteries. For a long time, they have not constituted an important class of electrode materials, partly because of the large success and rapid development of inorganic intercalation compounds. It is now becoming mandatory to develop renewable organic electrodes through eco-efficient processes and to decrease the consumption of non-renewable inorganic resources, the amount of waste produced as well as energy consumption [1]. In recent years, however, exciting progress has been made, bringing organic electrodes to the attention of the energy storage community [168]. Especially, the biomass-derived organic materials have the potential to boost the capacity. Recently, the feasibility of using several active organic molecules that can be simply prepared from natural products common in living systems as electrode materials has been successfully developed by Tarascon and colleagues.

Tarascon et al. firstly investigated the oxocarbon salt, Li<sub>2</sub>C<sub>6</sub>O<sub>6</sub>, as a candidate for lithium-inserting positive electrodes. It can electrochemically react with Li<sup>+</sup> by using carbonyl groups as redox centres, and can be synthesized from the natural organic sources through low-cost processes without using toxic solvents (Fig. 22). As compared with the few recent reports on carbonyl based organics, Li<sub>2</sub>C<sub>6</sub>O<sub>6</sub>, turned out to reversibly intercalate four extra lithium per unit formula at an average voltage of 2.5 V, leading to energy densities and power-rate performances that compare to conventional cathodes with the advantage of being fully sustainable

**Table 7**  
Small molecules derived from biomass as electrode materials for LIBs.

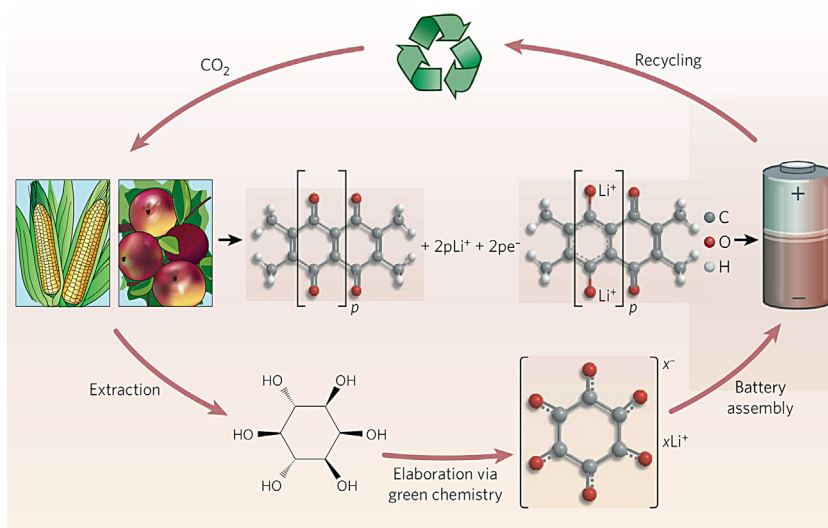
Compound	Structure	<i>E</i> (V) vs Li <sup>+</sup> /Li <sup>0</sup>	Capacity (mAh g <sup>−1</sup> )	Remarks	Ref.
Dilithium rhodizonate salt (Li <sub>2</sub> C <sub>6</sub> O <sub>6</sub> )		2.5	580	Contains carbonyl groups capable of reversibly reacting with four extra Li <sup>+</sup> per formula	[169]
Tetralithium rhodizonate salt (Li <sub>4</sub> C <sub>6</sub> O <sub>6</sub> )		1.8	~200	Contains carbonyl groups capable of reversibly reacting with two extra Li <sup>+</sup> per formula	[170]
Di-lithium trans-trans-muconate		1.4	150	With carboxylate groups capable of reversibly reacting with one extra Li <sup>+</sup> per formula	[171]
Di-lithium terephthalate		0.8	300	With carboxylate groups capable of reversibly reacting with two extra Li <sup>+</sup> per formula	[171]
Lithium 2,6-bis(ethoxycarbonyl)-3,7-dioxo-3,7-dihydro-s-indacene-1,5-bis(olate)		~1.96~1.67	125	With both carbonyls and ester redox centers capable of reversibly reacting with two extra Li <sup>+</sup> per formula	[172]



**Fig. 21.** (A) Schematic of the fabrication process of the graphene-cellulose paper membrane material. (B) Typical SEM image of the graphene-cellulose paper electrode, indicating the anchor of graphenes on the cellulose fiber surface. (C) Cyclic voltammetry (CV) curves of the graphene-cellulose paper electrode in 1 M H<sub>2</sub>SO<sub>4</sub>, showing an excellent capacitive behavior. (D) Cyclic performance of the graphene-cellulose paper electrode measured at 50 mV s<sup>-1</sup>. Inset: CV curves of the 1st and the 5000th cycle [163]. Copyright 2011. Reproduced with permission from WILEY-VCH Verlag GmbH & Co., KGaA.

as it is made from the oxidation of the sugar inositol [169]. Consequently, Li<sub>4</sub>C<sub>6</sub>O<sub>6</sub> [170], Li<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub> (Li terephthalate) [171], Li<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sub>4</sub> (Li trans-trans-muconate) [171] and lithium 2,6-bis(ethoxycarbonyl)-3,7-dioxo-3,7-dihydro-s-indacene-1,5-bis(olate) [172] compounds were reported as key electrode materials for LIBs with attractive performances (Table 7). These molecules can also

be readily prepared from biomass via eco-efficient processes. However, to realize green, sustainable, fully-organic LIBs with comparable energy densities and power-rate performances and to completely understand the structure-function relationship of these small molecule compounds, further investigations currently remains necessary.



**Fig. 22.** The proposed sustainable organic-based LIBs on the basis of biomass-derived electrode materials. Electrochemically active Li<sub>2</sub>C<sub>6</sub>O<sub>6</sub> can be prepared from corn-extracted myo-inositol, whereas electrochemically active polyquinone can be polymerized from apples-extracted malic acid (center) [1]. Copyright 2008. Reproduced with permission from the Nature Publishing Group.



## 6. Conclusion and perspectives

Recent investigations have resulted in a significantly improved comprehension of the critical challenges for electrochemical energy storage systems. Biomass-derived materials have been demonstrated as very promising alternatives to conventional polyolefin separators, binders and substantial electrode materials in electrochemical energy storage devices and the recent processes have been emphasized in this review. Owing to their sustainable, environmental friendly, cost-effective characteristics, the application of biomass-derived materials opens up new possibilities for the production of green, low-cost, up-scalable and lightweight energy storage systems, even fully recyclable paper-based batteries on a large industrial scale.

Although the implementation of biomass-derived materials in green and sustainable electrochemical energy storage systems holds great promise in a number of applications ranging from separators, binders to electrode materials, it is clear that considerable critical challenges still remain to be solved:

- (1) The principal challenge in the use of biomass-derived separators is the control of thickness and porosity (particularly pore size and distribution, and thermal shutdown property). In addition, the hygroscopic nature, low mechanical strength and flammable property, are also the challenges need to be overcome for the development of biomass-derived separators for energy storage.
- (2) For the biomass-derived binders, some critical drawbacks have to be overcome such as variable quality, weaker adhesion on foils, stiffness at low temperature and high moisture uptake. Strict quality standards need to be issued to control the production quality and utilization, and the combination of biomass-derived binders with some other flexible binders can improve the dispersion and adhesion on foils and ameliorate the flexibility at low temperature.
- (3) The energy densities of biomass-derived energy devices are normally quite lower than those of conventional metal-based systems. The critical issue in the use of biomass-derived materials as electrode materials is the fact that they by themselves are electronically insulating and usually limited in functionalities, and thus the proper integration with other conductive and functional materials is prerequisite and faces many challenges. In addition, the stability, conformability and self-discharge of biomass-derived energy devices deserve intensive fundamental research.

Future research can emphasize the following key areas of development, which might favor the realization of more intriguing electrochemical energy storage devices on the basis of biomass-derived materials:

- (1) Until now, most attention was paid to very numbered biomass materials, especially cellulose and its derivatives. However, numerous other biomass materials (e.g. lignin, marine polysaccharides, and biomass from agro-forestry wastes), with their own specific

structures and properties, also possess the potential applications as key materials for energy application, and thus merit intensive research devotion in the future. Additionally, large-scale production of biomass-derived materials with finely tuned structures and properties in even more low-cost and environmental friendly manners is critical for their applications in the energy storages.

- (2) It is obligatory to further improve their individual performance of biomass-derived key materials for energy devices, even to endow them with additional functions by physical or chemical manipulation to biomass. For instance, by incorporating the biomass-derived separator with proper electro-active polymers, it is expected that the fabricated switchable separator can transform from an isolating state to a conducting state at a defined charging voltage to bypass the overcharging current and further improve the safety of the batteries.
- (3) It can be expected that the biomass-derived materials can also play promising roles in the next-generation electrochemical energy devices, such as all-solid-state LIBs, Li-S batteries and Li-air batteries, with more significance and more challenges. The all-paper-device, in which all components are made by cellulose-derived materials, is also very promising and deserves intensive research efforts as a flexible, sustainable and high-performance energy device candidate. More importantly, the large-scale and low-cost fabrication of paper-based energy devices potentially can be realized by using 3-D printing and other high-throughput nanofabrication techniques in the future [173].

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