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Polymeric Binder Design for Sustainable Lithium-ion Battery Chemistry

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Abstract: The design of binders plays a pivotal role in achieving enduring high power in lithium-ion batteries (LIBs) and extending their overall lifespan. This review underscores the indispensable characteristics that a binder must possess when utilized in LIBs, considering factors such as electrochemical, thermal, and dispersion stability, compatibility with electrolytes, solubility in solvents, mechanical properties, and conductivity. In the case of anode materials, binders with robust mechanical properties and elasticity are imperative to uphold electrode integrity, particularly in materials experiencing substantial volume changes. For cathode materials, the selection of a binder hinges on the crystal structure of the cathode material. Other vital considerations in binder design encompass cost-effectiveness, adhesion, processability, and environmental friendliness. Incorporating low-cost, eco-friendly, and biodegradable polymers can contribute significantly to sustainable battery development. This review serves as an invaluable resource for comprehending the prerequisites of binder design in high-performance LIBs and offers insights into binder selection for diverse electrode materials. The findings and principles articulated in this review can be extrapolated to other advanced battery systems, charting a course for the development of next-generation batteries characterized by enhanced performance and sustainability.

Keywords: Li-ion battery; polymer binders; anodes; cathodes; bio-polymer; water-soluble binder; ultra-thick electrode

1. Introduction

The advent of lithium-ion batteries (LIBs) has ushered in innovation in the realm of mobile electronic devices, catalyzing a significant industrial transformation extending beyond the core markets of modern industry [1]. The market share and application areas of LIBs are experiencing rapid expansion, with a growing global demand for advanced LIBs characterized by high performance and sustainability, posing a current major challenge in LIBs chemistry [2]. Traditionally, LIBs chemistry has concentrated on active electrode materials to achieve higher energy densities. However, the cathode design based on layered materials is reaching its theoretical limit, and the graphite anode incorporating silicon (Si) faces challenges related to poor cycling stability [2,3]. These technical barriers pose a threat to the advancement of the LIBs industry, potentially leading to a recession in associated industries. Additionally, there is a mounting concern regarding the non-environmentally friendly components in current LIBs systems, particularly fluorine-based polymers, which can have critical impacts on human health and the environment throughout the entire production, manufacturing, and disposal processes [4]. Despite these concerns, the binder market is largely dominated by polyvinylidene fluoride (PVdF) due to its well-balanced material properties required in LIBs and their fabrication processes [5]. A novel research approach has recently been focused on substituting polymer binders for both the anode and cathode due to inadequacies in electrochemical performance and environmental considerations [6,7].

Overcoming the theoretical capacity limitation of active cathode materials involves creating a thicker cathode, which can double the energy density of LIBs by reducing the loading contents of other inactive cell components with electrode thickening [8-10]. Additionally, addressing the insufficient capacity of the graphite anode (~372 mA h g^{-1}) involves incorporating high-capacity Si, with the effectiveness of these improvements relying heavily on the performance of binder materials [11,12]. For thick cathodes, issues such as electrode cracking and flaking during the fabrication process, as well as insufficient ionic transfer rates and electrode stability during repetitive cycling, must be addressed through the design of high-performance polymer binders [13-17]. In the case of composite anodes, the suppression of large volume expansion and the continuous formation of solid-electrolyte-interface (SEI) byproducts necessitate the introduction of functional polymer binders. Numerous case studies underscore the importance of polymer binders and their positive roles in thick cathodes and composite anodes [18].

The design of new polymer binders also presents an avenue toward sustainable LIBs chemistry. The conventional slurry-based electrode fabrication process, which utilizes toxic organic solvents and generates volatile organic compounds, can be mitigated by employing water-soluble polymer binders or developing solvent-free binder materials based on a drying process [4,7,19,20]. Additionally, some bio-compatible and bio-degradable polymer binders exhibit high potential as functional binders for thick cathodes and composite anodes [14,15]. This review centers on the fundamental requirements for sustainable polymer binders in both conventional electrodes and next-generation thick electrode systems in LIBs.

2. Essential properties of binders

2.1. Stability

2.1.1. Thermal Stability

Thermal stability constitutes a crucial property in polymer binders designed for LIBs [21]. Despite the typical operating temperature range remaining below 55 °C, polymer binders may be exposed to higher temperatures exceeding 100 °C during the fabrication process and unexpected increases in operational temperature [22]. Consequently, a high level of thermal stability is imperative across a broad temperature spectrum. In contrast to conventional PVdF binders, which tend to loosen or weaken under high temperatures, diminishing the mechanical strength needed to bind together the active material, conducting agent, and current collector, most cross-linked and/or cyclic polymers exhibit elevated thermal stabilities (Figure 1a,b) [23]. For instance, Zhang et al. reported that polyacrylic acid (PAA) cross-linked with hydroxyl propyl polyrotaxane demonstrates notable thermal stability for Si-based anodes. Polyimide (PI) stands out as a representative cyclic binder with high thermal stability, and various PI-based binders have been proposed (Figure 1c,d) [24]. Notably, fluorinated PI has been suggested as a binder with high thermal stability. The incorporation of heterocyclic imide rings and fluorine functional groups on the backbone of PI enhances its thermal stability [25]. Furthermore, Zhang et al. conducted a study comparing different binders for their thermal diffusivity and thermal expansion. They found that the PAA binder exhibits the highest thermal diffusivity among the tested binders, with a value of 3.1×10^{-3} cm^2 s^{-1}, surpassing the values (1.0×10^{-3} and 9.1×10^{-4} cm^2 s^{-1}, respectively) of carboxymethyl cellulose (CMC) and PVdF. The heightened thermal diffusivity of the PAA binder facilitates faster heat transfer to the electrode exterior, aiding in the dissipation of heat generated during battery operation and thereby enhancing battery stability [24]. Moreover, in the mixed state with active materials and conductive agents, the intra- and inter-molecular interactions between polymer binders and other components can influence their secondary structures, leading to a significant change in thermal stability [26]. Thus, the thermal stabilities of polymer binders are intricately linked not only to their primary and secondary structures but also to their kinetic motion, highlighting a need for systematic studies on the effects of key parameters on thermal stabilities.

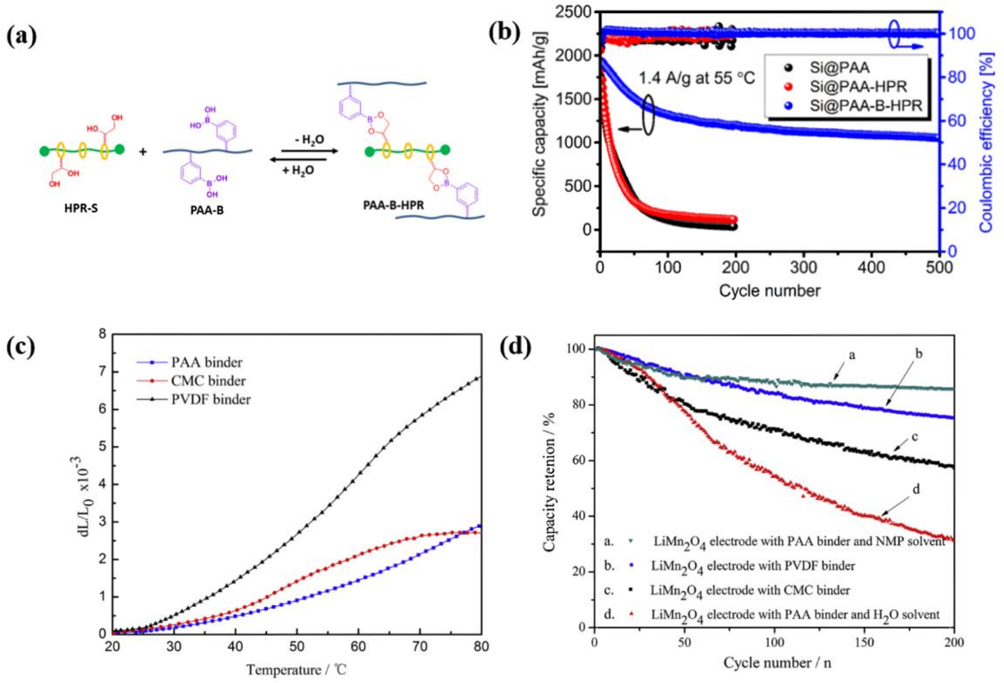

Figure 1. (a) Schematic Illustration of the Synthesis of PAA cross-linked by hydroxypropylpolyrotaxanes (PAA-B-HPR) (b) Cycling performance of Si anodes at 1.4 A g^{-1} under 55 °C. Reprinted with permission from reference [23], 2021, American Chemical Society. (c) Thermal expansion rate curves of PAA, PVdF and CMC binders at the temperature range from 20 C to 75 C. (d) Discharge cycle performances of LMO cathodes with the four different binder systems at the rate of 1 C between 3 V and 4.3 V at 25 C. Reprinted with permission from reference [24], 2014, Elsevier B.V.

2.1.2. Electrochemical Stability

Polymer binders undergo direct reduction or oxidation at low or high potentials, respectively, during the charge/discharge cycling of LIBs. Additionally, the decomposition of electrolytes on active surfaces can generate active radicals that may react with polymer binders, resulting in the decomposition of binder materials [5, 27]. While conventional PVdF exhibits strong and symmetric C–F$_2$ functional groups in a polyolefin structure, providing relatively high oxidation/reduction stabilities, its halogen bonding group lacks sufficient intermolecular interaction with active materials or conductive agents on their surfaces [28,29]. This deficiency leads to poor passivation behaviors for the active surfaces, causing significant electrolyte decomposition on both cathodes and anodes and contributing to poor cycling stabilities. To mitigate this issue, carboxyl-rich polymer (CRP) binders have been employed in conjunction with typical polyethylene oxide (PEO) and PVdF binders (Figure 2a) [30-32]. The CRP fully coats the active cathode surfaces, facilitating the passivation of electrode surfaces. A similar passivation strategy is applied using lithium polyacrylate (LiPAA) binder. Additionally, polymer binders with anti-oxidation properties are introduced onto active cathode surfaces through in situ cross-linking reactions [33]. A natural sericin binder has also demonstrated high voltage stability [34]. On the anode side, more severe electrolyte decomposition occurs due to the substantial volume expansion of Si during charge/discharge cycling [35]. Consequently, polymer binders with multiple hydrogen bonding sites and high stretchability have been designed to fully coat active anode materials and accommodate the large volume change [30].

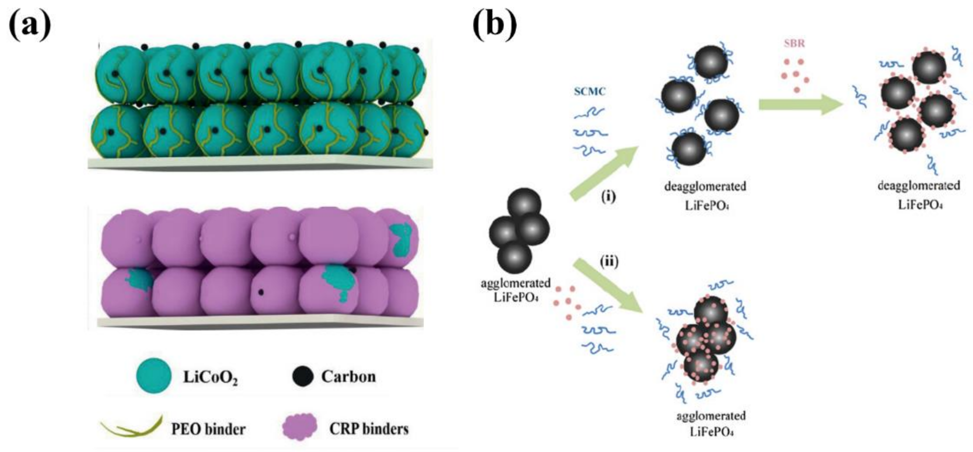

Figure 2. (a) Schematic diagrams for the binding capability/mechanism of PEO and CRP (carboxyl-rich polymer) binders. Reprinted with permission from reference [30], 2020, Wiley-VCH GmbH. (b) Diagrams showing dispersion mechanisms of $LiFePO_4$ in an aqueous suspension with the presence of SBR and sodium carboxymethyl cellulose added via the sequence of (i) sequenced adding and (ii) simultaneous adding process. Reprinted with permission from reference [47], 2012, Elsevier B.V.

2.1.3. Chemical stability

Chemical stability is a critical requirement for polymer binders to prevent corrosion or decomposition under the operating conditions of a battery. Even in the case of PVdF binders known for their high chemical stability, an exothermic reaction between the C–F bond and lithiated carbon can lead to the formation of LiF [28,29]. Additionally, LiOH generated by residual impurities, such as water, can react with PVdF to produce LiF [36]. While by-products resulting from the chemical instability of binders can be utilized as components of the SEI layer on the electrode surface, excessive accumulation can reduce Coulombic efficiency (CE) and contribute to poor cycling stability through electrode collapse [37]. In certain cases, the chemical reactivity of binders has been harnessed for electrode fabrication. Binder precursors are mixed with active electrode materials, and in situ polymerization is initiated through various methods such as ultraviolet (UV) irradiation or heating [38-40]. This in situ polymerization enhances the adhesion properties of binders towards active materials through a mechanical interlocking effect or the formation of robust crosslinked networks [38-40].

The solubility of binders in the electrolyte also significantly affects battery performance. PVdF, for example, exhibits swelling in organic solvents like ethylene carbonate, diethyl carbonate, and dimethyl carbonate [41]. While the swelling phenomenon of binders in electrolytes can contribute to the improvement of ionic conductivity across binders, excessively high solubility that leads to the dissolution of binders in the electrolyte may have a detrimental effect on the integrity of the electrode [42].

2.1.4. Dispersion Stability

The dispersion state of electrode materials, including the polymer binder in the slurry, plays a crucial role in ensuring the uniformity of electrode components. An uneven coating of active material, conductive additives, and polymer binder can have adverse effects on electron/ion conductivity, potentially leading to local current overloads and increased charge transfer resistances (R_{ct}) [43,44]. In the slurry process, the polymer binder serves as a dispersant to stably distribute active materials and conductive additives [45]. The amphiphilic properties of the binder and its strong interactions with other components are key factors in achieving the proper slurry viscosity and uniform coating.

Studies by Gordon et al. explored the impact of CMC and a fluorine/acrylate hybrid polymer (FAHP) on the dispersion of $LiFePO_4$ (LFP) and carbon black particles in an aqueous slurry. CMC acted as a dispersant, influencing slurry viscosity to achieve effective particle dispersion in the manufacturing process, while FAHP binder improved adhesion to the current collector [46]. Li et al. delved into the interaction between LFP, carbon-based conductive agents, and CMC/styrene–butadiene (SBR) binder in an aqueous slurry. Similar to Gordon et al.'s findings, CMC played a role as a dispersant for LFP particles in the aqueous system, with LFP preferring interaction with SBR, resulting in complementary binding behaviors. The enhanced dispersibility of LFP particles with CMC was attributed to the electrostatic repulsion induced by increased negative charge density, with electrostatic force serving as a crucial factor for achieving dispersion stability of electrode materials (Figure 2b) [47].

Furthermore, slurry properties and preparation techniques have a notable impact on electrode morphology, influencing electrochemical performances. Research by Kraytsberg et al. highlighted the relationship between shear stress applied by a mixer and cluster size in slurries. Notably, specific slurry techniques can modify the structure of electrode components, leading to diverse electrochemical performances [48]. Consequently, changes in binder material, solvent systems, or specific slurry techniques can affect the dispersion properties of electrode materials in the slurry. Thus, a tailored engineering process is essential to establish an optimal dispersion state for electrode fabrication.

2.2. Mechanical Properties

The mechanical properties of binders, encompassing factors such as adhesive force, tensile strength, elasticity, and flexibility, are crucial considerations for their performance in LIBs. These properties directly impact the electrode fabrication process and the cycle life of LIBs, making it essential to select binders with specific mechanical attributes for the optimization of LIBs performance [49].

Ideally, a binder should possess high adhesion, mechanical strength, elasticity, and flexibility. However, achieving a balance among these properties is challenging, particularly in the wet state under electrolyte soaking [50]. Additionally, the pursuit of high mechanical properties in polymers often involves promoting high intramolecular interaction or increasing crystallinity [51]. While these characteristics enhance the mechanical strength of the polymer, they may have a downside-deteriorating the intermolecular interactions between the polymer and active material or conductive additive [52]. This, in turn, can lead to adverse effects on electrode stability. Therefore, striking the right balance between desirable mechanical properties and maintaining effective interactions with other components is a critical aspect of binder selection for LIBs [53]. The optimization of these properties ensures not only the successful fabrication of electrodes but also contributes to the overall stability and performance of LIBs throughout their cycle life.

2.2.1. Adhesion

Adhesive force is a critical parameter extensively used to assess the performance of binders due to its significant influence on the electrochemical performance of LIBs [44,50,54-56]. Binders with high adhesive force play a pivotal role in maintaining robust contact between the components of electrodes, even amidst the volume expansion and contraction inherent in charge/discharge cycles [57-61]. Several theories have been proposed to elucidate the mechanism of binder adhesion, including mechanical, chemical, and thermodynamic models [5,62]. The mechanical mechanism involves physical interlocking following the diffusion or penetration of the binder into the irregular or porous surface of electrode materials. The effectiveness of mechanical interlocking is highly contingent on the surface roughness of the electrode materials [63]. Thermodynamic models describe adhesion through surface adsorption via van der Waals forces between two materials, without forming chemical bonds [52]. The chemical model explains adhesion by the formation of surface chemical bonds, such as ionic, covalent, and hydrogen bonds [64,65]. To comprehensively describe the adhesion of polymer binders, these various mechanisms must be considered in combination under different circumstances. In general, the adhesion of low-polarity polymers, such as PVdF without nitrogen- and oxygen-containing functional groups, is primarily governed by mechanical interlocking and van der Waals forces [66]. On the other hand, polymers like CMC, PAA, and alginate, which form robust chemical bonds such as hydrogen or ionic bonds, have demonstrated higher adhesive force compared to PVdF [6,64]. The interaction between the binder and the active material can also impact the bonding state during wetting and drying processes. Techniques such as atomic force microscopy have been employed to study these interactions in detail [67]. Understanding and optimizing adhesive forces are crucial for enhancing the overall performance and durability of LIBs.

2.2.2. Tensile strength

The tensile strength of polymer binder-based electrode materials is indicative of their maximum force resistance against mechanical failure and is closely tied to their structural stability facilitated by the polymer binder [68]. The tensile strength of polymers is significantly influenced by their chemical structure, molecular weight, and crystallinity. Generally, higher molecular weight, crystallinity, crosslinking density, or intermolecular interaction contributes to the higher tensile strength of polymers [64]. In the context of LIBs, binders with high tensile strength offer advantages as they can endure repeated cycles of mechanical stress without undergoing deformation or failure [49]. This characteristic is particularly beneficial for polymer binders with high tensile strength, such as alginates and PI, which can mitigate the pulverization of Si-based anodes experiencing significant volume changes during battery operation [69-72]. However, it's important to note that polymers with high tensile strength may exhibit drawbacks, such as low ionic conductivity, which can diminish battery performance, or poor solubility, which can impede electrode processability. Striking a balance between tensile strength and other critical properties is essential for designing polymer binders that enhance the mechanical robustness of LIBs electrodes while maintaining overall electrochemical performance [73-76].

2.2.3. Flexibility and elasticity

Elasticity and flexibility are crucial properties of binders, playing a significant role in maintaining a stable electrode structure during the volume changes that occur during battery operation [77,78]. Elasticity refers to a material's ability to return to its original state after deformation, while flexibility describes a material's capacity to bend without breaking. Binders with high elasticity and flexibility, typically characterized by polymers with low glass transition temperatures (T_g), can effectively minimize electrode deformation caused by volume changes during charging and discharging cycles [79,80]. Physical or chemical crosslinking is a strategy that can dramatically enhance the elasticity of polymers, enabling them to endure mechanical deformation. For instance, physical crosslinking achieved through hydrogen bonding, pi-pi interactions, or host-guest interactions results in a three-dimensional network structure of polymer binders when mixed with active materials, leading to significant mechanical robustness [81-84]. Chemical crosslinking, involving the formation of covalent bonds (e.g., ester bonds between PAA and poly(vinyl alcohol)(PVA)) or ionic bonds (e.g., alginate with calcium ions), has been shown to enhance the cycling performance of LIBs [85-88]. These strategies contribute to improving the elasticity and flexibility of polymer binders, ensuring the structural integrity of electrodes over repeated charge and discharge cycles in LIBs.

2.3. Ionic Conductivity

The ion conductivity of a binder is a critical factor influencing the electrochemical performance of LIBs. When the binder uniformly and densely coats the active material, the impact of ion conductivity on battery performance increases due to the enhanced probability of ion transport through the binders [89]. Particularly for active materials with low ionic and electronic conductivity, such as olivine LFP, the introduction of polymer binders with high ionic conductivity can significantly enhance battery cycling performance [90,91]. In general, the ionic conductivity of polymers is closely associated with the T_g. Below T_g, polymers may exhibit poor ionic conductivity due to limited chain mobility. Additionally, polymers with higher crystallinity generally show low ionic conductivity due to their reduced free volume for ion transport [79-80,92-95]. Consequently, strategies such as lowering T_g or crystallinity are employed to enhance the ionic conductivity of polymers.

The affinity of the binder with the electrolyte and the wetting amount of the electrolyte are also crucial parameters influencing the ion conductivity of the binder [43,44]. While a higher wetting amount of the electrolyte can be advantageous for lithium-ion transport, excessive wetting can degrade the adhesive performance of the binder and the mechanical strength of the electrode [89]. Recent research has focused on improving the ion conductivity of binders to achieve high-performance LIBs. For instance, the use of a binder system involving poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) crosslinked by PEO with polyethyleneimine coating has shown significantly higher electronic conductivity (~895 S cm^{-1}) and ionic diffusion coefficient (4.0×10^{-8} cm^2 s^{-1}) compared to traditional binder systems like CMC/acetylene black (~3 S cm^{-1} of electronic conductivity and 2.8×10^{-9} cm^2 s^{-1} of ionic diffusion coefficient) for Si-based anode [43]. Measurement techniques such as galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) can be employed to determine the ion transport characteristics of the binder. GITT provides information about the lithium-ion diffusion coefficient, a crucial parameter for understanding the ion transport behavior of the binder. Higher lithium-ion diffusion coefficients indicate faster ion transport, contributing to better battery performance [96]. EIS analysis is valuable for evaluating the ion transport characteristics of the binder by measuring the resistance of the electrodes [90,97]. The measurement of electrode resistance using EIS enables the indirect identification of changes in lithium-ion movement during charge and discharge processes. The ohmic resistance of the electrode, primarily influenced by the binder, may increase due to binder degradation or alterations in the electrode structure. Film resistance can also arise from the repetitive regeneration of the SEI layer, resulting in an elevation of R_{ct} and deterioration in battery performance. In summary, a comprehensive analysis of the ion transport characteristics of the binder is crucial for understanding its role in the electrochemical performance of the battery [89,91]. Achieving high ion conductivity and diffusion coefficient in the binder can contribute to improved battery performance, but it is equally important to balance other factors such as adhesive performance and structural stability of the electrode [98].

3. Typical Binders

3.1. Anode Binders

3.1.1. PVdF

PVdF is a widely used polymer binder in secondary batteries, known for its thermal and electrochemical stability, making it suitable for various battery applications. However, when used as a binder for Si-based electrodes, PVdF does have certain limitations. One limitation of PVdF stems from its nonfunctional linear chain structure, which can result in low adhesive force and weak interaction with Si-based materials, potentially leading to degradation in battery performance [53]. Additionally, PVdF exhibits low mechanical characteristics and flexibility, making it susceptible to the breakage of adhesive bonds during the volume changes occurring during the charging and discharging of Si-based electrodes, further impacting battery performance [77,78,89]. The non-reactive C-F structure of PVdF may also result in weak interactions between electrode materials, hindering the formation of conducting channels [99,100]. The high viscosity of PVdF in solvents like *N*-methyl-2-pyrrolidone (NMP) used in the slurry process can lead to accumulation with the active material, potentially blocking charge-transfer pathways and degrading charge-transfer rates. However, researchers have demonstrated that adjusting the molecular weight of PVdF can influence its performance as a binder. Increasing the molecular weight of PVdF can lead to higher binding strength and improved long-term cycling performance of the battery electrode [100].

Efforts have also been made to address the limitations of PVdF by developing composite materials. For example, synthesizing PVdF with other materials, such as lithium lanthanum titanate, has been explored to achieve improved conductivity for solid-state electrolytes [101]. In the broader context, it is crucial to carefully consider the characteristics of the polymer binder and select an appropriate one based on the specific requirements of the battery electrode and electrolyte system. Additionally, researchers are actively working on addressing environmental concerns associated with the use of solvents like NMP in the slurry process and exploring more sustainable alternatives [102]. Understanding both the properties and limitations of PVdF, as well as other binder materials, is essential for designing high-performance batteries with improved electrochemical performance and environmental sustainability [6]. Ongoing research and development in this area will contribute to the advancement of battery technologies.

3.1.2. PAA

PAA has emerged as a promising alternative binder to PVdF, particularly for electrodes experiencing substantial volume expansion, such as Si-based anodes [42]. PAA boasts several advantages, including its applicability in a broad voltage range from graphite electrodes to Si anodes and its solubility in both water and ethanol. This solubility feature reduces the reliance on toxic solvents like NMP, contributing to its environmental friendliness [102]. The functional group of PAA contains carboxyl groups, imparting robust mechanical properties and facilitating interaction with Si particles through non-covalent bonding. This characteristic makes PAA well-suited for binding Si-based materials, particularly in scenarios where materials with severe volume expansion, like Si anodes, are employed [103]. PAA has demonstrated versatility as a binder, finding application in replacing PVdF for alloy or conversion materials in batteries. To enhance the performance of PAA as a binder, ongoing research has explored innovative approaches [104]. For instance, Song's group developed an interpenetrating gel polymer binder by creating a chemical structure bridge between PAA and PVA around Si particles. This network polymer binder exhibited exceptional cycle stability, showcasing a capacity retention of 1,663 mA h g^{-1} after 300 cycles and a high CE of 99.3%. These advancements underscore the potential of PAA as a high-performance binder for Si anodes, offering solutions to some of the limitations associated with PVdF [86].

3.1.3. CMC/SBR

CMC is a linear polymer derivative of natural cellulose extensively investigated as a binder for Si electrodes across various industries [105,106]. CMC, being water-soluble, has the capability to establish robust hydrogen and covalent bonds with surfaces containing hydroxyl groups, such as Si. This unique property enables CMC to maintain high mechanical integrity within the battery cell without undergoing expansion in liquid electrolytes. In terms of solubility, hardness, and elastic modulus in electrolyte solvents, CMC exhibits behavior akin to PAA [86]. To enhance the flexibility of CMC as a binder, researchers have explored combinations with other polymers, such as SBR. The utilization of a CMC/SBR mixed binder has demonstrated an increase in maximum elongation, leading to improved adhesion strength. Lee's findings indicate that, while the tensile strength and modulus of the CMC/SBR binder may be slightly lower compared to PVdF, the maximum elongation and adhesive force are elevated. This mitigated the volume expansion of Si, resulting in significantly enhanced cycle performance, highlighting the benefits of employing CMC as a binder for Si electrodes [107]. Further studies, such as those conducted by He et al., have extended the application of CMC/SBR as an efficient binder for lithium-sulfur (Li-S) batteries, showcasing improved cycling performance with higher capacity retention compared to PVdF binder. The electrode utilizing the CMC/SBR binder exhibited a capacity retention of 580 mA h g^{-1} after 60 cycles, outperforming the 370 mA h g^{-1} retention achieved with PVdF binder. Additionally, it was noted that the anode using CMC/SBR exhibited lower resistance and charge transfer impedance, contributing to a more stable interface structure and an efficient electron transport network [108]. However, a challenge associated with binders like PAA and CMC/SBR is the potential uneven coverage of the active material on the electrode surface, leading to localized mechanical stress and potential particle breakage [51]. Therefore, achieving uniform adhesion of the binder remains crucial, and ongoing research is dedicated to developing strategies to address this issue.

3.1.4. Binders for Si/Graphite (Si/G) Anodes

The utilization of nickel-rich materials as cathodes in LIBs has garnered attention due to their high energy density and cost-effectiveness compared to cobalt-based counterparts [4]. However, these nickel-rich cathodes often encounter challenges such as capacity retention issues and the development of an unstable cathode-electrolyte interface layer [109-111]. To address these concerns, extensive research is underway to enhance the performance of nickel-rich cathodes [112]. In parallel, researchers are exploring alternative anode materials to replace graphite, which has a limited theoretical capacity of 370 mA h g^{-1} [113-116]. Si has emerged as a promising anode material due to its abundance, low operating voltage (~0.2 V vs Li/Li^{+}), and high theoretical capacity (3,572 mA h g^{-1}) [117,118]. Nevertheless, However, Si undergoes significant volume expansion (approximately 300%) during the intercalation/deintercalation process of lithium ions, in stark contrast to the volume expansion of graphite (around 10%). The substantial volume expansion of Si during cycling brings about structural alterations in the electrode, leading to reduced adhesive force between the substrate and active material, electrode peeling, and the formation of an unstable SEI layer [77,78]. These challenges may result in capacity decay, decreased CE, and heightened internal resistance of the electrode. Consequently, for Si to be successfully commercialized as a high-capacity anode material, it is imperative to restrict volume expansion to within 10% to minimize structural transformations, with a compression density of approximately 1.65 g cm^{-3}. Moreover, the Si anode should exhibit a performance of ≥500 mA h g^{-1}, achieve ~99% CE, and maintain ≥80% capacity retention even after 500 cycles to meet the criteria for large-scale energy storage systems [119].

Recently, both industry and academia have directed their research efforts toward the design of Si anodes, employing a combination of Si and graphite along with suitable binders and electrolytes. This strategy aims to enhance battery performance and tackle the inherent challenges associated with Si anodes [121-124]. The anticipated outcome of this approach is the development of LIBs characterized by high performance, cost-effectiveness, and safety, making them well-suited for large-scale energy storage applications.

Table 1. The electrochemical properties of various Si/G electrodes according to the Si/G ratio, and different types of binders and electrolytes.

Si/G ratio	Binder	Electrolyte	CE (%)	Cycle	Ref.
Si/G (10:90)	Ur	1M $LiPF_6$ EC/EMC/DMC (1:1:1) (3wt% FEC)	99.6	400	[73]
Si/G (2.5:97.5)	PAA-VTEO	1M $LiPF_6$ EC/DMC (1:1) (3wt% FEC)	89.4	477	[74]
Si/G (50:50)	reDNA/ALG	1M $LiPF_6$ EC/DEC (1:1) (5wt% FEC)	99.1~99.6	300	[125]
Si/G (19:57)	*c*-Alg-*g*-PAAm	1.15M $LiPF_6$ EC/DEC/DMC (3:5:2) (5wt% FEC, 2wt% VC, 5wt% $LiBF_4$)	72.8	100	[126]
Si/G (15:73)	SSC4SA	1M $LiPF_6$ EC/DEC/FEC (1:1:0.2)	99	200	[45]

Si/G (15:73)	GC-g-LiPAA	1.2M $LiPF_6$ EC/DMC (3:7) (10wt% FEC)	90.3	100	[76]
Si/G (19:57)	Alg-g-PAMAT	1.5M $LiPF_6$ EC/DEC/DMC (3:5:2) (5wt% FEC, 2wt% VC, 0.4wt% $LiBF_4$)	56~62 (capacity retention)	200	[127]
Si/G (43:43)	PAA	1M $LiPF_6$ DMC/FEC (7:3)	88~91	40	[99]
Si/G (30:50)	Li-PGlu	1M $LiPF_6$ EC/DMC (1:1) (2v% FEC)	73	30	[100]
Si/G (15:73)	CMC/SBR=4:6(w/w)	1.2M $LiPF_6$ EC/DEC (3:7) (30wt% FEC)	99.8~99.9	400	[128]
Si/G (15:73)	LiPAA	1.2M $LiPF_6$ EC/EMC (3:7) (10wt% FEC)	91	50	[129]
Si/G (20:65)	LiPAA	1M $LiPF_6$ EC/DEC/FEC(3:6:1)	79.1	50	[130]

Table 1 provides a summary of the electrochemical properties of Si/G composite materials, detailing the Si/G ratio, binder utilized, and electrolyte [75,73,74,76,99,100,125-130]. The data indicates that an increase in Si content leads to higher capacity but lower CE and cycle retention. However, it is observed that the currently employed commercial binders and electrolytes may not be optimal for Si/G anodes, lacking the necessary stability during cycling for viable commercialization. This underscores the necessity for further research and development endeavors aimed at identifying and optimizing suitable binders and electrolytes tailored specifically for Si/G composite anodes. This may involve the creation of novel binders or electrolytes designed to address the challenges associated with Si-based anodes, such as significant volume changes during cycling and the formation of an unstable SEI layer [105,106]. The quest for appropriate binders and electrolytes capable of ensuring stable cycling performance for Si/G composite anodes is pivotal for the successful commercialization of LIBs featuring Si-based anode materials. Continued research efforts in this domain can significantly contribute to the progress of Si/G composite anodes, addressing the challenges inherent in Si-based anode materials [97,131]. Ultimately, this research may bring us closer to the realization of LIBs characterized by high capacity, low cost, and suitability for large-scale energy storage applications [130]. The challenges associated with the volume changes during lithiation and delithiation of Si and graphite in a Si/G composite anode can indeed impact the stability and cycling performance of LIBs. The substantial volume expansion of Si and the moderate volume expansion of graphite can induce mechanical stress, cracks, and the loss of electrical contact between active materials and conducting agents [73,75,125,126,132]. These issues result in elevated internal resistance and irreversible cycling. Additionally, the repeated cracking and regeneration of the SEI layer during cycling may lead to the formation of an unstable and thick SEI, further compromising the battery's performance and capacity. This phenomenon can also contribute to the consumption of lithium ions, leading to a gradual depletion of the usable electrolyte over time. To tackle these challenges, researchers are actively exploring the use of different binder materials with diverse polymer characteristics in Si/G composite anodes [76,99,100,127-129]. The binder assumes a crucial role in upholding the structural integrity of the composite electrode, mitigating volume changes, and enhancing the cycling stability of the battery [77,78]. The meticulous selection and optimization of binder materials aim to minimize the stress and cracks induced by volume changes, enhance the electrical contact between active materials and conducting agents, and facilitate the formation of a stable and thin SEI layer [119,120]. This strategic approach can alleviate the issues of irreversible cycling and capacity fading linked with Si/G composite anodes, paving the way for stable cycling performance, even with higher Si content (up to 10%) in real-world commercial applications. The ongoing development of advanced binder materials and their effective integration into Si/G composite anodes remains a dynamic area of research [122,123]. Continued progress in this direction holds the potential to usher in the commercialization of high-performance LIBs featuring Si-based anode materials, effectively addressing the challenges associated with volume changes and SEI formation.

Mochizuki et al. and Wang et al. conducted research focusing on enhancing the performance of Si/G composite electrodes in LIBs using different binder materials [100,133]. In their study, Mochizuki et al. employed lithium poly-γ-glutamate (Li-PGlu) and four natural polymers as binders in Si/G composite electrodes with a mass loading of 1 mg cm^{-2} [100]. The initial reversible capacities achieved ranged from 800 to 1200 mA h g^{-1} (1.3 mA h cm^{-2}), with a maximum CE of 51% to 79%. Li-PGlu emerged as an effective binder for suppressing electrolyte decomposition, providing uniform coverage of the active material surface. The binder was intentionally designed with a robust structure featuring polarized functional groups (-COOH and -NH-CO) (Figure 3a-e), promoting smooth lithium-ion movement in the electrolyte/electrode interface through coordination functional effects of oxygen and nitrogen atoms. Surface chemical and binding characteristics were confirmed using hard X-ray photoelectron spectroscopy (XPS) in Figure 3f-h. On the other hand, Luo et al. utilized UV-cured urushiol monomers as binders in a Si/G composite electrode with a Si/G ratio of 90:10 and a mass loading of 0.8 mg cm^{-2} (Figure 4) [73]. The resulting electrode demonstrated a capacity of 603.3 mA h g^{-1} and excellent capacity retention of 96.1% even after 400 cycles. The binder facilitated Si-O-C bond formation on the surface of Si powder, and strong interaction between the surface of Si particles and phenolic hydroxyl groups improved adhesion, limiting volume change and mitigating capacity loss and electrode degradation during volume expansion [119,120]. In another approach, Liu et al. synthesized a functional aqueous binder, PAA-vinyl triethoxy silane (VTEO), using lithium acrylate and VTEO. This binder was utilized in a composite electrode with a Si/G ratio of 97:3 and a mass loading of 0.8 mg cm^{-2} [74]. The PAA-VTEO binder exhibited a specific capacity of 470 mA h g^{-1} and high cycle retention of 99% after 100 cycles. XPS analysis confirmed the formation of a strong 3D cross-linked network between the binder and silanol groups on the surface of Si nanoparticles, resulting in the formation of Si-OH groups and Si-O-Si covalent bonds. This highlighted the solid mechanical and binding properties of the PAA-VTEO binder, effectively mitigating volume expansion and enhancing electrochemical cycling stability.

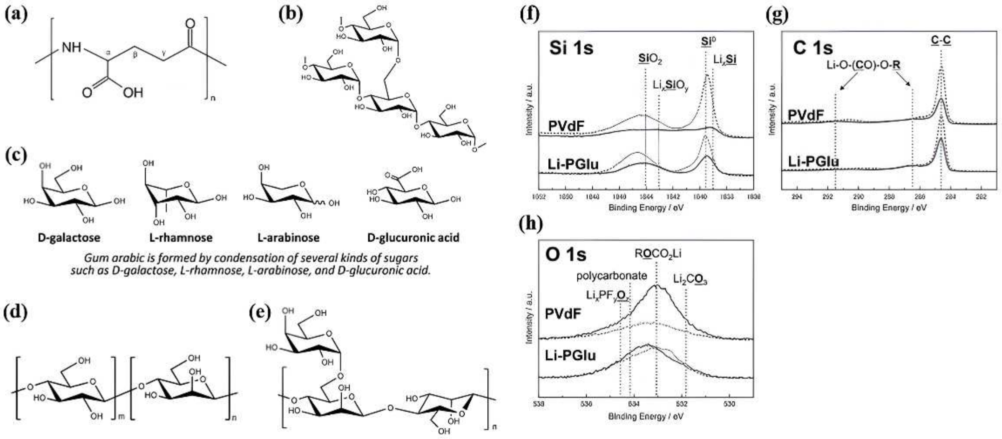

Figure 3. Molecular structures of natural polymers or the monomers: (a) poly-y-glutamic acid, (b) amylopectin, (c) constituent monomers of gum arabic: d-galactose, L-rhamnose, L-arabinose, and D-glucuronic acid, (d) guar gum, and (e) glucomannan. HAXPES results of (f) Si 1s, (g) C 1s, (h) O 1s

core level spectra for Si/G composite electrodes with PVdF and Li-PGlu binders. Reprinted with permission from reference [100], 2017, American Chemical Society.

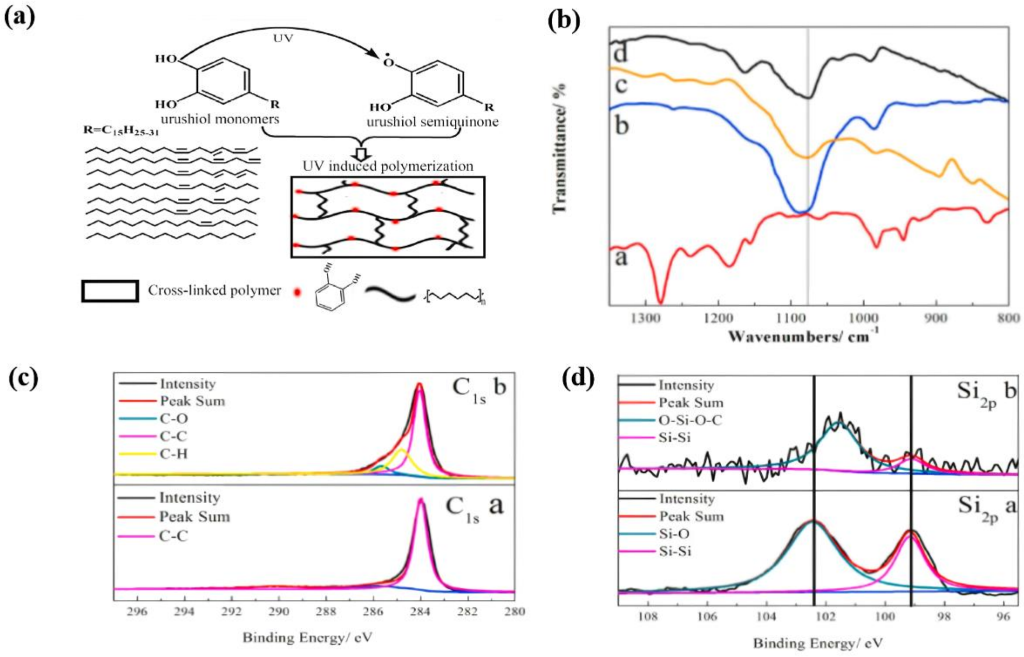

Figure 4. (a) Structure of the urushiol and its UV curing mechanism, (b) FT-IR spectra for the expanded Si–O region (800–1300 cm^{-1}) of urushiol monomers, (c,d) XPS Si 2p and C 1s spectra for the Si/G powders and the powders scraped from the electrode with the Ur Binder. Reprinted with permission from reference [73], 2018, Elsevier.

Each of these studies underscores the crucial role of binder materials in enhancing the performance and stability of Si/G composite electrodes in LIBs [119]. Binders possessing robust mechanical strength, elasticity, and effective adhesion to both Si and graphite particles are essential to suppress the volume expansion of Si during cycling and maintain the structural integrity of the electrode [73,74,125]. The careful selection and design of binders, considering appropriate functional groups and chemical characteristics, can significantly influence the electrochemical performance of composite electrodes. This impact extends to key aspects such as capacity retention, cycling stability, and the adhesion between active materials and conducting agents [99,100,127,128]. Continued research and optimization of binder materials hold the promise of advancing the development of high-performance Si/G composite electrodes for the batteries of the future. It's crucial to recognize that the interaction not only with Si but also with graphite plays a pivotal role in determining the overall performance of Si/G composite electrodes [77,78]. Further exploration is necessary to gain a comprehensive understanding of the intricate interactions between different binders and both Si and graphite particles. This understanding will shed light on their effects on the mechanical and electrochemical properties of composite electrodes [97,131,134-136]. Through meticulous optimization of binder selection and properties, the cycle stability and overall performance of Si/G composite electrodes in advanced LIBs can be improved.

3.2. Cathode binders

While extensive research has concentrated on the development of high-performance cathode materials for LIBs, the significance of the binder in the cathode formulation should not be underestimated [6,91]. The binder assumes a vital role in upholding the structural integrity of the cathode electrode, ensuring effective adhesion between the active materials and the current collector, and enhancing the overall electrochemical performance of the cathode [46]. Several challenges accompany the practical implementation of high-performance cathodes, including the detachment of active materials from the current collector, the dissolution of transition metal ions from cathode materials, and the creation of an uneven SEI. These challenges can detrimentally impact the performance and cycle stability of LIBs [90,137]. The judicious selection of the binder can effectively address and overcome these issues. For instance, binders characterized by high adhesive strength and compatibility with both cathode materials and electrolytes can prevent the detachment of active materials from the current collector during cycling. Binders capable of adequately coating the cathode materials and forming a stable interface can impede the dissolution of transition metal ions from the cathode materials, thereby enhancing the long-term stability of the cathode [91]. Furthermore, binders with suitable mechanical properties play a crucial role in maintaining robust contact between the cathode and electrolyte, facilitating the development of a more uniform SEI and augmenting electrochemical performance. It is imperative to consider the type and crystal structure of the cathode material during binder selection, as distinct cathode materials may impose varying requirements on binder properties [46]. The binder should be meticulously chosen based on its compatibility with the cathode material, electrolyte, and other components of the battery, as well as its capability to address specific challenges associated with the cathode material. In conclusion, the selection of an appropriate binder is paramount for attaining high-performance LIBs, particularly in the cathode [90,138]. A judicious binder choice can effectively mitigate issues such as peeling, dissolution, and SEI formation, thereby contributing to enhanced cycle stability and the overall electrochemical performance of the cathode electrode. Ongoing research and the development of advanced binders tailored to specific cathode materials and battery requirements are pivotal for advancing the next generation of LIBs [139].

3.2.1. Binders for NCM

$LiNi_{1-x-y}Co_xMn_yO_2$ (both x and y are ≤0.1, NCM) is a layered oxide under active research for use in high-energy LIBs. The performance of NCM cathodes can be improved by adjusting the ratio of the central atoms Ni, Co, and Mn, which directly influences capacity, performance, and safety [138]. Increasing the Ni content has been explored to enhance the capacity of NCM cathodes. However, a significant challenge when using Ni-rich cathodes at high voltages is the choice of the binder material that holds the cathode together. PVdF is a commonly used binder for layered cathode materials; however, it has limitations when applied to high-voltage cathode materials, especially Ni-rich cathodes that are sensitive to moisture [140-142]. Exposure to water molecules can lead to structural collapse and corrosion of Ni-rich cathodes, resulting in the production of alkaline chemical residues such as LiOH or Li_2CO_3. Therefore, there is a growing need for non-aqueous binders to replace PVdF and other aqueous binders in Ni-rich cathodes [6].

Recent research has shown promising results with the use of PI and an amphiphilic bottlebrush polymer (BBP) as alternative binders for NCM cathodes. Pham et al. demonstrated stable operation at high voltages using PI as a binder in NCM811 [138]. PI forms a robust binding environment through chemical bonding on the surface of NCM811, resulting in a high capacity of 203 $mA\ h\ g^{-1}$ when charged up to 4.4 V. The strong interaction between $-CF_3$ and PI bonds suppressed oxidation stability and metal dissolution, showcasing the potential of PI as a binder for Ni-rich layered oxides. In another study, Kim et al. developed an amphiphilic BBP as a binder applicable to NCM811 cathodes [140]. The BBP combines hydrophobic polynorbornene backbones with hydrophilic PAA sidechains. The BBP cleverly integrates hydrophobic polynorbornene backbones with hydrophilic PAA sidechains. These hydrophilic PAA groups establish robust hydrogen bonds with alkaline collectors, resulting in exceptional adhesion properties. In a 180° peel-off test, the adhesion force of the BBP binder with the aluminum current collector was quantified at 3.76 $N\ cm^{-1}$, showcasing a substantial improvement compared to the PVdF film (0.18 N). Impressively, the BBP binder exhibited consistent cycling performance over 240 cycles at a high mass loading of 27 $mg\ cm^{-2}$, with a minimal content of 1 wt%. Furthermore, it displayed electrochemical stability akin to that of the PVdF binder, underscoring its outstanding performance. This implies that nonaqueous solvent-based binders like PI and the amphiphilic BBP hold promise for application in NCM811 cathodes, known for their nickel richness and the necessity for robust structural stability [138,140]. Further exploration and research

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into binder materials stand to significantly contribute to the advancement of LIBs with high performance, particularly those featuring nickel-rich cathodes [141].

3.2.2. Binders for LFP

LFP, as a cathode material, showcases a distinctive one-dimensional channel movement of lithium ions within its olivine crystal structure, enabling a theoretical capacity of 170 mA h g^{-1} through insertion/extraction processes [90,91]. Renowned for its robust covalent bonds and minimal volume alterations during charging and discharging, LFP exhibits remarkable stability, especially when compared to cathode materials with layered structures like NCM. Unlike anode materials such as Si, which undergo substantial volume expansion, LFP typically doesn't necessitate binders with high mechanical strength [143]. However, despite its advantages, LFP grapples with challenges associated with its low electrical conductivity (approximately 10^{-9} to 10^{-10} S cm^{-1}) and Li^+ ion diffusivity (around 10^{-14} to 10^{-16} cm^2 s^{-1}), factors that can impact its overall performance. Consequently, ongoing research is directed toward exploring low-cost, water-soluble binders, and conductive binders tailored for LFP cathodes [144].

In a study conducted by He et al., an environmentally friendly water-soluble binder called Xanthan gum (XG), a natural and non-toxic polysaccharide, was applied in the cathodes of LFP [102]. Although XG has lower adhesive force compared to conventional PVdF binder, it possesses abundant functional groups such as carboxyl and hydroxyl, resulting in higher slurry viscosity. The functional groups in XG may promote electron and ion conduction by providing more active binding sites between LFP, conducting agents, and the substrate, and improving dispersion in the slurry manufacturing process. The XG binder exhibited excellent cycling stability and performance at high speeds, maintaining 55.3% of its capacity at 5 C speeds. In comparison, PVdF and CMC binders maintained 34.8% and 57.8% of their capacity, respectively. This suggests that XG has the potential to be a new water-soluble binder for LFP cathodes, offering advantages such as low cost, high viscosity at low concentration, and excellent processability.

4. Sustainable binders for LIBs

4.1. Bio-based Eco-friendly binder

The choice of an eco-friendly binder, replacing commonly used binders like PVdF, is essential for the design of sustainable batteries. The environmental impact of battery disposal has become a significant concern, with conventional binders potentially releasing harmful factors [133,145,146]. Therefore, there is a growing interest in researching natural binders based on biopolymers, aiming to develop more sustainable battery technologies that minimize environmental impact throughout their lifecycle, including disposal.

In a recent study, Yoon et al. utilized a biodegradable polymer, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (PHA), as a binder for LIBs [147]. The chemical structure of the PHA binder, containing 47% of 4-hydroxybutyric acid in the monomer 3-hydroxybutyric acid, demonstrated favorable properties for electrode maintenance and smooth ion transfer. When compared to PVdF, even with a reduced amount of binder and increased active material, the PHA binder maintained a capacity of 324 mA h g^{-1} and a CE of 94.1%, showcasing its viability as an alternative binder due to its biodegradable properties. Similarly, Nowak et al. employed a biodegradable polymer, poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), as a binder for a lithium-ion battery with a graphite anode [148]. Compared to the conventional binder PVdF, PHBV exhibited similar specific capacity and lithium-ion diffusion coefficient in the graphite electrode. After 100 cycles, PHBV showed a specific capacity of 357 mA h g^{-1} and 99.1% capacity retention, highlighting its potential as a replacement binder for anodes in LIBs. These findings suggest that biopolymer-based binders have the potential to be the next-generation binders for LIBs, offering durability to the electrodes while promoting the development of sustainable batteries.

4.2. Water-based process

The pursuit of sustainable manufacturing for LIBs has led to significant attention on water-soluble polymeric binders. Traditional binders like PVdF often require specific organic solvents like NMP in the LIBs manufacturing process [5,149]. The use of PVdF dissolved in NMP during the slurry process has drawbacks such as high boiling point, toxicity, flammability, cost, and environmental damage [149,150]. To address these issues and eliminate the use of conventional PVdF binders and organic solvents, research has focused on water-soluble binders [149-151]. A variety of water-soluble binders have been explored, including both natural and synthetic polymers. Natural polymers such as polysaccharides (CMC [105,106], carrageenan [152], alginate [69,88,153], chitosan [154,155], gums [150,156-158], and cyclodextrins [159,160], gelatin [161-163], and lignin [164]) and synthetic polymers (PAA [86,97,131,134-136], PVA [40,86,165,166], polyacrylamides [11,12,167], PI [70-72] and SBR [41,151]) have been investigated for water-based processes in LIBs. These water-soluble binders typically contain hydrophilic polar functional groups such as hydroxyls, carboxylic acids, amides, and amines. These functional groups not only enhance water solubility but also improve adhesion strength to electrode materials through the formation of hydrogen bonds. It's worth noting that while water-soluble binders like CMC are often used in combination with SBR due to their brittle nature, the polar functional groups may reduce binder flexibility through strong intramolecular interactions, increasing T_g and brittleness [41]. Additionally, while water-soluble polymeric binders have found success with carbonaceous anode materials, their utilization in cathode fabrication remains challenging due to the hygroscopic degradation of cathode active materials. While recent reports indicate success with non-hygroscopic cathode materials such as LFP and spinel-type $LiMn_2O_4$ using CMC binders, the hygroscopic nature of Ni-rich cathode materials, such as NCM, poses challenges for water-soluble polymers [143,168]. The high voltage and energy capabilities of Ni-rich cathode materials make them promising for LIBs, but their susceptibility to water-induced degradation complicates the use of water-soluble polymers. Overcoming these challenges is crucial for advancing the application of water-soluble binders in the sustainable manufacturing of high-performance LIBs [141,142].

4.3. Dry process and ultra-thick electrode

The ultimate objective of binder research is to enable the design of ultra-thick electrodes, with the goal of increasing the energy density per weight of LIBs [137,169]. The conventional cell design involves stacking multiple layers of anodes and cathodes, each with a thickness of 15-25 μm. Researchers are exploring ways to minimize inactive parts, such as current collectors and separators, by increasing the thickness of the active material in the anode and cathode to 200 μm or even thicker. This approach aims to reduce dead volume, increase energy density, and potentially lower manufacturing costs by eliminating the need for assembling multiple layers [15-17,170,171]. Empirical investigations have demonstrated that augmenting the electrode thickness, escalating from 70 to 320 μm, can yield a substantial 19% enhancement in volume energy density [13]. While increasing electrode thickness has shown promise in increasing volume energy density, challenges arise, including crack generation during drying and the fragile mechanical properties of thick electrodes [172]. Additionally, thicker electrodes face increased charge transport distance and resistance, making it challenging to achieve electrochemical performance comparable to standard thickness electrodes [9,10,173]. To overcome these challenges, various strategies, such as electrode design to promote ion transport and electrode design with low tortuosity, have been explored. However, using a suitable binder with excellent interfacial adhesive force between the anode and cathode materials is considered a promising solution for designing high-energy density batteries with thick electrodes. This would enable strong adhesion with only a small amount of binder, addressing the challenges associated with thick electrodes. Recent research has focused on dry-coating processes as an efficient production method for thick electrodes without the use of solvents [174]. Dry-coating processes offer the advantage of eliminating the need for toxic organic solvents, enabling the manufacture of high-loading electrodes with increased active materials [175,176]. The binder plays a crucial role in providing adhesive force between particles within the electrode and forming a network of particles, whether in dry-coating or wet-coating processes. In wet-coating processes, conductive materials and binders with relatively low density can rise above the electrode during solvent evaporation, resulting in non-uniform distribution [177-179]. In contrast, dry-coating processes, which do not involve solvent evaporation, allow for uniform distribution of electrode materials even in thick electrodes. Micro- computed tomography observations conducted by Ryu et al. have confirmed that dry-coating electrodes form a denser and more continuous conductive network. In wet-coating electrodes, the binder undergoes dissolution in a solvent, encasing the active material particles [176]. Conversely, in dry-coating electrodes, the binder and agglomerates of conductive material are interspersed among the active material particles, covering only a fraction of their surface. This differentiation allows dry-coating electrodes to expedite ion transfer, ultimately augmenting electrochemical performance [14,180].

In contrast to wet-coating, which relies on a solvent, dry-coating electrodes rely on particle cohesion established through surface energy. Consequently, the particle distribution in dry-coating electrodes is dictated by interparticle bonding arising from surface energy, rather than solvent effects (Figure 5). This results in a cohesive interaction between the binder and the active material, surpassing the cohesion between the binder and the conductive material. As a consequence, agglomerates composed of the binder and the conductive material form between the active material particles [180]. The establishment of a well-connected network between active materials through the binder is particularly crucial in dry-coating electrodes. Li et al. introduced a hot-press-based method to manufacture thick dry-coating electrodes by affixing electrode particles onto a current collector [50]. Furthermore, they achieved a robust adhesive force between the active material and the current collector in the electrode by employing phenoxy resin as a binder. EIS measurements revealed an R_{ct} value of 40.15 Ω for the dry-coating electrode using phenoxy resin as a binder, in contrast to 44.06 Ω for the dry-coating electrode using PVdF as a binder, which exhibited lower resistance to charge transfer. Additionally, cyclic voltammetry measurements demonstrated that phenoxy resin exhibited electrochemical stability within the operating voltage range and was deemed suitable as a binder for thick electrodes. The dry-coating electrode produced using phenoxy resin (~40 mg cm^{-2}) displayed stable cycling performance for 50 cycles at 0.1 C [14]. In the application of the dry-coating method to electrode manufacturing, achieving a uniform distribution of electrode powders is feasible, thereby enhancing cycle stability.

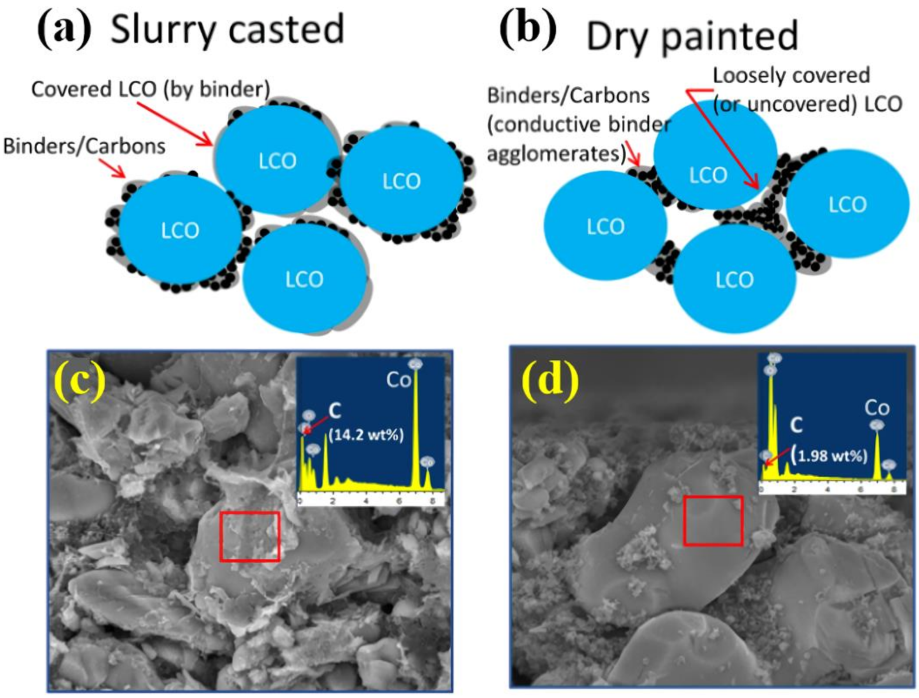

Figure 5. Schematic illustrations of characteristic binders/carbons distribution in (a) dry-coating electrodes and (b) wet-coating electrodes. SEM micrograph showing the representative $LiCoO_2$

particles in cross-sectioned (c) dry-coating electrodes and (d) wet-coating electrodes. Reprinted with permission from reference [180], 2016, Springer Nature Limited.

5. Conclusions and outlook

The review emphasizes the critical characteristics that binders should possess for their application in LIBs, catering to both anode and cathode materials. When choosing a polymer binder, numerous factors come into play, including electrochemical stability, thermal stability, compatibility with electrolytes, solubility in solvents, mechanical properties, ion conductivity, and dispersion stability. For anode materials, binders must showcase excellent mechanical properties and elasticity to uphold the structural integrity of the electrode, especially in materials like Si that undergo substantial volume changes. It is crucial to understand the interaction mechanism with both graphite and Si surfaces for effective binder selection. The choice of binder for cathode materials varies depending on the crystal structure of the cathode material. Different polymers, such as aqueous or non-aqueous binders, conductive polymers, or others, may be suitable for different cathode materials. Additional considerations in binder design include cost-effectiveness, strong adhesion, ease of processing, and eco-friendly properties. The adoption of low-cost, environmentally friendly, and biodegradable polymers contributes to sustainable development and helps mitigate the environmental impact of batteries, even after disposal. This review serves as a valuable reference for understanding the fundamental requirements in binder design for high-performance LIBs, offering insights into selecting the appropriate binder for various electrode materials, particularly in the context of thick electrodes. The principles and findings established in this review can extend to other advanced battery systems, such as lithium-air, Li-S batteries, and solid-state batteries. This paves the way for the development of next-generation batteries that not only exhibit improved performance but also adhere to sustainability principles.

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