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Advances Toward Sustainable Lignin-based Gel for Energy Storage and Smart Sensing

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Abstract: Polymers obtained from biomass are promising alternatives to petro-based polymers owing to their low cost, biocompatibility, and biodegradability. Lignin, a complex aromatic polymer containing several functional hydrophilic and active groups including hydroxyls, carbonyls, and methoxyls, is the second most abundant biopolymer in plants. In particular, sustainable lignin-based gels are emerging as an appealing material platform for developing energy- and sensing-related applications owing to their attractive and tailorable physiochemical properties. This study describes the preparation strategies of lignin-based gels according to previously reported methods, with significant attention on the diverse performance of lignin-derived gel materials. Additionally, a detailed review of lignin-based gels utilized as an important resource in diverse fields is provided. Finally, a future vision on challenges and their possible solutions is presented.

Keywords: lignin; gels; sustainable materials; smart sensing; energy storage
DOI: 10.26599/PBM.2023.9260007

1 Introduction

The rapid development in flexible wearable devices in the past decade has driven the demand for all forms of power, such as batteries [1], sensors [2], triboelectric nanogenerators (TENGs) [3], and supercapacitors [4], which are commonly used energy suppliers. The selection of appropriate electrode materials is a significant challenge faced in flexible-device industry. Owing to the energy crisis and environmental problems arising from using traditional fossil fuels, alternative, eco-friendly biomass-derived biopolymers and other natural materials must be determined. Biopolymer-based gels, as emerging and renewable electrolyte materials, are considered competitive candidates for

Received: 21 March 2023; accepted: 5 April 2023.

flexible and smart electrochemical energy storage and conversion devices owing to their low cost, eco-friendliness, and degradability. Biopolymers, such as cellulose, chitosan, chitin, alginate, and lignin, have been explored for fabricating functional gel electrolytes [5]. Lignin, the second most abundant plant polymer, after cellulose, in all terrestrial vascular plants, is a complex organic polymer comprising aromatics [6]. Furthermore, lignin can be an excellent candidate for chemical modifications and reactions owing to its high functionality (i.e., rich in phenolic and aliphatic hydroxyl groups) [7].

Gels are defined as crosslinked network systems that exhibit properties ranging from soft and weak to hard and tough. Conventionally, gels, particularly hydrogels, consist primarily of homopolymer or copolymer chains crosslinked by either physical interactions or chemical bonds [8]. Physical gels are networks formed through noncovalent interactions, which typically lead to junction zones because separated polymer chains interact over a certain length but not in a pointwise manner [9]. Typical interactions include hydrogen bonds, hydrophobic interactions, ionic/electrostatic interactions, and metal coordination [10]. When the crosslinking effects are covalent in nature, the gels thus formed can be regarded as chemical gels, which typically exhibit enhanced mechanical stability because the covalent interactions are much stronger [11]. Chemical crosslinking methods include radical polymerization, redox reactions, and base-catalyzed ring-opening reactions according to their distinct mechanisms. The introduction of lignin into the gel system can not only realize the effective substitution of lignin raw materials for fossil materials in the field of gel materials but also affect the biocompatibility and degradability of the gel. However, most as-prepared lignin gels exhibited inferior mechanical strength, limited extensibility or recoverability, and poor toughness.

To the best of our knowledge, a comprehensive overview focusing on lignin-based gels for flexible energy storage and conversion devices is still lacking. In particular, multifunctional gels using various polymerization methods must be urgently developed for energy applications. This review, as shown in Fig. 1, summarizes the preparation process, progressive properties, and application of lignin-based gels as biopolymer-based gel electrolytes for various energy storage and conversion devices, including electrochemical supercapacitors (SC), lithium-ion batteries (LIBs), zinc-ion batteries (ZIBs), sensors, and TENGs. First, various crosslinking methods, classified into either noncovalent (i.e., physical) or covalent bonding (i.e., chemical), were comprehensively reviewed, analyzed, and discussed. Next, the performance of lignin-based gels was characterized in terms of the role of lignin in the system. More importantly, the current applications of lignin gel electrolytes for energy storage and conversion devices were extensively reviewed. Finally, the relevant challenges and perspectives were summarized and analyzed, and some underlying approaches to overcome these challenges of lignin gels were proposed.

2 Fabrication of lignin-based gels

Crosslinking strategies of gels allow a further degree of tuning of their molecular structures, morphologies, and properties for application as desirable components in energy and water-related technologies. In general, the synthesis of gels from lignin includes noncovalent (i.e., physical) or covalent bonding (i.e., chemical). Note that in most cases, multiple crosslinking methods were combined to form functional gels. As depicted in Fig. 2, a combination of noncovalent and covalent crosslinking (a), or the coexistence of different interactions (b), is feasible in designing specific functional gels for target applications.

2.1 Physical crosslinking

According to their various crosslinking methods, gels can be classified as physical or chemical gels. The majority of physical gelation methods depend on the intrinsic properties of the polymers. Physical-entanglement gels form their 3D networks through the dynamic formation of reversible noncovalent interactions, such as hydrogen bonds, hydrophobic,

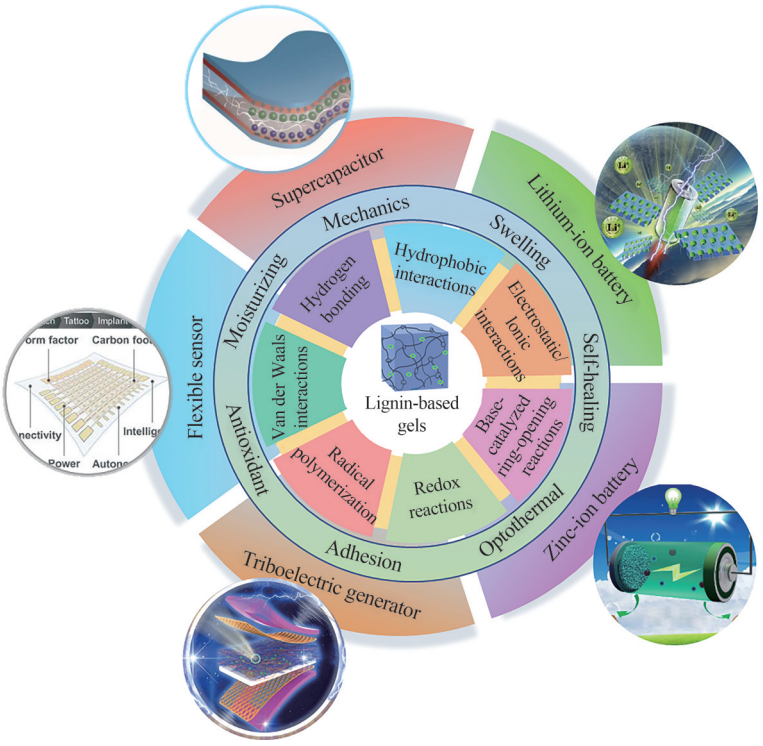

Fig. 1 General fabrication, properties, and applications of lignin-based gels used for various electrolytes in energy storage and conversion systems

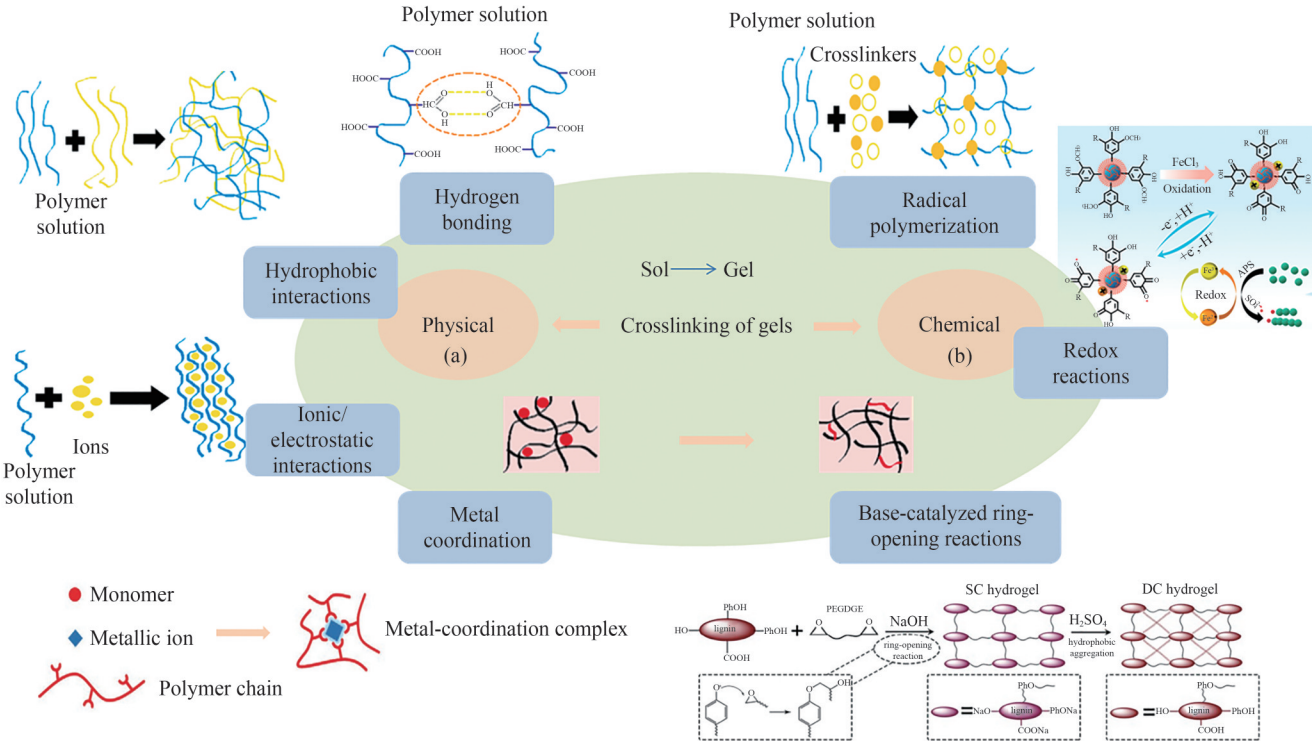

Fig. 2 Preparation of gels by physical and chemical crosslinking techniques (adapted from references [11−14])

ionic/electrostatic, and van der Waals interactions.

2.1.1 Ionic/electrostatic interactions

Constructing gels via ionic/electrostatic interactions requires an initial solution containing at least two molecules with opposite electric charges. Electrostatic interactions also occur between charged biological

macromolecules or between natural and synthetic polymers. Wang et al [15] fabricated a novel double-layer polyvinyl alcohol (PVA)-borax (dynamic crosslinked agent)-freezing-thawing (FT) gel, with polyanionic lignosulfonate sodium (LS) as the bottom layer and quaternary hydroxyethyl cellulose (QHEC) as the top layer. The multiple interactions between the two layers result in excellent asymmetrical adhesion, strength, and electrical properties. Ravishankar et al [16] prepared biocompatible gels by mixing an aqueous-acidic solution of chitosan with alkali lignin (AL). Electrostatic interactions between the phenoxide groups in lignin and the ammonium groups on the chitosan backbone were found to be responsible for ionotropic crosslinking. These products are biocompatible and provide an appropriate surface for cell attachment and growth, thus making them highly suitable for application as scaffolds in tissue engineering and wound healing.

2.1.2 Hydrophobic interactions

Hydrophobic interactions occur in gels when water-soluble precursors contain hydrophobic units, side chains, or functional groups [17]. Hydrophobic interactions can be achieved in the following two ways. First, gel can be fabricated by promoting a sol-gel phase transition, which is the thermal induction based on the lower critical solution temperature (LCST) or upper critical solution temperature (UCST) of polymers, such as poly(N-isopropylacrylamide) (PNIPAM), poly (hydroxyethyl methacrylate) (PHEMA), and their derivatives. In addition, some amphiphilic copolymers combining hydrophilic polyethylene oxide (PEO) with hydrophobic poly(propylene oxide) (PPO) or polyglycolide and polylactide also formed thermoresponsive gel [18]. For instance, a pluronic [PEO-b-PPO-b-PEO] aqueous solution dissolved with ions transforms to a gel when the temperature increases beyond its LCST. You et al [19] constructed a novel lignin/poly(N, N-dimethylacrylamide) (PDMA) gel with high lignin content, excellent toughness, and ultrahigh antioxidative performance by employing a facile dissolve-dry-swell solvent exchange method. The PDMA chains both interpenetrated inside and adhered to the surface of these domains through hydrophobic interactions.

2.1.3 Metal coordination

Metal coordination is another supramolecular crosslinking method used for fabricating gel. It is generally be referred to as metal-ligand interaction, i.e., a noncovalent, special Lewis-acid based interaction that is weaker compared with covalent bonding [20]. As the bond energy of metal-ligand bonds is moderated, they can dynamically assemble/disassemble or associate/dissociate, thus exhibiting great potential for features, such as self-healing properties and sol-gel phase transitions [21–23]. Xiu et al [24] reported a robust and adhesive gel constructed primarily using silver nanoparticles (AgNPs)@lignin, polyacrylamide (PAM), and sodium alginate (SA). The gel strength was improved via the reaction between AgNPs@lignin and Fe^{3+}. This lignin hybrid gel can detect various human motions and small physiological signals (such as breathing and pulse). Given its excellent sensing property, antibacterial performance, and biocompatibility, this gel may be used as a high-performance sensing material for the design of flexible wearable electronics. Yu et al [14] developed a simple and effective approach for fabricating tough metallosupramolecular gel films of poly(acrylic acid) by one-pot photopolymerization of the precursor solution in the presence of Zr^{4+} ions that form coordination complexes with carboxyl groups and serve as physical crosslinkers of the matrix.

2.1.4 Hydrogen bonding

Hydrogen bonding is the most common noncovalent interaction in numerous physically crosslinked gel. Numerous functional groups, such as amide, phosphate, carboxylic, urea, carbazole, and hydroxyl, can form hydrogen bonds or interact with electron donor groups, such as pyridine and imidazole groups. For example, Li et al [25] prepared a lignosulfonate-modified graphene gel (LS-GH) using a one-step method. In their LS-GH network, lignosulfonate provided a competent active fraction, and graphene offered sufficient surface area and larger pore diameter. Furthermore, LS could be decorated on the surface of reduced graphene oxide

(GO) sheets via strong noncovalent interactions, such as hydrogen bonding and π-π conjugation between LS and reduced GO sheets, to form a 3D porous structure. Therefore, as an excellent adsorbent, LS-GH has great potential for water purification applications. Cao et al [26] fabricated a novel self-healing and adhesive gel driven by noncovalent interactions between LS and polyvinylpyrrolidone (PVP), including hydrogen bonding and hydrophobic interactions. Multifunctional lignin-based gel with desirable mechanical properties, self-healing ability, adhesion strength, and biocompatibility can be prepared for biomedical applications. Huang et al [27] synthesized a strong shape-memory gel through solvent exchange after the homogeneous copolymerization of dopamine methacrylamide (DMA), N, N-dimethylacrylamide (DMAA), and N, N-methylenebisacrylamide (BIS) crosslinker in a mixed solvent of water and dimethyl sulfoxide (DMSO). Immersion in water induced solvent exchange to reinforce the gel by the association of DMA to provide external reversible crosslinking, which endowed the gel with interesting shape-memory and bio-inspired actuating behaviors. Further, a more complicated actuation was attempted by combining solvent exchange with coordination of DMA and Fe^{3+}.

Li et al [28] prepared AL/polyethylene elastomer (POE) composites by a solvent-free melt compounding process. The formation of π-π conjugation and molecular interactions among lignin molecules endowed the lignin with unique optical properties, including aggregation-induced emission, ultraviolet (UV) absorbance, and great potential for sustainable photothermal conversion. The sustainable development and high-value utilization of biomass lignin provide considerable application prospects in smart materials for precise remote driving of robots, machines, sensors, sterilization, and self-repairing equipment. Chen et al [29] developed castor oil-derived functional polyamide (PA) elastomers with ultrahigh mechanical strength by controlling programmable supramolecular hydrogen bonding and tunable crystallinity. The presence of abundant hydrogen bonding between lignin and poly[N, N′- (2-hydroxypropane-1, 3-diyl)bis(undec-10-enamide)] (PUDA)-co-[1,3-di(undec-10-enamido)propan-2-yl butyrate] (BUDA) facilitated stress transfer during tensile deformation, thus significantly improving tensile toughness. The gel produced via this method is a high-value-added material with photoresponsive capabilities and can be used in various applications. Wang et al [30] developed high-performance lignin/carbon black (CB)/nitrile rubber (NBR) elastomers with high strength, excellent elasticity, and good energy dissipation by constructing a dual-crosslinking network consisting of hydrogen bonding and dynamic coordination sacrificial bonds. They presented a novel method for preparing high-performance green lignin/rubber elastomers. Huang et al [31] presented a new class of lignin-based thermoplastic elastomer (TPE) using a saturated POE as the rubber matrix. The coordination bonds between lignin and the POE matrix promoted the dispersion of lignin, improved the interfacial interactions, and facilitated the orientation of chain segments during stretching. The lignin-based TPE exhibited enhanced toughness and excellent shape-memory performance, thus offering a promising methodology for the facile production of high-performance but cost-effective TPE materials. Wang et al [32] attempted to employ a highly resilient lignin-containing polyurethane (PU) foam by partially substituting petroleum polyols with chemically modified AL. The modified lignin structure influenced the mechanical properties and thermal stability of the PU foams. Thus, their proposed methodology can be used to develop biopolymer lignin for application in flexible and highly resilient PU foams. Lin et al [33] fabricated a novel redox-active and self-healing PVA/PA/Fe^{3+} (PPFe) gel containing a dual crosslinking network through the formation of both metal coordination bonds and hydrogen bonds via the FT method. Using their methodology, multifunctional gel with simultaneously promoted self-healing and electrochemical activity can be designed.

2.2 Chemical crosslinking

Compared with physically crosslinked gels, chemically

crosslinked gels are prepared by a chemical reaction between a crosslinking agent and lignin, which has the advantages of mechanical stability and permanency. During the reaction, they form a stable covalent bond, and most of the process is irreversible. Crosslinking agents are required for almost all covalent crosslinking approaches, and some polymerizations also require initiating chemicals. Chemical crosslinking methods include radical polymerization, redox reactions, and base-catalyzed ring-opening reactions according to their distinct mechanisms.

2.2.1 Radical polymerization

Several gel can be synthesized by crosslinker-involved radical polymerization of monomers. It typically begins with initiating agents to produce active radicals and then propagates through the bonds of monomers, thereby forming polymer chains. The polymer chains terminate when the propagating radicals react by combination, disproportionation, or transfer [34–35]. Depending on the types of monomers, solvents, reaction conditions, and initiators, radical polymerization can vary significantly with case. For instance, Meng et al [36] introduced a super-swelling biopolymer gel with lignosulphonate-and-polysaccharide-contained papermaking spent liquor and acrylic acid (AA) via a simple and low-cost method. These gels were proven to be excellent candidates for plants and vegetables for water retention in agriculture. Xue et al [37] synthesized a new type of acrylamide (AM)-based gel with ethanol organosolv lignin (EOL) used as a reactive filler in the presence of N, N methylene-bis-acrylamide (MBA) as the crosslinker and ammonium persulfate (APS) as the initiator. With increasing EOL content in the gel, an interpenetrating polymer network may be formed primarily by hydrogen bonding between EOL and AA and/or AM molecules. The gel can be used as a good water retention material with high water absorption, high stretch modulus, and excellent elongation at break. Li et al [38] studied a novel method for preparing lignin-based antibacterial gel through crosslinking of lignin amine (LA) with PVA. Next, the silver ions were reduced *in situ* to obtain a polymer gel containing silver nanoparticles. The biocompatible gel possessed good broad-spectrum antibacterial properties toward both *E. coli* and *S. aureus* owing to the enhanced antibacterial effect of both the gel and silver nanoparticles. Additionally, the gel exhibited good strength and elasticity, and is expected to have wide applications in the medical field.

2.2.2 Redox reactions

Novel dynamic oxidation and coordination systems composed of polyphenols and high-valent metal ions (Fe^{3+}, Al^{3+}) have been widely reported over the past years. This gelling system is highly advantageous as it produces low-cost lignin-based gel for the fast fabrication of multifunctional gel under facile conditions and effectively decreases energy loss; thus, it can be used for mass-scale production. Additionally, this system can activate the initiator to promote monomer polymerization, and then dynamically crosslink the polymer chains. Sun et al [39] designed a facile and universal lignin-based self-catalytic system (AL-Cu^{2+}) to initiate the polymerization of AM monomers in an alkaline water-ethylene glycol (EG) binary solvent. The conductive and transparent organogel was designed by introducing anti-freezing, nondrying, self-adhesive, and stretchable properties. Feng et al [40] constructed a eutectogel using a dynamic oxidation and coordination system composed of sulfonated lignin (SL) and Fe^{3+} immersed in a deep eutectic solvent (DES). The dynamic redox system containing SL (reducing agent) and Fe^{3+} (oxidizing agent) can trigger rapid gelation (approximately 30 s) of monomers without external stimulus by self-catalytic APS to generate radicals. By the subsequent one-pot solvent replacement in DES, the obtained eutectogel exhibited remarkable freezing tolerance, and could retain stable mechanical flexibility (450% strain) and electrical conductivity (up to 8.70 mS/cm) in a wide temperature range, from −80 to 25 ℃. Zhao et al [12] constructed a highly elastic conductive gel with the dynamic redox reaction between the catechol groups of SL-coated silica nanoparticles (LSNs) and Fe^{3+}, which could promote the rapid gelation of the AM monomers in 60 s. The gels

exhibited integrated mechanical robustness, self-adhesiveness, UV filtering, and stable electrical performance. Wang et al [41] directly dissolved lignin into a DES composed of betaine and EG, and utilized the dynamic redox reaction between lignin and $Fe_2(SO_4)_3$ in DES to catalyze the polymerization of AA at 25 ℃ within minutes. The as-prepared ionic gel exhibited high strength, high temperature stability, and good electrical conductivity.

2.2.3 Base-catalyzed ring-opening reactions

As is well known, lignin possesses excellent solubility in alkaline solutions because of the phenol, carboxyl, and hydroxyl groups [42]; moreover, precipitation can be easily induced upon adding the acid solution because of hydrophobic aggregation. Numerous researchers have utilized stepwise alkali/acid treatment to purify lignin [43–45]. Inspired by the different solubilities of lignin in alkaline and acid solutions, and the hybrid physically double-crosslinked approach, some studies synthesized a chemically crosslinked lignin gel through base-catalyzed ring-opening polymerization and crosslinking reaction, and then applied a simple acid soaking strategy to convert the lignin gel into a high-mechanical hybrid double-crosslinked (DC) lignin gel via lignin hydrophobic aggregation interactions. Liu et al [13] reported a facile and feasible method to construct a hybrid DC lignin gel electrolyte with superior compressibility via the simple treatment of a single chemically crosslinked lignin gel using H_2SO_4 solution. This synthetic DC lignin gel exhibited significant improvement in mechanical strength, remarkable shape-recovery property, and high ionic conductivity.

3 Lignin-based gels in practical applications

Lignin is extracted from the plant fiber, which is nontoxic and biodegradable, and does not affect the biocompatibility of materials. The features of lignin include huge reserves, low cost, and favorable renewability because of the wide range of plant resources and industrial processes [46]. Recently, gels, as indispensable constituents, have undergone rapid development from synthetic to natural polymers [47]. Among different natural polymers, lignin is an attractive candidate for gels because of its advantages, as mentioned previously. Therefore, gels prepared from lignin are also expected to be used for extensive applications in various fields [48]. Polymeric lignin-based gels have been demonstrated as novel materials with devisable 3D network structures that are adaptable and inclusive, thus exhibiting great potential for applications in various fields, such as rechargeable batteries, supercapacitors, flexible sensors, and TENGs [49–50]. Therefore, the following sections summarize the most common applications of lignin-based gels in detail.

3.1 Applications in rechargeable batteries

Low-carbon economy has drawn considerable attention and comprehensive interest in an environmentally friendly society, and the use of eco-friendly, biomass-derived biopolymers and other natural materials, instead of traditional petroleum-based materials, has accelerated to circumvent the challenges regarding global warming and climate change [51–53]. Biopolymer-based gels are regarded as competitive candidates for emerging and renewable electrolyte materials owing to their low cost, bio-friendliness, and recyclability, which render them suitable for use as energy storage devices. Rechargeable batteries are among the most important energy storage devices, and tremendous research efforts have been devoted to investigating the three main components of batteries (cathode, electrolyte, and anode) during the charging/discharging process. Generally, alkaline metal ions (e.g., Li^+, Na^+, and K^+) exhibit broad application prospects in battery systems owing to their high reactivity, low standard reduction potential, and high specific capacity. However, several major bottlenecks still exist in the further application of LIBs; these include the scarcity of lithium resources, safety-related problems, and the high cost of battery raw materials [54]. In addition to alkaline metals, multivalent ions (e.g., Mg^{2+}, Ca^{2+}, Zn^{2+}, and Al^{3+}) have also been widely researched to solve the issues of LIBs; however, further efforts are necessary for their

practical uses [55]. The electrolyte, an important part of the battery, is responsible for ionic transportation between the two electrodes. To a large extent, it determines the device properties, including cycling stability, electrochemical stability, potential window, and ionic conductivity [56–57]. The polymer gel electrolytes consist of polymer networks, solvent, and conductive salt dissolved in the solvent. As a substrate in the liquid, swollen, or even solid state, the polymer networks can exist in the solutions or substrates. Gel electrolytes, as solid-state electrolytes, overcome the shortcomings of liquid electrolytes, such as electrolyte leakage and blast, while exhibiting the advantages of high ionic conductivity and ion mobility [58–59]. Therefore, several studies have been conducted to further develop solid-state electrolytes. The next section provides a detailed overview focusing on biopolymer-based gel electrolytes and lignin as a renewable and low-cost bioresource used in recent rechargeable battery technologies.

3.1.1 Applications in LIBs

The development of rechargeable LIBs have been witnessed in recent years, which is due to greater energy density, higher operating voltage, and longer cycle life. The polymers currently utilized in gel polymer electrolytes (GPEs) mostly are difficult to biodegrade [60–62]. Owing to the extensive use of GPEs in commercial LIBs and the undegradability of these polymer substrates, their use can eventually lead to serious "white pollution" in the environment. Consequently, lignin has gained increasing attention for replacing synthetic polymers as the GPE matrix [63].

Gong et al [64] first explored a truly green and environmentally friendly GPE used in LIBs with higher performance. The membrane was obtained as a matrix by simply drying the suspension of lignin in distilled water. Next, a gel-like polymer electrolyte was prepared by pouring the liquid electrolyte onto a dry lignin membrane. With high liquid electrolyte upholding (230 wt%), the lignin-based GPE exhibited an excellent ionic conductivity of 3.73 mS/cm at room temperature. More importantly, the lignin-based GPE was thermally stable up to 250 ℃ with a high Li^+ transference number of 0.85 owing to the strong interactions between the massive phenol hydroxyl units in lignin and anions in lithium salts. However, pure lignin membranes have limited potential applications in several GPEs owing to their poor mechanical properties. To obtain better mechanical properties, Liu et al [65] fabricated a biodegradable composite polymer membrane by synthesizing PVP on the matrix of lignin, and then the corresponding gel polymer electrolyte (LP-GPE) was further prepared by absorbing the liquid electrolyte. The composite lignin/PVP membrane exhibited better mechanical strength compared with the pure lignin membrane. The battery based on the LP-GPE exhibited outstanding capacities, rate and cycle performance; thus, it is sustainable and desirable from an environmentally friendly and economic perspective. Similarly, Uddin et al [66] prepared a lignin/PVA membrane as a separator for LIBs using a simple, low-cost, environmentally friendly, water-based method. The lignin/PVA membrane exhibited excellent electrochemical performance with a good capacity retention of 95.3% and specific capacity of 135 mAh/g after 100 cycles at a current density of 0.2 C, which can be used as separators for LIBs with various different anodes. Wang et al [67] further extended the free-standing lignin-based film by mixing lignin and poly(N-vinylimidazole)-co-poly(PEG methyl ether methacrylate) via a facile blending and casting method. Through the activation of the lignin-based membrane by an organic electrolyte, an electrolyte membrane with high ionic conductivity, superior Li^+ transference number, and wide electrochemical window was obtained. The $LiFePO_4$/lignin-based electrolyte/Li cell exhibited excellent long cycle performance (approximately 150 mAh/g at 1 C for more than 450 cycles) and rate capacity (110 mAh/g at 10 C) at room temperature for wide application in high-performance and high-safety LIBs.

Zinc oxide (ZnO) is considered as the next generation LIB anode material owing to its high theoretical capacity, low potential, abundant resources, and low toxicity. Yu et al [68] prepared a porous carbon

skeleton using lignin and ZnO nanoparticles by a simple solvothermal method. This lignin has a unique structure, excellent stability, and high electrical conductivity for LIBs with a discharge capacity of 898.1 mAh/g at 0.2 C after 110 cycles, which is very close to the theoretical specific capacity of ZnO (978 mAh/g).

3.1.2 Applications in ZIBs

LIBs have the advantage of high energy density and are currently widely used as energy storage devices. However, major bottlenecks still exist in their further application. First, the total production capacity of lithium electricity is limited owing to the scarcity of lithium resources and large amount of lithium consumption. Second, electrolyte battery materials are highly toxic and harm to the environment. Thus, zinc ions are considered as a promising alternative for LIBs because of their low-cost and abundant zinc (Zn) resources. The zinc anode has a low redox potential (0.76 V vs. standard hydrogen electrode) and high mass specific capacity (820 mAh/g); thus, it exhibits great application potential in aqueous electrolytes. Aqueous ZIBs suffer from short-circuit and self-discharge due to leakage of the aqueous electrolyte and instability of the zinc anode (such as dendrite formation and growth, and corrosion) [69]. Therefore, stable and durable gel electrolytes must be developed for Zn-based flexible aqueous batteries. Among the promising biopolymers, lignin-based gels have been employed as green renewable candidates to prepare durable and multifunctional ZIBs. Yuan et al [70] reported a feasible way to design an effective solid-electrolyte interface for advancing the use of Zn anodes in rechargeable ZIBs. Nafion membranes were synthesized by introducing biomass lignin, and they exhibited impressively long stripping/plating cycle life. The benefits of the membranes were further confirmed in β-MnO_2|Zn rechargeable ZIBs. Unfortunately, the structural instability and poor electrical conductivity of MnO_2 impede their further applications. Zhou et al [71] developed an LPC/δ-MnO_2 nanocomposite by hybridizing lignin-derived porous carbon (LPC) with δ-MnO_2 exhibiting enhanced structural stability and improved electrical conductivity through a facile hydrothermal method. This LPC/δ-MnO_2 cathode material benefits from the high electrical conductivity of porous carbon and can offer a high discharge capacity (332.3 mAh/g at 0.2 A/g) and excellent high-rate capability (196.1 mAh/g at 5 A/g). Moreover, the assembled Zn-MnO_2 battery exhibited good long-term cycling stability (82% capacity retention after 1000 cycles). To further improve the cycle performance of ZIBs, Xu et al [72] constructed Al-doped α-MnO_2 coated with lignin (L+Al@α-MnO_2) via a hydrothermal method to stabilize the structure of α-MnO_2. The L+Al@α-MnO_2 cathode achieved a durably higher reversible capacity of 188 mAh/g at 1.5 A/g and good cycle stability with lower fluctuations.

3.2 Applications in supercapacitors

Supercapacitors have gained increasing research attention for application in diverse energy storage and conversion devices because of their advantageous characteristics, such as high-power density (>10000 W/kg), extremely long cycle life (>100000 cycles), and simple structure [73–75]. Based on the mechanisms of energy storage, supercapacitors can be classified into two categories: electrical double-layer capacitors (EDLC) and pseudocapacitors [76]. In general, the positive and negative electrodes constitute a supercapacitor, which is separated by an electrically insulating separator with an ion-conducting electrolyte. Traditional active electrodes are prepared using a uniform mixture of active materials, polymer binders, and conductive additives. However, several factors have limited its development, such as the decrease in volumetric/gravimetric capacitance and mechanical flexibility. These problems have drawn extensive attention and interest in the energy storage field. For portable and wearable electronics, the device must be miniaturized and its flexibility must be improved. Among the various electrode materials for supercapacitors, porous carbonaceous materials have received significant attention, whereas lignin is an abundant aromatic polymer with a carbon content of

nearly 60 wt%. The merits of these porous carbonaceous materials are their interconnected 3D porous network, superior conductivity, and strong mechanical flexibility. Therefore, lignin has been considered as a carbon precursor and electrolyte additive for supercapacitors.

Li et al [77] prepared a metal-free supercapacitor from LS-GH, which had twice the conductivity of a pure graphene gel, primarily owing to the reversible redox charge transfer of the quinone groups in lignin. In addition, a flexible solid-state supercapacitor was rationally designed using symmetric LS-GH electrodes with PVA gel as the electrolyte. The integrated flexible device maintained high capacitive performance (408 F/g at 1 A/g, 75.4% capacitance retention at 20 A/g and 84.0% capacitance retention over 10000 cycles) and exhibited excellent mechanical flexibility. Peng et al [78] assembled a flexible supercapacitor (FSC) using lignosulfonate/single-walled carbon nanotube pressure-sensitive gel as electrodes and cellulose gel as electrolyte separators. The assembled biomass-based FSC exhibited a high specific capacitance (292 F/g) at a current density of 0.5 A/g, excellent rate capability, and outstanding energy density of 17.1 Wh/kg at a power density of 324 W/kg. In addition, the FSC exhibited outstanding electrochemical stability even after 1000 bending cycles. Park et al [79] fabricated all-lignin-based flexible supercapacitors by integrating chemically crosslinked lignin gel electrolytes with electrospun lignin/PAN nanofiber electrodes. The crosslinked networks of lignin-based gel electrolytes exhibited high ionic conductivity and mechanical integrity, whereas the free-standing flexible composite electrode achieved outstanding charge storage capability and kinetics arising from interconnected porous channels. The resulting devices exhibited a high capacitance of 129.23 F/g and capacitance retention of 95% over 10000 cycles, as well as flexibility and durability under diverse bending angles. Moreover, these renewable flexible supercapacitors delivered a maximum energy and power density of 4.49 Wh/kg and 2.63 kW/kg, respectively. Fu et al [80] developed a lignin-derived carbon/zinc oxide (LDC/ZnO) composite prepared through a facile electrostatic self-assembling carbonization process. The prepared LDC/ZnO composites possessed a unique 3D porous framework structure, where ZnO nanoparticles were enchased by LDC nanosheets. The LDC/ZnO composites exhibited high gravimetric capacitance (193 F/g at 0.5 A/g), outstanding durability, and superior rate capability in a two-electrode system using PVA/KOH gel as the electrolyte. Recently, Du et al [81] proposed a controllable and effective strategy to fractionate lignin by only changing the ratio of ethanol/water (*V*/*V*) as a mixture solvent. This gradient extraction method effectively removed the part of lignin with a small molecular weight and branching structure, thus selectively obtaining fractionated lignin with a high molecular weight, narrow polydispersity index, and good linear structure. High-quality lignin-based carbon nanofiber (LCNF) supercapacitors were obtained with a large specific surface area, independent filamentous morphology networks, and excellent electrochemical properties. LCNF-L60 exhibited the best electrochemical performance with a high specific capacitance (405.8 F/g, 3 E) and outstanding energy density (53.7 Wh/kg at 600 W/kg power density, 2 E).

3.3 Applications in flexible sensors

Flexible wearable sensors have gained increased research attention for their application in realizing human movement detection, artificial intelligence, and smart/soft robotics. In particular, conductive gels have been demonstrated as promising sensing materials for accurately detecting human body activities and physiological signals [82–87]. Recently, various biomacromolecule-based gels have made significant progress in the field of wearable electronics. However, the application of lignin-based gels in flexible devices is still limited. The common operating mechanism of gel-based electronics is the conversion of external stimulus signals (such as pressure and strain) into measurable electrical signals (voltage, current, resistance or capacitance) to realize the detection and identification of stimuli [88]. Therefore, conductivity is fundamental for gel electronics. In addition, the gel

requires certain properties, including excellent adhesion, remarkable stretchability, and the ability to resist bacteria and UV irradiation [89]. In fact, lignin contains abundant active groups, which have excellent reactivity and processability [90]. In addition, lignin has excellent natural properties, including UV shielding, biodegradability, antibacterial, and anti-oxidation [91]. Therefore, lignin has excellent application prospects in the development of suitable gel-based electronics.

At present, numerous studies on the application of lignin gels in different sensors according to their different characteristics are ongoing. Inspired by the intercellular material—lignin, which cements lignocellulosic plants, Wang et al [15] fabricated a novel lignin-based double-layer gel with potential applications in numerous fields, including wearable bioelectrodes and self-powered sensors. Feng et al [92] developed a robust and conductive lignin-based nanocomposite organogel with extreme temperature tolerance and long-lasting moisture; they prepared the composite in a binary-solvent system composed of DMSO and water. The PVA-lignin nanoparticle (PVA-LN) organogel was assembled into flexible strain sensors to detect large human motions and subtle physiological signals, even in extreme environments. To simplify the tedious preparation process of gels, Zhao et al [12] assembled the LSN-Fe/PAM gel into flexible sensors to detect various human motions with conformal skin contact and reported high sensitivity (GF = 1.22), linearity (R^2 = 0.995), and excellent reliability with a wide strain range (10%−200%) and stability over 400 stretching cycles. Although considerable efforts have been devoted to developing conductive gels with good performance, the mechanical properties of conductive gels and their adhesiveness toward other materials (such as tissue) need to be further improved. Xiu et al [24] prepared the lignin-based gel comprising (AgNPs) @lignin, PAM, and SA; the resultant lignin hybrid gel exhibited stress, strain, and tearing energy of up to 0.055 MPa, 1000%, and 250 J/m^2, respectively. Furthermore, the gel adhered to different materials with adhesion energy higher than 230 J/m^2. This gel was demonstrated to be an ideal sensing material because it could detect both large-scale motions and small physiological signals, including breathing and pulse.

3.4 Applications in TENGs

To meet the ever-increasing energy consumption and the need for sustainable energy in modern life, the TENG is gaining popularity as a promising energy scavenging technology owing to its advantage of converting ambient mechanical energy into electric energy [93–94]. The TENGs based on coupling contact electrification (CE) and electrostatic induction is superior in harvesting low-frequency and micromechanical energy [95–96]. Various environment-based mechanical energies, including human motion [97–98], rotating motion [99], vibration [100], water drops [101], sea waves [102], and wind [103–104], can be harvested effectively using TENGs. Typically, contact-separation TENGs are composed of a substrate, electrodes, and tribo-positive/negative friction layers. To replace conventional petroleum-based friction materials and reduce their impact on the natural environment, sustainable biomaterials have been used to prepare “green” TENGs. At present, TENGs based on lignin and its derivative gels have gained extensive attention for their application to wearable electronics owing to their attractive mechanical flexibilities and conductive properties. To adapt to extreme environments, Sun et al [39] designed a conductive and transparent organogel in alkaline water-EG binary solvent using a facile and universal self-catalytic system (AL-Cu^{2+}) based on AL macromolecules, which exhibited extreme environment applicability (from −40 to 60 ℃), eligible stretchability (approximately 800% elongation), and robust self-adhesion (approximately 31.4 kPa). The assembled organogel-based TENGs (O-TENGs) achieved a maximum output voltage of 220 V, current of 4.5 pA, and charge of 0.07 pC. After storing in −40 or 60 ℃, the O-TENGs still maintained a stable and competitive signal output, thereby confirming its workable application in a wide temperature range. More promisingly, the electrical output capacity of the O-TENGs could be restored without delay during the continuous flapping process (approximately 6000

cycles), thus suggesting impressive signal stability. By harvesting biomechanical energy using the O-TENGs in extreme environments, the generated electricity can be used directly or stored to drive commercial electronics. In addition, the O-TENGs can be installed on human joints for movement monitoring at temperature as low as −40 ℃.

To optimize the tedious polymerization process and freezing below zero temperature, the research of Feng et al [40] reported that the obtained eutectogels with high stretchability (approximately 450%), transparency (93.5%), and ionic conductivity (8.70 mS/cm) could be retained even in extreme temperatures, as low as −80 ℃. Notably, the eutectogel-assembled TENGs (E-TENGs) exhibited high and stable electrical output performances, including an open-circuit voltage of 105 V, short-circuit current of 0.5 μA, short-circuit charge of 10 nC, and power density up to 53 mW/m^2. The E-TENGs with a self-charging system can easily light up 20 light-emitting diodes (LEDs) and charge capacitors to drive commercial electronics by harvesting energy. Moreover, as a proof of concept, the flexible E-TENGs can serve as a self-powered biomechanical sensor to realize real-time monitoring of various human motions, thus providing a promising and versatile platform for environment-adaptable gel-based TENGs with reliable output performance and self-healing ability. To further develop TENGs with improved power generation, Wang et al [105] fabricated sustainable hybrid lignin-based nanofibers (LNFs) via electrospinning and prepared LNF-based TENGs. The obtained TENGs exhibited enhanced output performance owing to the strong tribo-positivity of lignin and the high specific surface area of the 3D-network LNFs. The optimized output was realized after the trade-off between improved tribo-positivity and formed beads that impact the surface area of LNFs when increasing lignin concentration. Moreover, the correlation between the electrical performance of the LNF-based TENGs and the external pressing force/frequency was explored. Additionally, they demonstrated the practical applications of LNF-based TENGs in efficient energy harvesting and self-powered pressure sensing. Their work showed the feasibility of using LNFs to prepare sustainable TENGs with enhanced performance and provided novel insights into the high-value utilization of lignin.

4 Conclusion and future perspective

Gel materials with 3D crosslinked network structures have attracted considerable attention owing to their unique chemical/physical properties. Lignin is the second most abundant plant polymer that contains plentiful aromatic moieties; moreover, it is the major byproduct in the pulp and paper industry. Introducing lignin and its derivatives into gel networks represents a very promising approach to valorize this natural lignin. Lignin-based gel materials exhibit excellent mechanical, swelling, moisturizing, adhesive, self-healing, anti-oxidation, and photothermal properties. These advantageous features make gel materials promising candidates for use in energy storage and smart sensing systems, such as rechargeable batteries, supercapacitors, flexible sensors, and triboelectric nanogenerators. Unfortunately, the properties and practical applications of lignin-derived high-value materials are still considerably limited owing to some obstacles and challenges.

First, efficient, highly value-added, and high-quality production of lignin is critical for lignocellulose biorefinery; however, the complex and variable structure of lignin macromolecules, poor activity of reactions, and redundancy render difficulty in preparing polymeric materials with stable properties. With increasing research on lignin modification, different solvents for dissolving lignin, and other methods, some progress has been made in the preparation of lignin gels. However, introducing a hydrophilic structure into lignin is still challenging; consequently, preparing lignin composite gel materials with stable properties is challenging.

Second, among various biorenewable polymers used in the field of gels, lignin exhibits tremendous potential to reduce energy consumption/pollution by replacing traditional synthetic materials for biomedical and

various applications owing to its inherent advantages, such as being antioxidant, antibacterial, ecumenically available, abundance as a byproduct of industrial waste, and biodegradable. Nonetheless, studies on the feasibility of functional lignin gels are limited because the introduction of lignin into the gel system can destroy the structure of the gel, thus affecting some properties of the gel.

Third, applications in the area of lignin-based rechargeable batteries and supercapacitors can significantly improve complete high-value utilization of biomass, which can further progress the development of biorefinery. Thus far, only limited lignin sources (primarily alkali lignin, lignosulfonate, and organosolv lignin) have been investigated in these areas. Therefore, the lignin products of various plant types in different biorefinery processes must be extensively investigated, particularly for energy storage applications.

Overall, the progress achieved during the past decades has been significant, although numerous challenges still remain, which must be overcome before realizing the commercial application of lignin in the energy storage field. Major advances have been made in both enhancing the performance and understanding the mechanisms of using lignin-derived materials. We believe that further studies by the research community will lead to more exciting results and, eventually, practical high-value lignin-derived materials.

Acknowledgments

This work was financially supported by grants from the National Natural Science Foundation of China (22108023), NSFC-CONICFT Joint Project (No. 51961125207), Innovation Support Program for High-level Talents of Dalian (Top and Leading Talents) (201913), Liaoning Province "Xingliao Talent Plan" Outstanding Talent Project (XLYC1901004), Scientific Research Startup Funds for High-level Talents of Dalian Polytechnic University (6102072112), Natural Science Foundation of Liaoning Province (2021-BS-227), and the State Key Laboratory of Pulp and Paper Engineering (South China University of Technology, No. 202202).

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