DOI:
Article type: Review

Rational design of binders for stable Li-S and Na-S batteries

*Qianyi Guo, and Zijian Zheng**

Qianyi Guo, Prof. Z. Zheng
Laboratory for Advanced Interfacial Materials and Devices
Research Centre for Smart Wearable Technology
Institute of Textiles and Clothing
The Hong Kong Polytechnic University
Hung Hom, Kowloon 999077, Hong Kong SAR, China
E-mail: tczzheng@polyu.edu.hk

Keywords: binder, lithium-sulfur battery, sodium-sulfur battery, sulfur cathode, energy storage.

Binder plays a critical role in stabilizing the sulfur cathode of Li-S and Na-S batteries. Over the past decade, the design of binder molecules has gone through tremendous evolution from primarily maintaining the structural integrity of the electrode against volume change to rationally immobilizing polysulfide intermediate and facilitating electron/ion transport in the charge and discharge process. This article reviews the development of binder for Li-S and Na-S batteries from the perspective of molecular design, and comprehensively discuss the correlation between the functions of the binder molecules and the cell performance. It also points out the future challenge and the potential solutions to address them.

1. Introduction

The pursuit of clean and renewable energy and the electrification of lifestyle significantly promote the need for cost-effective and high-energy-density rechargeable batteries in recent years.[1] Lithium-ion battery (LIB) is the dominant rechargeable battery technology to date. In LIBs, the commonly used cathode materials are lithium metal oxides such as $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$, $LiNi_xMn_yCo_zO_2$ (NCM), and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). The theoretical capacity of these cathodes is typically in the range of 148 to 280 mAh g^{-1}, which are much lower than the anode materials including graphite (372 mAh g^{-1}) and silicon (4200 mAh g^{-1}).[2-3] The limited capacity of cathode materials has largely hindered the further enhancement of the energy density of the battery. As such, it imposes great necessity for developing alternative cathodic materials with much higher capacity and cost-effectiveness to meet the ever-growing demand for energy.[4-6]

Sulfur is a promising cathodic material because of its ultrahigh theoretical specific capacity (1672 mAh g^{-1}), low cost, and environmental friendliness.[7-9] A series of metal-sulfur batteries with alkali metal anodes have been proposed as high-energy-density batteries for different applications.[10-11] Among them, lithium-sulfur (Li-S) and sodium-sulfur (Na-S) batteries are recognized as the most promising technologies. Li-S battery can reach ultra-high theoretical energy density as much as 2600 Wh kg^{-1}, which is ideal for being used in consumable electronics and electrical vehicles (EVs).[7, 12-13] Na-S battery, which also shows a high theoretical energy density (760 W h kg^{-1}),[10, 14] is very suitable for grid-scale storage as backup power because of the natural abundance of Na.[15-17]

The cathodic charge/discharge reaction of Li-S and Na-S batteries involves the phase transitions of sulfur to metal sulfides based on the two-electron-transfer mechanism ($xM+S_8+2e^- \rightarrow xM_2S$), which is largely different from the intercalation chemistry of conventional lithium metal oxide cathodes. This has led to several critical challenges including the physical shedding and electrical isolation of sulfur from current collectors, shuttle effect of polysulfide, low electrical conductivity and large volumetric change of sulfur during the charge/discharge process that cause the irreversible capacity loss, low Coulombic efficiency and short cycling life of sulfur cathodes.[16, 18]

Great efforts have focused on the design of the binder of the sulfur cathode to address the challenges in recent years. Binder typically occupies a small portion of the electrode (≤10 wt%). It functions as a matrix for binding sulfur and other components (e.g., conductive carbon) of the electrode to the current collectors to guarantee a good electrical contact between the constituent electrode components.[19] Binder is commonly designed with strong bonding strength, high thermal/electrochemical stability, and sufficient mechanical properties to accommodate volume deformation.[20] Driven by the deeper understanding of multi-phase conversion chemistry in the sulfur-based battery system, the role of binder has shifted from simple mechanical stabilizer to electrochemical regulator which prevents the polysulfide shuttling and facilitates the electron-/ion- transport.[20-22] These advances have significantly enhanced the capacity and electrochemical stability of the sulfur cathodes.

Here, we aim at providing a comprehensive review of the progress in the design and function of the binder of the sulfur cathode of both Li-S and Na-S batteries. We first introduce the principle of Li-S and Na-S batteries and discuss the challenges of the sulfur cathode. We then review the development of the binder, with a focus on the functionality of materials. The specific design principles to achieve the different functions are comprehensively discussed. In the end, we provide perspectives on the challenges and the research direction to the further design of binders of sulfur cathodes.

2. Principles and Challenges of Sulfur Cathodes

Li-S and Na-S batteries are both alkali metal-sulfur batteries that share a similar conversion chemistry between the sulfur cathode and metal anode. In a typical discharge process, the electrons in the external circuit are captured by sulfur cathode through a two-step reduction reaction with Li^+/Na^+: a higher reduction process corresponding to conversion of cyclo-S_8 to high-order polysulfides (M_2S_x, $4 \leq x \leq 8$, M=Li, Na), and a lower reduction process involving the conversion of M_2S_x to lower-order species, which are assumed to ultimately convert to solid M_2S (**Figure 1A**). The actual discharge products and energy conversion in each step are different between Li-S and Na-S, as shown in **Figure 1B** and **Figure 1C**. For Li-S batteries, the formation of a series of soluble polysulfides (Li_2S_x, $4 \leq x \leq 8$) at the first step (≈2.3 V) and solid Li_2S_2/Li_2S at the second step (≈2.1 V) achieves a theoretical capacity of 418 mAh g^{-1} and 1254 mAh g^{-1}, respectively. In comparison, although Na-S follows the similar conversion of solid→liquid→solid process, the lower-order intermediates (Na_2S_m, $m \leq 4$) is formed at deep discharge (<1.65 V), which induces an increased resistance and prevents the further discharge process to fully release the theoretical capacity of sulfur electrode (1675 mAh g^{-1}).[23]

The critical challenges arising from a similar cathodic reaction in Li-S and Na-S systems can be concluded into the following aspects (**Figure 1D**). Firstly, the insulating nature of sulfur and some short-chain products induces the low utilization of active materials, as well as the sluggish kinetics related to the poor electrochemical contact and slow reaction kinetics.[24-26] The Na^+ with a larger ionic radius than Li^+ can induce a more sluggish reaction.[18] Secondly, the notorious "shuttle effect", which is originated from the migration and diffusion of electrolyte-soluble polysulfide species, causes an irreversible loss of sulfur, poor cycling stability, low Coulombic efficiency, and self-discharge phenomena.[27] The shuttle reaction becomes even more severe in Na-S batteries due to the higher mobility of the Na polysulfide species. Thirdly, the reduplicative volume expansion related to the density difference of sulfur and intermediate products can reach as large as ≈80% in Li-S batteries and ≈170% in Na-S batteries, leading to serious structural instability of the electrode, rapid capacity decay, and safety problems, especially for Na-S batteries.[10, 12, 28] The rational design of binders applied in the battery system aims for addressing the core problems of poor electrical contact, poor reaction kinetics, polysulfide dissolution and shuttling, and volume expansion.

3. Development of Binders for Li-S Batteries

Binder molecules are typically mixed with sulfur species and conductive additives to form a sticky slurry, which is coated onto current collectors with necessary post-treatment. **Figure 2** illustrates the evolution of binders of sulfur cathodes, in which the research was mainly explored in Li-S systems and then extended to Na-S batteries. As early as the 1980s, binder was utilized in Li-S cells to provide the basic function of fixing sulfur and conductive agent on the current collector.[29-30] It was found later that the insulating characteristic of sulfur species such as polysulfide and Li_2S and the shuttling effect of polysulfide also significantly deteriorate the electrode performance. Along with a better understanding of those electrochemical processes, the development of binders has gone through a remarkable journey in terms of their functional design for improving and stabilizing the electrochemical performance. These functions are discussed in the following three aspects in this section: 1) structural and mechanical stabilizer; 2) immobilization of polysulfide to prevent shuttling effect; and 3) improvement of electron and ion transport. Multiple functions are often integrated to stabilize the sulfur electrodes by designing one binder molecule with multiple functional groups or by mixing binders with different functionalities. The following sections will discuss these functions in detail.

3.1 Structural and Mechanical Stabilizer

The primary role of binder in the cathode's configuration is to maintain the steady attachment of loaded sulfur and to avoid structural pulverization when the cathode undergoes volume change. Binder molecules are designed to acquire strong adhesion with both sulfur and the current collector, and a strong skeleton to accommodate the stress/strain during the electrochemical process. At the early stage (before 2013), researchers used those linear binders in conventional lithium metal oxide cathodes - including polyethylene oxide (PEO)[31-32], fluoropolymers such as poly(vinylidene fluoride) (PVDF) and poly(tetrafluoroethylene) (PTFE)[33] - for making sulfur cathodes. The electronegative polar groups of these binder molecules promote the adhesion among the different components including sulfur, conductive additives and current collector without galvanic corrosion.[34] Meanwhile, the good elasticity originated from the van der Waals forces among the polymer chains provides a certain level of mechanical strength to withstand the volume fluctuation during the repeated discharge/charge process. However, because the volume expansion of sulfur cathode in a charge/discharge process is much larger than those of lithium metal oxides, these conventional binders face a significant challenge in ensuring long-term stability of the cathode especially when the sulfur loading is high.

Based on the preliminary understanding of the binder as a structural and mechanical stabilizer, researches explored alternatives with better mechanical properties by rational design of the molecular structure and surface chemistry. The most common strategy to improve the mechanical strength is incorporating binder molecules with functional groups to form covalent bonds with S/C composite and the substrate. Polar groups such as -OH, -COOH, $-NH_2$, -CN and $-SO_3$ can form strong covalent bonds with the cathodic materials.[35-36] As such, a series of linear polymers with these functional groups including polyvinylpyrrolidone (PVP),[37] polyvinyl alcohol (PVA),[33] carboxymethyl cellulose (CMC),[38] polyethyleneimine (PEI),[37] gelatin,[39-40] polyacrylic acid (PAA),[41] and poly(acrylamide-co-diallyldimethylammonium chloride) (PAMAC)[42] were used as binders (**Figure 3A**). Among them, gelatin is particularly promising.[39] Being a natural biomacromolecule composed of peptide, gelatin contains a large number of ionizable groups such as -COOH and $-NH_2$. The great hydrophilic feature endows gelatin with water-solubility, strong adhesion, and insolubility in organic electrolyte, which are important to improve the electrode stability.

The second strategy to improve mechanical stability is forming a hybrid binder such as CMC/PTFE[33] and PEI/PVP,[37] which combines desirable attributes of the individual component. Importantly, the addition of a small amount of plasticizing reagents with lower Young's modulus into linear binder molecules can effectively improve flexibility, ductility, and toughness.[43] For example, adding elastic styrene-butadiene rubber (SBR) into brittle CMC significantly increased the elasticity of the electrode. The swelling ratio of CMC/SBR hybrid was only 1/3 of that of PVDF, even with high areal loading (3-7 mg cm^{-2}) of sulfur. [38, 44] Cairns et al. demonstrated the use of the CMC/SBR hybrid to reach high-rate capability (~800 mAh g^{-1} at 6.0 C) and long cycling performance (0.039% decay per cycle for 1500 cycles) of Li-S cells.[43] A similar hybrid consisting of CMC and nitrile-butadiene rubber hybrid binder (CMC/NBR) was also reported later.[45]

In recent years, branch-type molecular designs, as compared to the abovementioned linear polymer design, are introduced; typical examples include dendrimer and cross-linked polymer network. Branch-type structures possess more functional groups than linear polymers, which improve the adhesive ability of the binder. For example, the dendritic structure of water-soluble polyamidoamine (PAMAM) provides a high degree of surface functionality and polarity and ensures a high interior porosity when mixed with sulfur (**Figure 3B**). Bhattacharya et al. demonstrated that PAMAM capped with 4-carbomethoxy pyrrolidone (G4CMP)could deliver a high specific capacity of 1045 mAh g^{-1} (0.05C) at a high sulfur loading (4.38 mg cm^{-2}) and the capacity retained at 98% after 100 cycles. It should be noted that increasing branched degrees of and molecular weights will lead to poor solubility and therefore a balance between the branches and the solubility should be considered in the synthesis.[46]

On the other hand, cross-linked networks constructed by intermolecular ionic or covalent bonds are proposed to provide a mechanically robust 3D skeleton to withstand the volume change. Na alginate-Ca^{2+} is the first ionically cross-linked network developed for sulfur-cathode.[47]. Other divalent transition metal cations such as Cu^{2+} can also act as a crosslinker to replace Ca^{2+}.[48] In comparison with ionic crosslinking, covalent cross-linking yields stronger binders. For example, the crosslinked network formed by the hydrolysis of guar gum (GG) and xanthan gum (XG) showed remarkable adhesion (evaluated by nanoscratch and nanoindentation), which could afford ultrahigh sulfur loading of 19.8 mg cm^{-2} and high areal capacity of 26.4 mAh cm^{-2} without surface cracking of the electrode (**Figure 3C**).[49] Up to now, other covalently crosslinked binders such as self-cross-linked polyacrylamide (c-PAM)[50] and cross-linked CMC with citric acid[51], are also reported.

3.2 Immobilization of Polysulfide

Overall, linear or cross-linked binder molecules with electron-withdrawing or cationic groups can effectively suppress the shuttling of polysulfides. In 2013, a study with ab initio simulation provided the first prediction that functional groups in binders could chemisorb polysulfide species by polar-polar interaction to alleviate the polysulfide dissolution.[52] In this work, the interactions between polysulfides and different functional groups were systematically studied to suggest molecular structures possessing a strong affinity to both soluble sulfur species and insoluble Li_2S (Table 1). They found that electron-rich groups with lone electron pairs on O, N and halogen heteroatoms exhibited high affinity with lithium polysulfides because of the hard acid nature of Li^+. Especially, carbonyl groups (>C=O) on esters, ketones, and amides delivered the highest binding energies with lithium polysulfides in the range of 0.95-1.26 eV. In comparison, electron-withdrawing -CF of PVDF showed relatively low binding energy to polysulfide (0.23-0.40 eV). As a proof-of-concept experiment, >C=O containing PVP was used as binder of Li_2S for testing the electrode performance, showed higher initial capacity (760 mAh g^{-1}, 0.2C), capacity retention (94%, 100 cycles) and average Coulombic efficiency (97%) than those made with PVDF.

Since then, researches have explored many kinds of binders with polysulfide--anchors. The abovementioned linear binders such as PEO,[53] PVA,[33] PEI [54] and CMC,[38] also show polysulfide-anchoring ability because of the existence of the lone electron pairs on O and N of the molecules. Zhang et al. reported that water-soluble Gum arabic (GA) derived from *Acacia Senegal* are bifunctional binder for the longevity of Li-S batteries because these bio-molecules are rich in hydroxyl and acylamido groups.[55] This hydrophilic property is favorable considering environmental friendliness.[56] Later on, other linear polymers including sulfonated poly(ether ether ketone) (SPEEK),[57] poly(vinylidene difluoride-trifluoroethylene) (P(VDF-TRFE)),[58] PEDOT:PSS[59], polyamide-6 (PA6), chitosan sulfate ethylamide glycinamide(CSEG),[60] benzimidazole-containing poly(arylene ether ketone) (PAEK-BI) and sulfonated poly(arylene ether ketone-co-benzimidazole) (SPAEK-BI)[61] also have been reported to show good polysulfide anchoring ability.[62] Recently, Cui et al. reported an aqueous inorganic polymer binder, ammonium polyphosphate (APP), which acquires not only polysulfide adsorption capability but also the flame-retardant property (**Figure 4D**).[63] The strong polar P-O bond in APP polymer contributes to high binding energies towards sulfur/polysulfide (2.16-2.30 eV). It allows APP to efficiently suppresses the out-diffusion of polysulfide meanwhile promoting the hopping of Li^+ for ion transport, resulting in the excellent cycling stability for 400 cycles with low capacity decay rate of ~0.038% and high Coulombic efficiency >99%. When being ignited, the APP decomposes and cross-links to form an insulating polymer layer as shield to protect the cell which greatly improve the cell safety.

Designing binder molecules with branched structures can future increase the density of the functional groups and enhance the anchoring ability. In 2017, Yan et al. reported a cross-linked hyperbranched binder with amino functional groups (AFG) by copolymerization between the amine groups of PEI and isocyanates of hexamethylene diisocyanate (HDI) (**Figure 4B**).[64] This binder showed good mechanical elasticity and strong capability of absorbing different polysulfide intermediates with binding strength in the range of 0.94-1.29 eV. Consequently, sulfur cathodes using this binder reached almost 100% capacity retention and ~99 % Coulombic efficiency after 200 charge/discharge cycles at 1C (S loading: 0.7 mg cm^{-2}). Similar binders copolymerized using PEI and epoxide compounds (ER) could future improve the cycling performance; testing cells reached a high Coulombic efficiency >99% and a low capacity decay rate of 0.020% at 0.5C after 1000 cycles (S loading: 1.9 mg cm^{-2}).[65] Very recently, Xiong et al. reported a more environmental friendly hydrophilic binder (denoted as PPA) by cross-linking poly(ethylene glycol) diglycidyl ether (PEGDGE) with polyethylenimine (e-PEI).[66]

Apart from polymers with electron-withdrawing functional groups, cationic polymers are alternatives to anchor polysulfides, by taking advantage of the strong electrostatic interaction between the cations and polysulfide anions. Zeng et al. first reported a hyperbranched binder (β-CDp-N$^+$) containing hydroxyl-enriched β-cyclodextrin and quaternary ammonium cation, which provided additional electrostatic adsorption towards soluble polysulfide intermediates (**Figure 4A**).[67] Other cationic polymers with higher density of positively charged quaternary ammonium (R_4N^+) but less oxygen-containing groups, have also been investigated; these examples include poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA),[68] poly[bis(2-chloroethyl) ether-alt-1,3-bis[3(dimethylamino) propyl]urea] quaternized (PQ) with a high density quaternary ammonium cations[69], poly(diallyldimethylammonium triflate) (PDAT)[70], cationic PEI.[71] However, these polymers often swell or dissolve in the electrolyte which also contains anionic species, and result in the short cycle life of the electrode. The binding energy between the cationic polymer and the anionic species of the electrolyte should be minimized. Helms et al. reported that poly[(N,N-diallyl-N,N-dimethylammonium) bis(trifluoromethanesulfonyl)imide] (PEB-1) could regulate the transport of polysulfides through anion metathesis between the counterions ($TFSI^-$) of PEB-1 and polysulfide because of the less binding free energy of TFSI-PEB-1, which resulted in the preferentially binding with LiS_n^- or S_n^- (**Figure 4C**).[72] They claimed that some LiS_n could undergo second anionic exchange to induce inter- or intramolecular crosslinks and allow better confinement of the polysulfide. These attributes allow the promising capability (1004 mAh g^{-1}, 0.2C) with extreme high sulfur loadings of 8.1 mg cm^{-2}. Further study showed that the cationic polymers containing $TFSI^-$ counter ions offer the best polysulfide adsorption compared to polymers containing other smaller counter anions such as BF^{4-}, PF^{6-} and Cl^-.[73] Besides, the polymer backbone of cationic polymer has impact on the binding affinity with polysulfide, which increases in the order of styrene backbones, vinyl-based, and cross-linked cationic polymer.[74]

3.3 Improvement of the Electron and Ion Transport

The electrochemical reaction in Li-S batteries involves a serial of mass transport and electron transfer. The rate capacity of batteries is highly related to the ion diffusion; faster ion diffusion can efficiently reduce the voltage polarization generated due to the mass transfer impedance. The kinetics of electrochemical reactions occurring in sulfur cathodes largely depend on the electron transfer because of the insulating nature of sulfur/Li_2S. Note that traditional binders are nonconductive. Therefore, incorporating binder molecules with functions of facilitating the electron and ion transport can further improve the conductivity and lower the impedance of sulfur cathodes. It should be noted that ion conductivity relies on the interaction between the Li^+ and ionic groups of the binder molecular.[75-76] Especially, the ability to transport ion can be improved by enhancing the uptake of Li ions in the electrolyte.[77-78] Therefore, most binder molecules showing a high affinity to lithium polysulfides are inherently ion-conductive and the research focus has been placed on how to improve the electric conductivity of the binder.

Based on the conduction mechanism, the electric conductivity of binder molecules can be enhanced by introducing conductive conjugated segment to the backbone of the polymer. However, the rigid conjugated structure usually fails to meet the basic requirement of the binder as a mechanical stabilizer. It was reported that some common conductive polymers such as polyaniline (PANI),[79] polypyrrole (Ppy),[80-81] poly(3,4ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)[82] are too rigid to sever as good binder. To further improve their mechanical elasticity and binding affinity to sulfur species, one strategy is to incorporate soft segments into the backbone of the conductive polymer. For example, poly(9, 9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) was designed, in which the methylbenzoic ester segment was responsible for enhancing the elasticity, while the octyl side chains and fluorenone functional groups provided high conductivity.[83] Another simple and efficient method of reducing the rigidity of conductive binders is to blend with another polymer with better mechanical properties. For example, composite binders integrating conductive and adhesive agents including PPy/PU[84] and PEDOT:PSS/PAA[59] were demonstrated. Yan et al. synthesized a novel double-chain polymer network binder composed of CMC and 4,4'-biphenyldisulfonic acid connected polypyrrole (Sul-PPy). With the addition of a small amount of cross-linked Sul-PPy (<6.4 wt%) into the viscous CMC binder, the composite binder exhibited reduced resistance meanwhile maintaining its mechanical characteristics and polysulfide trapping ability, thus enabling a high rate performance (1326.9 mAh g^{-1}), good sulfur loading ability (9.8 mg cm^{-2}) under a low electrolyte/sulfur ratio (5:1, μL mg^{-1}).[85]

It is noted that the introduction of soft segments or soft polymers inevitably reduces the electric conductivity of the binder. Therefore, a third strategy based on cross-linking conductive binder was developed. Positively charged conjugated polymers are promising candidates taking account of their multiple functions including high conductivity, ample immobilization sites of polysulfide and good mechanical durability. Wang et al. reported an acid doped PANI with polar amine groups and positively charged features.[78] Instead of forming compact layer morphology with undoped PANI, the charged PANI cross-linked to form a "cobweb" structure, which decreased the loading amount of the PANI in the electrode, mitigated the brittle feature of PANI, and improved the electrical contact between the binder and the sulfur. PEDOT:PSS cross-linked with Mg^{2+} was also reported to improve the binder's mechanical stability maintaining high conductivity.[86]

4. Development of Binders for Na-S batteries

In the field of Na-S battery, most researches focus on the study of the cathode's configuration and electrolyte, and less effort has been made on the development of binders. In general, the development of binders for the Na-S system shares similar features with that of Li-S batteries, with the functions evolving from simple mechanical stabilizers to electrochemical regulators for regulating the Na polysulfide migration and electron/ion transport. Even though the multiphase conversion chemistry of sulfur is similar, most binders developed for Li-S batteries are not suitable direct use in Na-S batteries, because of the more severe polysulfide shuttling, volumetric variation and sluggish charge transfer.

Most reported studies on Na-S battery used PVDF as the binder, which is a sole mechanical stabilizer. Not until very recently did the researcher report the bifunctional binder to solve the notorious Na polysulfide shuttling, which is the main reason for the poor stability in Na-S batteries. In 2018, Wang et al. first reported the study of CMC as a binder for obtaining stable and high-performance Na-S batteries.[87] CMC molecules acquired high binding energy with Na polysulfide by forming strong S-O bonds with Na polysulfide, which preventing the dissolution of Na polysulfide into the electrolyte (**Figure 5A**). The performance of Na-S batteries made with CMC was much better than those with PVDF as the binder, in terms of better specific capacity (1170 mAh g^{-1}), higher energy density (1477 Wh kg^{-1}), and longer cycling stability.

Copolymerization between pentaerythritol tetraacrylate (PETEA) and sulfur via an inverse vulcanization-like process could yield a cross-linked polymer, poly(S-PETEA) (**Figure 5B**).[88] The PETEA rich in ester groups could immobilize Na polysulfides during cycling to suppress the polysulfide shuttling. It is noted that the poly(S-PETEA) is rigid and it has a low binding affinity to the current collector. As such, it should be further combined with CMC to obtain the poly(S-PETEA)-based cathode for fabricating a stable quasi-solid-state Na-S battery. This inverse vulcanization strategy offers a significant insight for stabilizing the polysulfide species.

A recent study reported a hybrid binder fabricated by mixing Na alginate and PANI, which has a particular advantage of high electric conductivity (**Figure 5C**).[89] Na alginate is a high-modulus polysaccharide with appropriate swelling property. It served as a structural stabilizer to endure volume fluctuation during the insertion and extraction of Na^+ ions. Doping PANI into Na alginate provided additional electric conductivity, leading to the reduced internal resistance of the electrode and fasten redox reactions. As a result, Na-S batteries with such a hybrid binder achieved improved electrochemical performances (e.g., higher specific capacity and better capacity retention) in comparison with those using PVDF.

5. Binder Using Conductive 2D Materials

Compared with conductive polymers, conductive 2D materials with high specific surface area, high electric/ionic conductivity, abundant functional sites and mechanical flexibility are promising to be used as binder's additive or multifunctional binder. Graphene-based materials including reduced graphene oxide (rGO) and doped graphene, are representative 2D materials with a good ability to adhere sulfur species to the current collector.[90] They exhibit prominent advantages of strong polysulfide chemisorption and fast Li^+/electron transport. It is noted that the early reports rarely use such materials in the binder considering their relatively low viscosity to guarantee the attachment of sulfur to the substrate. Not until recent years were graphene-based materials developed to improve the adhesive property by means of blending with polymer or chemical modulation.[90-97]

Binders using rGO was firstly used in Li-S battery. Xu et al. reported a conductive binder by direct mixing of rGO nanosheets with PAA.[90] Oxygen-containing groups of rGO and PAA showed a strong affinity to polysulfides and suppressed their migration. Besides, the functional groups of PAA (-COOH) and rGO (-OH, -COOH and C-O-C) formed hydrogen bonds to obtain a cross-linked network (**Figure 6A**), which significantly improved the electrical conductivity and mechanical property of the whole sulfur cathode. Even with only 1 wt% of rGO in the mixture, the specific capacity of the sulfur cathode exhibited was 30% higher than that made with pure PAA. The initial specific capacity was ~820 mAh g^{-1} (0.5 C), with a capacity decay rate of 0.22% per cycle for 100 cycles. Adding rGO to Ppy also showed similar results.[91]

Chemically modulating graphene by doping with heteroatoms or grafting with functional groups can effectively improve the adhesion of graphene-based materials to sulfur/polysulfide. Nitrogen-doped graphene,[92-93] nitrogen/sulphur codoped graphene[94], ethylenediamine functionalized rGO,[95] anthraquinone modified rGO[96] have been demonstrated to facilitate the sulfur/polysulfide adhesion. For example, Chang et al. reported nitrogen and sulfur co-doped graphene (NSHG) to serve as a conductive binder in a flexible Li-S battery.[97] The NSHG binder strongly fixed the sulfur onto the current collector, nickel-coated fabrics (NiCF), though simple vacuum infiltration of concentrated ink containing sulfur and NSHG onto the fabric substrate (**Figure 6B**). The doping of N/S not only improved the mechanical affinity between graphene and sulfur but also provided chemically absorbed sites for anchoring soluble polysulfides. As the result, the NSHG/S_8/CF electrodes exhibited excellent capacity retention >99.82% over 400 cycles (S loading: 2.4 mg cm^{-2}), and high areal capacity of 3.51 mAh cm^{-2} (S loading: 4.2 mg cm^{-2}). Such stable and high-performance sulfur cathode further paired with Cu-deposited carbon fabric anode (CuCF) to fabricate the full battery. Importantly, the assembled full cell has achieved high energy density (6.3 mWh cm^{-2}), excellent cycling stability (capacity retention of 99.89%, 260 cycles) and remarkable structural stability even upon repeatedly bending at a small radius of curvature. Noted that although the rGO and doped graphene have strong adhesion to S/polysulfide, their adhesion to the current collector still needs to be further strengthened.

Other 2D materials have also been demonstrated with similar functions. For example, MXene, which composes of a transition metal, C and/or N, and surface termination group such as -O, -OH and/or -F, is of great potential to be the conductive additive of binder.[98-99]Upon a further modification, such kind of materials are expected to serve as binders with high adhesion, conductivity, polysulfide adsorption, and catalytic characteristic.

6. Conclusions and Prospective

In summary, although occupying only very small portions, binders are indispensable components to achieve stable sulfur cathodes for both Li-S and Na-S batteries. The functions of binders have experienced a remarkable development in the past two decades. **Figure 6** summarizes the characteristics of sulfur electrodes using binders designed with specific functions (mechanical stabilizer, immobilization of polysulfide, and improvement of electric conductivity). They are compared in terms of the electrode capacity, capacity decay rate, mass loading of sulfur, cycling life, and capacity enhancement factor in comparison with reference electrodes made with PVDF.

At the early stage, binders are designed to serve as mechanical stabilizers to provide the good electric contact between different cathode constituents (sulfur, conductive additives, and current collector) and to ensure the structural stability of the electrode during redox reactions. In this regard, the design principle of the binder molecule is to achieve stronger surface adhesion with sulfur and the current collector, and the molecular structures have evolved from linear to branch-typed polymers (dendrimers and cross-linked structures). The cross-linked structures of binders, especially the covalently cross-linked one, can bear high mass loading of sulfur and maintain the high capacity (**Figure 7A**).

With a better understanding of sulfur-based chemistries, the design of binders has been extended to bifunction and multi-function, which also aim for the chemical immobilization of polysulfides and the facilitation of electron and ion transport. Specifically, chemical adsorption of polysulfides is mainly achieved by introducing electron-withdrawing or cationic groups to the binder molecules, which have a strong binding affinity to polysulfides. The polysulfide-immobilizing skeleton plays a significant role in the enhancement of cycling performance (**Figure 7B**).

On the other hand, conductive polymers are used as electrically conductive binders, which can improve the redox kinetics and also enhance the capacity of sulfur (**Figure 7C**). However, a major drawback of using conductive polymers is the poor mechanical adhesion of the electrode. While introducing soft segments into the molecular backbone or mixing with soft binder molecules can improve the mechanical durability of rigid conjugated structure, a more effective way is to construct ionically or covalently cross-linked networks of the conductive polymer.

In addition, 2D materials such as rGO and doped graphene have also been applied in binders in consideration of their superior conductivity, large surface-anchoring sites, and mechanical flexibility. Simple addition of rGO into the polymer binder can effectively enhance the electric conductivity and polysulfide anchoring ability of the whole electrode while maintaining suitable mechanical properties for enduring volume change. The mechanical adhesion between sulfur and graphene can be further improved by doping graphene with a heteroatom (e.g., nitrogen and sulfur). Graphene-based materials provide a great possibility to obtain a multifunctional binder to achieve remarkably enhanced battery performance.

Despite the progress discussed above, it is still very challenging nowadays to simultaneously achieve high areal capacity (≥ 6 mAh cm^{-2}) and high cycling stability (capacity retention $\geq 80\%$ after 500 cycles) of the sulfur cathode, which is a critical milestone for the commercialization of the technology. In principle, the combination of cross-linked architecture, ample anchoring sites, and conductive segments in the molecular design should lead to multi-functional binders, which should provide more stable and higher capacity sulfur cathodes. Nevertheless, it is often a tradeoff between different functions, and there remains a large open space to obtain the optimal property. The correlation between the binder structure and the electrode performance of Li-S and Na-S batteries, in principle, can also be beneficial for the rational design of binders used in other sulfur-based batteries, such as Mg-S battery.

Acknowledgments
The authors acknowledge NSFC/RGC Joint Research Scheme (N_PolyU528/16) for financial support of this work.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References:

[1] J. B. Goodenough, K.-S. Park, *J. Am. Chem. Soc.* **2013**, *135*, 1167.

[2] J. M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359.

[3] N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, *18*, 252.

[4] Z. W. Seh, Y. Sun, Q. Zhang, Y. Cui, *Chem. Soc. Rev.* **2016**, *45*, 5605.

[5] M. S. Whittingham, *Science* **1976**, *192*, 1126.

[6] J. R. Dahn, T. Zheng, Y. Liu, J. S. Xue, *Science* **1995**, *270*, 590.

[7] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* **2011**, *11*, 19.

[8] R. Fang, S. Zhao, Z. Sun, D.-W. Wang, H.-M. Cheng, F. Li, *Adv. Mater.* **2017**, *29*, 1606823.

[9] A. Manthiram, Y. Fu, S. H. Chung, C. Zu, Y. S. Su, *Chem. Rev.* **2014**, *114*, 11751.

[10] X. Hong, J. Mei, L. Wen, Y. Tong, A. J. Vasileff, L. Wang, J. Liang, Z. Sun, S. X. Dou, *Adv. Mater.* **2019**, *31*, 1802822.

[11] H. Kim, G. Jeong, Y. U. Kim, J. H. Kim, C. M. Park, H. J. Sohn, *Chem. Soc. Rev.* **2013**, *42*, 9011.

[12] R. Fang, S. Zhao, Z. Sun, D. W. Wang, H. M. Cheng, F. Li, *Adv. Mater.* **2017**, *29*.

[13] M. Hagen, D. Hanselmann, K. Ahlbrecht, R. Maça, D. Gerber, J. Tübke, *Adv. Energy Mater.* **2015**, *5*, 1401986.

[14] Y. Zhao, K. R. Adair, X. Sun, *Energ. Environ. Sci.* **2018**, *11*, 2673.

[15] L. Li, S. Peng, J. K. Y. Lee, D. Ji, M. Srinivasan, S. Ramakrishna, *Nano Energy* **2017**, *39*, 111.

[16] Y.-X. Wang, B. Zhang, W. Lai, Y. Xu, S.-L. Chou, H.-K. Liu, S.-X. Dou, *Adv. Energy Mater.* **2017**, *7*.

[17] G. Nikiforidis, M. C. M. van de Sanden, M. N. Tsampas, *RSC Adv.* **2019**, *9*, 5649.

[18] Z. Wen, Y. Hu, X. Wu, J. Han, Z. Gu, *Adv. Funct. Mater.* **2013**, *23*, 1005.

[19] S. L. Chou, Y. Pan, J. Z. Wang, H. K. Liu, S. X. Dou, *Phys. Chem. Chem. Phys.* **2014**, *16*, 20347.

[20] H. Yuan, J.-Q. Huang, H.-J. Peng, M.-M. Titirici, R. Xiang, R. Chen, Q. Liu, Q. Zhang, *Adv. Energy Mater.* **2018**, *8*.

[21] J. Liu, Q. Zhang, Y.-K. Sun, *J. Power Sources* **2018**, *396*, 19.

[22] J. Zhu, P. Zhu, C. Yan, X. Dong, X. Zhang, *Prog. Polym. Sci.* **2019**, *90*, 118.

[23] X. Yu, A. Manthiram, *ChemElectroChem* **2014**, *1*, 1275.

[24] G. Li, S. Wang, Y. Zhang, M. Li, Z. Chen, J. Lu, *Adv. Mater.* **2018**, *30*, e1705590.

[25] D. Su, D. Zhou, C. Wang, G. Wang, *Adv. Funct. Mater.* **2018**, *28*, 1870273.

[26] S.-H. Chung, C.-H. Chang, A. Manthiram, *Adv. Funct. Mater.* **2018**, *28*, 1801188.

[27] K. Park, J. H. Cho, J.-H. Jang, B.-C. Yu, A. T. De La Hoz, K. M. Miller, C. J. Ellison, J. B. Goodenough, *Energ. Environ. Sci.* **2015**, *8*, 2389.

[28] X. Liu, J. Q. Huang, Q. Zhang, L. Mai, *Adv. Mater.* **2017**, *29*.

[29] R. D. Rauh, K. M. Abraham, G. F. Pearson, J. K. Surprenant, S. B. Brummer, *J. Electrochem. Soc.* **1979**, *126*, 523.

[30] H. Yamin, E. Peled, *J. Power Sources* **1983**, *9*, 281.

[31] J. Shim, K. A. Striebel, E. J. Cairns, *J. Electrochem. Soc.* **2002**, *149*, A1321.

[32] S.-E. Cheon, J.-H. Cho, K.-S. Ko, C.-W. Kwon, D.-R. Chang, H.-T. Kim, S.-W. Kima, *J. Electrochem. Soc.* **2002**, *149*, A1437.

[33] N.-I. Kim, C.-B. Lee, J.-M. Seo, W.-J. Lee, Y.-B. Roh, *J. Power Sources* **2004**, *132*, 209.

[34] A. Baldan, *J. Mater. Sci.* **2004**, *39*, 1.

[35] H. Yi, T. Lan, Y. Yang, Z. Lei, H. Zeng, T. Tang, C. Wang, Y. Deng, *J. Mater. Chem. A* **2018**, *6*, 18660.

[36] J. Pan, G. Xu, B. Ding, J. Han, H. Dou, X. Zhang, *RSC Adv.* **2015**, *5*, 13709.

[37] Y. Jung, S. Kim, *Electrochem. Commun.* **2007**, *9*, 249.

[38] M. He, L.-X. Yuan, W.-X. Zhang, X.-L. Hu, Y.-H. Huang, *J. Phys. Chem. C* **2011**, *115*, 15703.

[39] Q. Wang, W. Wang, Y. Huang, F. Wang, H. Zhang, Z. Yu, A. Wang, K. Yuan, *J. Electrochem. Soc.* **2011**, *158*.

[40] J. Sun, Y. Huang, W. Wang, Z. Yu, A. Wang, K. Yuan, *Electrochim. Acta* **2008**, *53*, 7084.

[41] Z. Zhang, W. Bao, H. Lu, M. Jia, K. Xie, Y. Lai, J. Li, *ECS Electrochem. Lett.* **2012**, *1*, A34.

[42] S. S. Zhang, *J. Electrochem. Soc.* **2012**, *159*, A1226.

[43] M. K. Song, Y. Zhang, E. J. Cairns, *Nano Lett.* **2013**, *13*, 5891.

[44] D. Lv, J. Zheng, Q. Li, X. Xie, S. Ferrara, Z. Nie, L. B. Mehdi, N. D. Browning, J.-G. Zhang, G. L. Graff, J. Liu, J. Xiao, *Adv. Energy Mater.* **2015**, *5*.

[45] S. Waluś, A. Robba, R. Bouchet, C. Barchasz, F. Alloin, *Electrochim. Acta* **2016**, *210*, 492.

[46] P. Bhattacharya, M. I. Nandasiri, D. Lv, A. M. Schwarz, J. T. Darsell, W. A. Henderson, D. A. Tomalia, J. Liu, J.-G. Zhang, J. Xiao, *Nano Energy* **2016**, *19*, 176.

[47] S. Zhu, J. Yu, X. Yan, E. Zhao, Y. Wang, D. Sun, Y. Jin, K. Kanamura, *J. Appl. Electrochem.* **2016**, *46*, 725.

[48] J. Liu, M. Sun, Q. Zhang, F. Dong, P. Kaghazchi, Y. Fang, S. Zhang, Z. Lin, *J. Mater. Chem. A* **2018**, *6*, 7382.

[49] J. Liu, D. G. D. Galpaya, L. Yan, M. Sun, Z. Lin, C. Yan, C. Liang, S. Zhang, *Energ. Environ. Sci.* **2017**, *10*, 750.

[50] X. Zhu, F. Zhang, L. Zhang, L. Zhang, Y. Song, T. Jiang, S. Sayed, C. Lu, X. Wang, J. Sun, Z. Liu, *Adv. Funct. Mater.* **2018**, *28*.

[51] Q. Pang, X. Liang, C. Y. Kwok, J. Kulisch, L. F. Nazar, *Adv. Energy Mater.* **2017**, *7*.

[52] Z. W. Seh, Q. Zhang, W. Li, G. Zheng, H. Yao, Y. Cui, *Chem. Sci.* **2013**, *4*.

[53] M. J. Lacey, F. Jeschull, K. Edstrom, D. Brandell, *Chem. Commun.* **2013**, *49*, 8531.

[54] L. Zhang, M. Ling, J. Feng, G. Liu, J. Guo, *Nano Energy* **2017**, *40*, 559.

[55] G. Li, M. Ling, Y. Ye, Z. Li, J. Guo, Y. Yao, J. Zhu, Z. Lin, S. Zhang, *Adv. Energy Mater.* **2015**, *5*.

[56] S. Tu, X. Chen, X. Zhao, M. Cheng, P. Xiong, Y. He, Q. Zhang, Y. Xu, *Adv. Mater.* **2018**, *30*.

[57] M. Cheng, L. Li, Y. Chen, X. Guo, B. Zhong, *RSC Adv.* **2016**, *6*, 77937.

[58] H. Wang, V. Sencadas, G. Gao, H. Gao, A. Du, H. Liu, Z. Guo, *Nano Energy* **2016**, *26*, 722.

[59] J. Pan, G. Xu, B. Ding, Z. Chang, A. Wang, H. Dou, X. Zhang, *RSC Adv.* **2016**, *6*, 40650.

[60] H. Yi, T. Lan, Y. Yang, H. Zeng, T. Zhang, T. Tang, C. Wang, Y. Deng, *Energy Stor. Mater.* **2019**, *21*, 61.

[61] J. Liao, J. Wang, Z. Liu, Z. Ye, *ACS Appl. Energy Mater.* **2019**, DOI: 10.1021/acsaem.9b01214.

[62] Z. Tang, Q. Yang, B. Liu, M. Wang, S. Wang, C. Xiong, *Macromol. Mater. Eng.* **2017**, *302*, 1700122.

[63] G. Zhou, K. Liu, Y. Fan, M. Yuan, B. Liu, W. Liu, F. Shi, Y. Liu, W. Chen, J. Lopez, D. Zhuo, J. Zhao, Y. Tsao, X. Huang, Q. Zhang, Y. Cui, *ACS central sci.* **2018**, *4*, 260.

[64] W. Chen, T. Qian, J. Xiong, N. Xu, X. Liu, J. Liu, J. Zhou, X. Shen, T. Yang, Y. Chen, C. Yan, *Adv. Mater.* **2017**, *29*.

[65] L. Yan, X. Gao, F. Wahid-Pedro, J. T. Ernest Quinn, Y. Meng, Y. Li, *J. Mater. Chem. A* **2018**, *6*, 14315.

[66] W. Chen, T. Lei, T. Qian, W. Lv, W. He, C. Wu, X. Liu, J. Liu, B. Chen, C. Yan, J. Xiong, *Adv. Energy Mater.* **2018**, *8*.

[67] F. Zeng, W. Wang, A. Wang, K. Yuan, Z. Jin, Y. S. Yang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 26257.

[68] H. Chen, C. Wang, Y. Dai, J. Ge, W. Lu, J. Yang, L. Chen, *Nano Energy* **2016**, *26*, 43.

[69] M. Ling, W. Yan, A. Kawase, H. Zhao, Y. Fu, V. S. Battaglia, G. Liu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 31741.

[70] H. Su, C. Fu, Y. Zhao, D. Long, L. Ling, B. M. Wong, J. Lu, J. Guo, *ACS Energy Lett.* **2017**, *2*, 2591.

[71] H. Wang, M. Ling, Y. Bai, S. Chen, Y. Yuan, G. Liu, C. Wu, F. Wu, *J. Mater. Chem. A* **2018**, *6*, 6959.

[72] L. Li, T. A. Pascal, J. G. Connell, F. Y. Fan, S. M. Meckler, L. Ma, Y. M. Chiang, D. Prendergast, B. A. Helms, *Nat. Commun.* **2017**, *8*, 2277.

[73] J. Liao, Z. Ye, *Electrochim. Acta* **2018**, *259*, 626.

[74] A. Vizintin, R. Guterman, J. Schmidt, M. Antonietti, R. Dominko, *Chem. Mater.* **2018**, *30*, 5444.

[75] W. Liu, S. W. Lee, D. Lin, F. Shi, S. Wang, A. D. Sendek, Y. Cui, *Nat. Energy* **2017**, *2*.

[76] W. Liu, D. Lin, J. Sun, G. Zhou, Y. Cui, *ACS Nano* **2016**, *10*, 11407.

[77] Y.-J. Zhong, Z. Liu, X. Zheng, S.-L. Luo, N.-Y. Yuan, J.-N. Ding, *Solid State Ionics* **2016**, *289*, 23.

[78] H. Gao, Q. Lu, Y. Yao, X. Wang, F. Wang, *Electrochim. Acta* **2017**, *232*, 414.

[79] G.-C. Li, G.-R. Li, S.-H. Ye, X.-P. Gao, *Adv. Energy Mater.* **2012**, *2*, 1238.

[80] Y. Zhang, Y. Zhao, T. N. L. Doan, A. Konarov, D. Gosselink, H. G. Soboleski, P. Chen, *Solid State Ionics* **2013**, *238*, 30.

[81] Y. Zhang, Y. Zhao, Z. Bakenov, M. Tuiyebayeva, A. Konarov, P. Chen, *Electrochim. Acta* **2014**, *143*, 49.

[82] W. Li, Q. Zhang, G. Zheng, Z. W. Seh, H. Yao, Y. Cui, *Nano Lett.* **2013**, *13*, 5534.

[83] G. Ai, Y. Dai, Y. Ye, W. Mao, Z. Wang, H. Zhao, Y. Chen, J. Zhu, Y. Fu, V. Battaglia, J. Guo, V. Srinivasan, G. Liu, *Nano Energy* **2015**, *16*, 28.

[84] C. Milroy, A. Manthiram, *Adv. Mater.* **2016**, *28*, 9744.

[85] X. Liu, T. Qian, J. Liu, J. Tian, L. Zhang, C. Yan, *Small* **2018**, DOI: 10.1002/smll.201801536e1801536.

[86] L. Yan, X. Gao, J. P. Thomas, J. Ngai, H. Altounian, K. T. Leung, Y. Meng, Y. Li, *Sustainable Energy & Fuels* **2018**, *2*, 1574.

[87] X. Xu, D. Zhou, X. Qin, K. Lin, F. Kang, B. Li, D. Shanmukaraj, T. Rojo, M. Armand, G. Wang, *Nat. Commun.* **2018**, *9*, 3870.

[88] D. Zhou, Y. Chen, B. Li, H. Fan, F. Cheng, D. Shanmukaraj, T. Rojo, M. Armand, G. Wang, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 10168.

[89] A. Ghosh, A. Kumar, A. Roy, M. R. Panda, M. Kar, D. R. MacFarlane, S. Mitra, *ACS Appl. Mater. Interfaces* **2019**, *11*, 14101.

[90] G. Xu, Q.-b. Yan, A. Kushima, X. Zhang, J. Pan, J. Li, *Nano Energy* **2017**, *31*, 568.

[91] Y. Lu, Y. Jia, S. Zhao, L. Chen, Y. Su, F. Wu, J. Li, X. Liu, S. Chen, R. Chen, *ACS Appl. Energy Mater.* **2019**, *2*, 4151.

[92] F. Pei, L. Lin, D. Ou, Z. Zheng, S. Mo, X. Fang, N. Zheng, *Nat. Commun.* **2017**, *8*, 482.

[93] M. Yu, J. Ma, M. Xie, H. Song, F. Tian, S. Xu, Y. Zhou, B. Li, D. Wu, H. Qiu, R. Wang, *Adv. Energy Mater.* **2017**, *7*.

[94] G. Zhou, E. Paek, G. S. Hwang, A. Manthiram, *Nat. Commun.* **2015**, *6*, 7760.

[95] Z. Wang, Y. Dong, H. Li, Z. Zhao, H. B. Wu, C. Hao, S. Liu, J. Qiu, X. W. Lou, *Nat. Commun.* **2014**, *5*, 5002.

[96] G. Li, X. Wang, M. H. Seo, M. Li, L. Ma, Y. Yuan, T. Wu, A. Yu, S. Wang, J. Lu, Z. Chen, *Nat. Commun.* **2018**, *9*, 705.

[97] J. Chang, J. Shang, Y. Sun, L. K. Ono, D. Wang, Z. Ma, Q. Huang, D. Chen, G. Liu, Y. Cui, Y. Qi, Z. Zheng, *Nat. Commun.* **2018**, *9*, 4480.

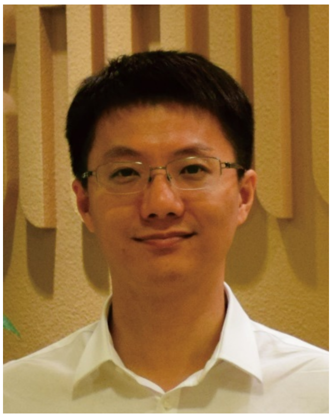
[98] W. Bao, X. Xie, J. Xu, X. Guo, J. Song, W. Wu, D. Su, G. Wang, *Chem. Eur. J.* **2017**, *23*, 12613.

[99] J. Song, X. Guo, J. Zhang, Y. Chen, C. Zhang, L. Luo, F. Wang, G. Wang, *J. Mater. Chem. A* **2019**, *7*, 6507.

[100] H. M. Kim, J. Y. Hwang, D. Aurbach, Y. K. Sun, *J. Phys. Chem. Lett.* **2017**, *8*, 5331.

Author biographies

Qianyi Guo received her BEng (2011) and MEng (2018) from South China University of Technology (China). Currently, she is pursuing her Ph.D. degree in the Institute of Textiles and Clothing at the Hong Kong Polytechnic University, under the supervision of Prof. Zijian Zheng. Her current research interests include the design and fabrication of high-performance flexible lithium-sulfur batteries.



Zijian Zheng is a Full Professor at the Institute of Textiles and Clothing at The Hong Kong Polytechnic University. He received his BEng (2003) in chemical engineering at Tsinghua University, Ph.D. (2007) in chemistry at the University of Cambridge, and postdoc training at Northwestern University (2008-2009). His research interests include surface and polymer science, nanofabrication, flexible and wearable materials, and devices.

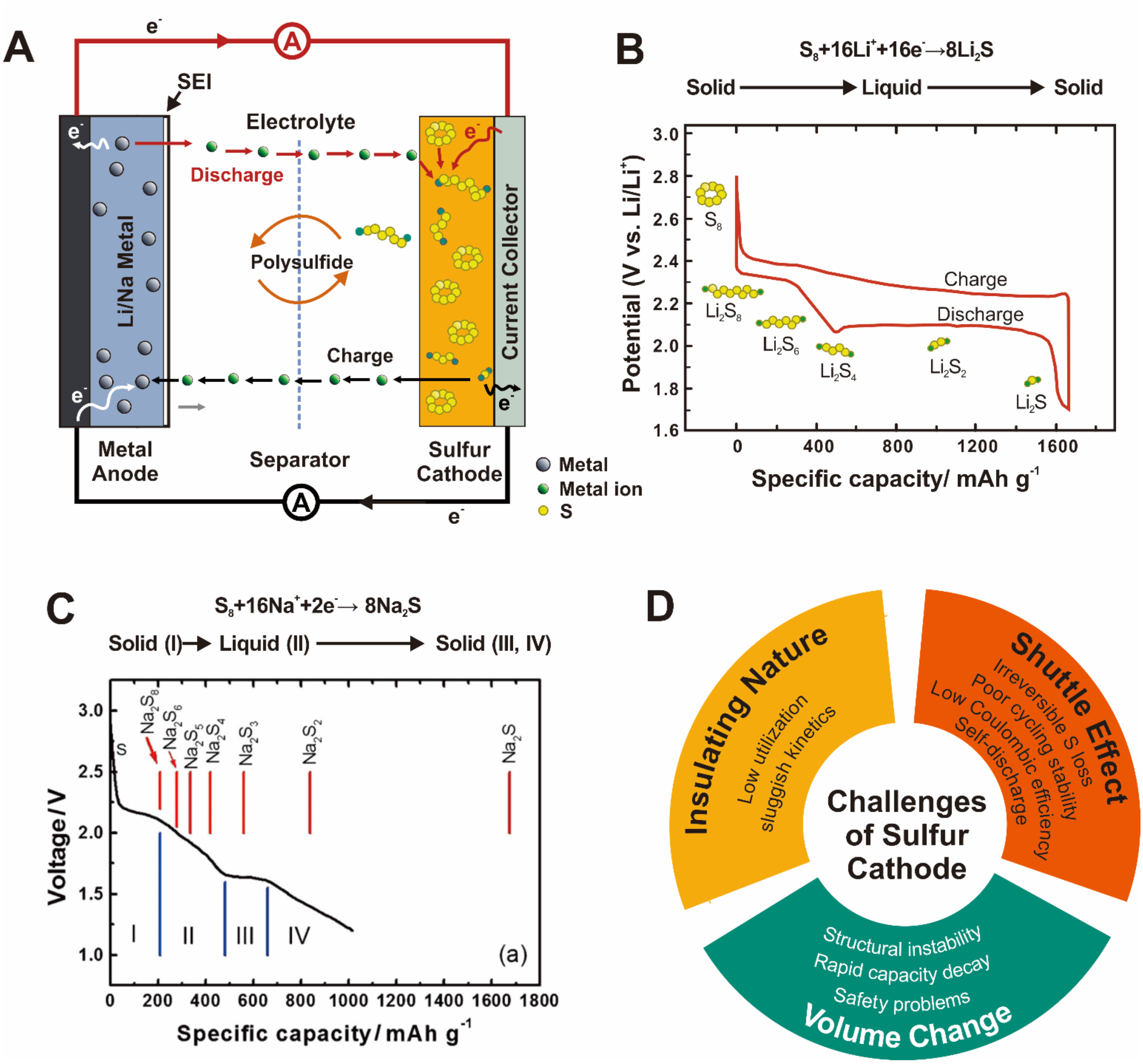


Figure 1. A) Diagram depicting the operation principle of the Li-S or Na-S system, which is typically composed of a metal anode, a sulfur cathode, a separator, and electrolyte. B) A typical charge/discharge voltage profile of Li-S battery. C) Theoretical versus practical discharge capacities of room-temperature Na-S battery. Reproduced with permission.[23] Copyright 2014, Wiley-VCH. D) Summary of the challenges in the sulfur cathode of Li-S and Na-S batteries.

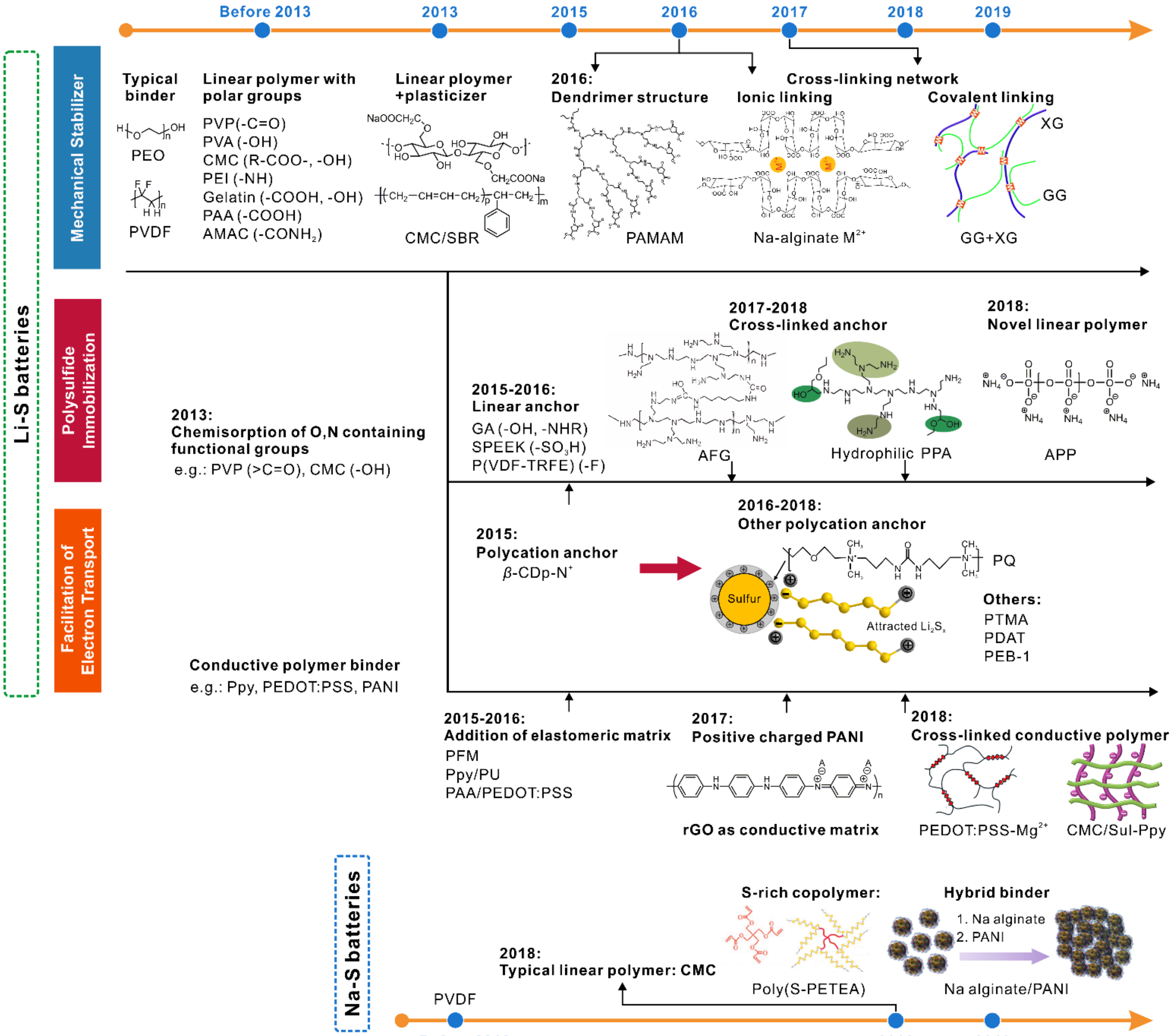


Figure 2. Timeline of the development of binders in terms of specific functions in Li-S and Na-S batteries. The binder in Li-S batteries has experienced a remarkable evolution in terms of functions, from fundamental structural and mechanical stabilizer (linear, hybrid,[38] dendrimer[46] and crossed-linked binder[48-49]), to versatile functions of polysulfide immobilization (polymer with functional groups [63-64, 66] or cation groups [69]) and facilitation of electron transport on the basis of conductive polymer.[85-86] It opens up the research of multifunctional binder. The analogous development route in the binder is found in Na-S batteries.[88-89] Reproduced with permission.[38] Copyright 2011, American Chemical Society. Reproduced with permission.[46] Copyright 2016, Elsevier. Reproduced with permission.[48] Copyright 2018, Royal Society of Chemistry. Reproduced with permission.[49] Copyright 2017, Royal Society of Chemistry. Reproduced with permission.[64] Copyright 2017, Wiley-VCH. Reproduced with permission.[66] Copyright 2018, Wiley-VCH. Reproduced with permission.[63] Copyright 2018, American Chemical Society. Reproduced with permission.[86] Royal Society of Chemistry Reproduced with permission.[85] Copyright 2018, Wiley-VCH. Reproduced with permission.[69] Copyright 2017, American Chemical Society. Reproduced with permission.[88] Copyright 2018, Wiley-VCH. Reproduced with permission.[89] Copyright 2019, Wiley-VCH.

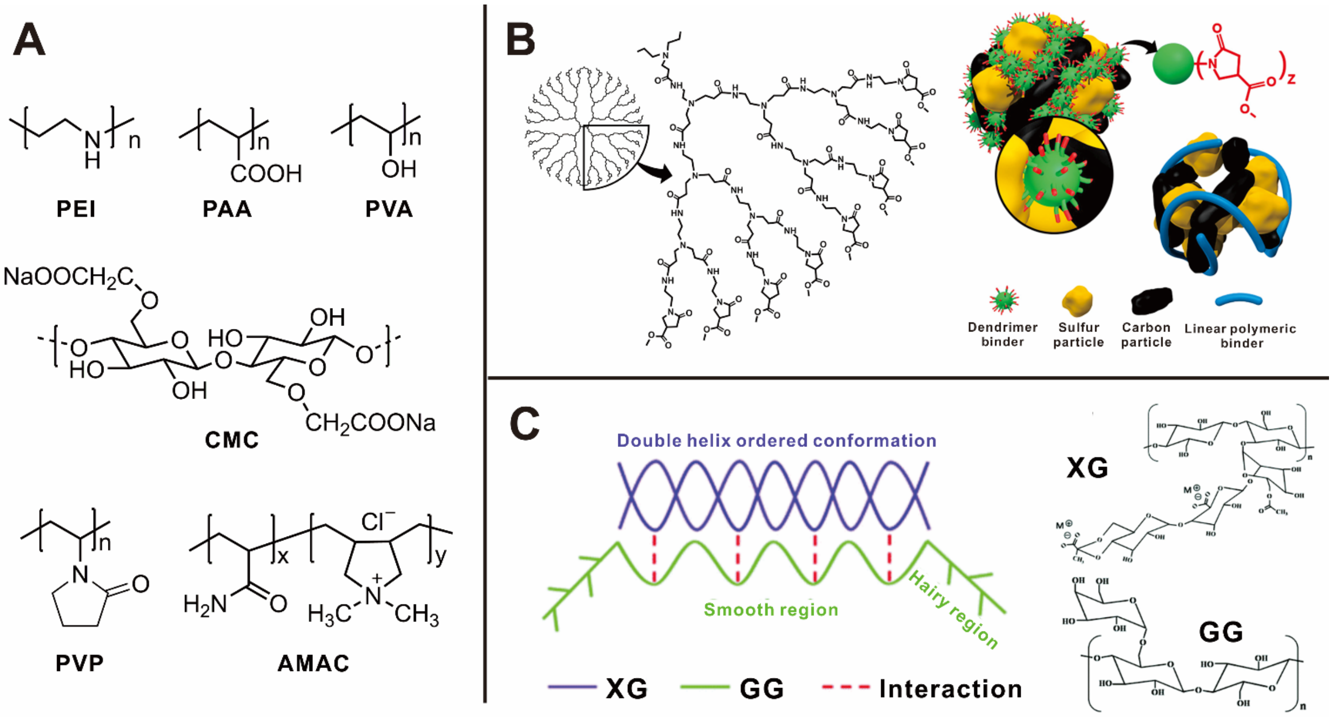
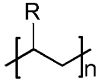
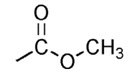
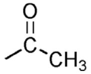
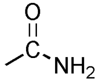
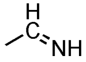
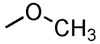


Figure 3. Binder as structural and mechanical stabilizer. A) Structures of some typical linear polymers used as binders. B) Schematic of polyamidoamine (PAMAM) dendrimer for used as branched-binder as compared with linear binder. Reproduced with permission.[46] Copyright 2016, Elsevier. C) Schematic of the intermolecular binding effect between guar gum (GG) and xanthan gum (XG), and corresponding chemical structures. Reproduced with permission.[49] Copyright 2017, Royal Society of Chemistry.

Table 1. The calculated binding energy of Li_2S and Li-S· species with various functional groups (R) based on the framework of vinyl polymers$–(CH_2–CHR)_n-$.[52]

 **R=**						$—C\equiv N$	$—F$	$—Cl$	$—Br$	$—CH_3$
Chemical class	Ester	Ketone	Amide	Imine	Ether	Nitrile	Fluoroalkane	Chloroalkane	Bromoalkane	Alkane
Binding energy with Li_2S	1.10	0.96	0.95	0.88	0.71	0.60	0.42	0.26	0.23	0.23
Binding energy with Li-S· species	1.26	1.20	1.23	1.02	1.01	0.77	0.62	0.46	0.42	0.30

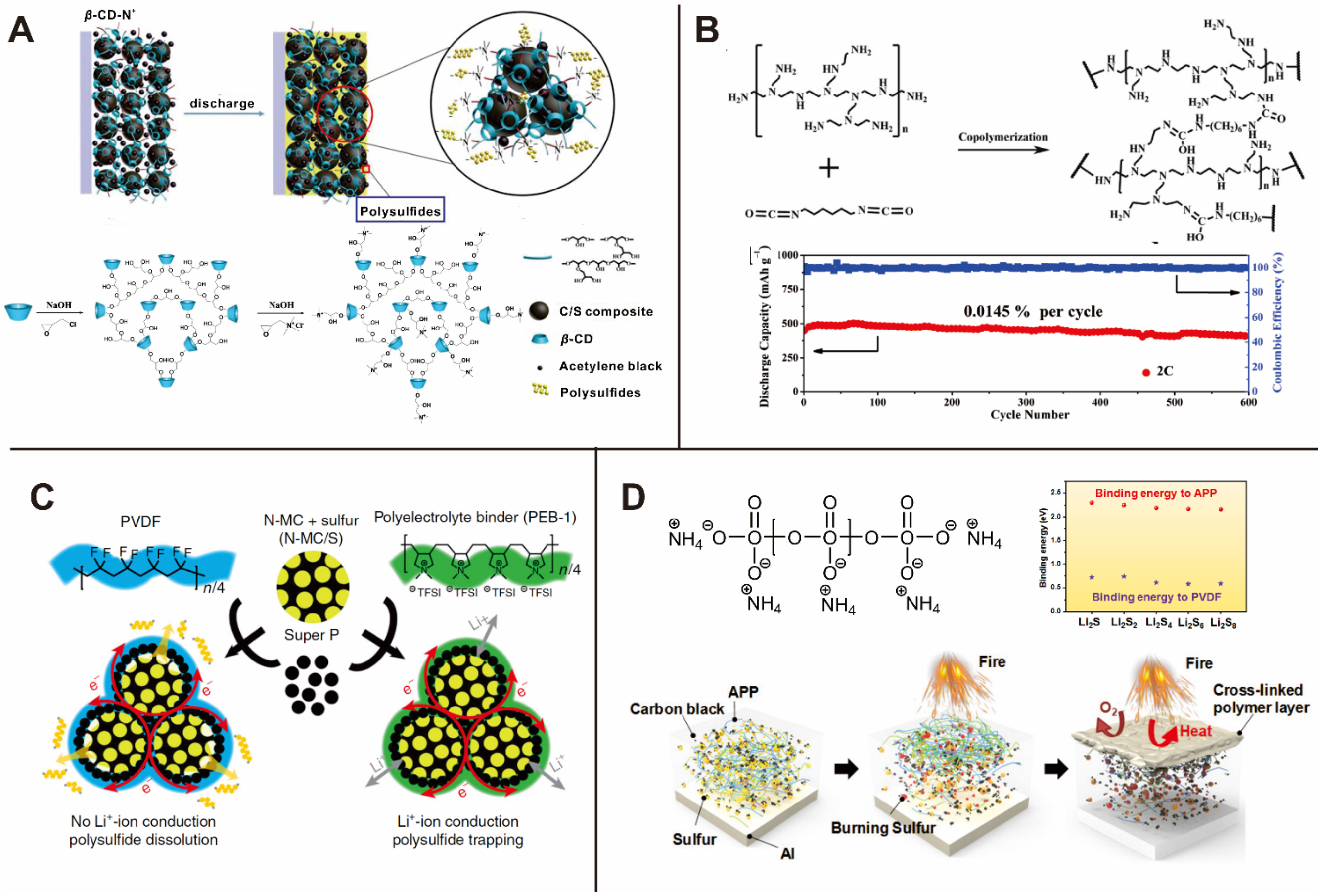


Figure 4. Binders for immobilization of polysulfide. A) Schematic representation of cathode configuration with the polycation β-cyclodextrin binder (β-CDp-N^+) and its synthesis. Reproduced with permission.[67] Copyright 2015, American Chemical Society. B) Synthesis scheme of amino-functional group (AFG) binder by copolymerization of PEI with HDI in DMF, and the long-term cycling performance of S@AFG cathode with 91.3% capacity retention at 2C (S≈0.7 mg cm^{-2}). Reproduced with permission.[64] Copyright 2017, Wiley-VCH. C) Illustration of the sulfur electrodes with PVDF or poly[(N,N-diallyl-N,N-dimethylammonium) bis(trifluoromethanesulfonyl)imide] binder (PEB-1). The cathode was comprised of sulfur-active materials loaded into N-doped mesoporous carbon (N-MC) hosts, 'Super P' as the conductive additive, and a polymer binder (PEB-1 or PVDF). Reproduced with permission.[72] Copyright 2017, Springer Nature. D) Ammonium polyphosphate (APP), the binding strengths of APP and PVDF with various Li-S species, and schematic of the flame-retardant mechanism of the APP binder. Reproduced with permission.[63] Copyright 2018, American Chemical Society.

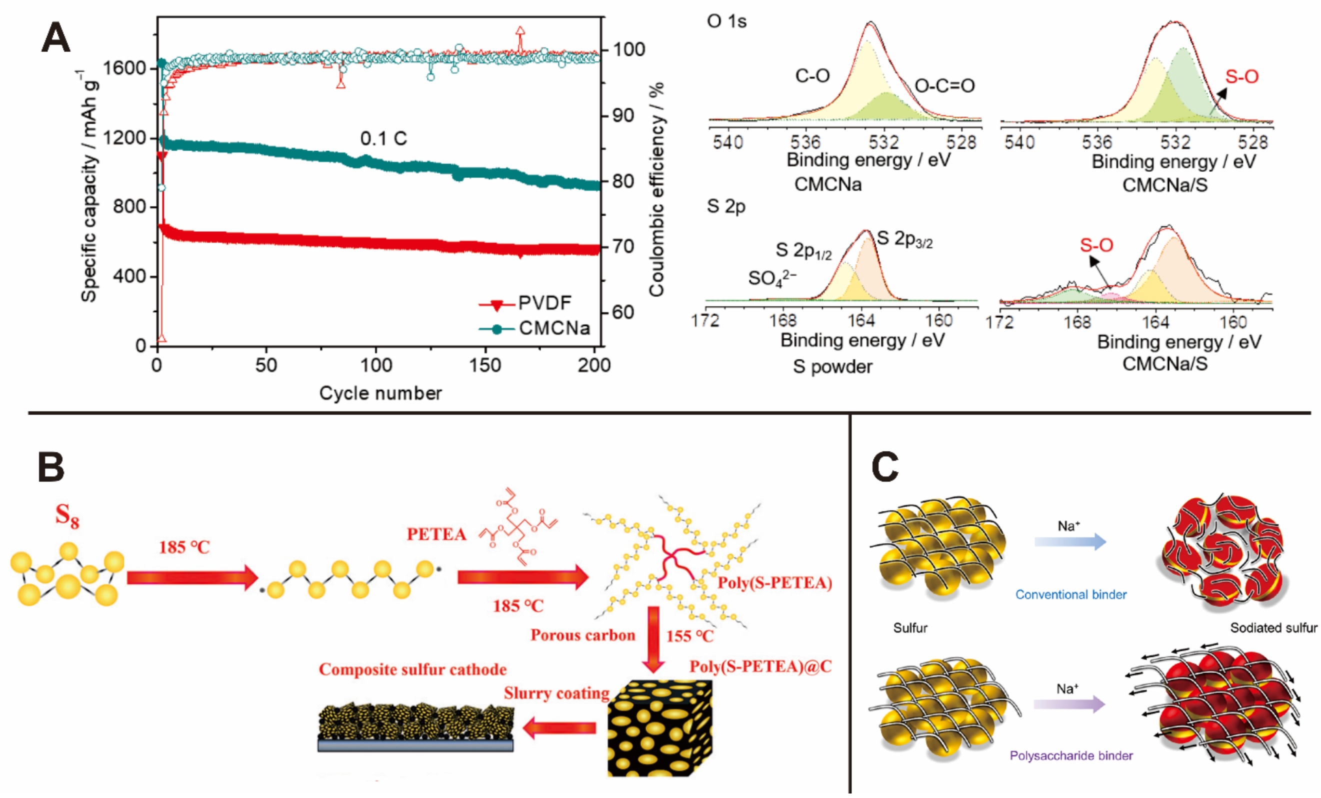


Figure 5. Binders developed for Na-S batteries. A) The comparison of cycling performances in Na-S cells using sodium carboxymethyl cellulose (CMCNa) or PVDF as binders. XPS spectra of O 1s and S 2p for sulfur, CMCNa, CMCNa/S mixture, illustrating of formation of strong S-O bond between binder and sulfur. Reproduced with permission.[87] Copyright 2018, Springer Nature. B) Schematic illustration of the preparation of poly(S-pentaerythritol tetraacrylate (PETEA)) binder in quasi-solid-state Na-S battery. Reproduced with permission.[88] Copyright 2018, Wiley-VCH. C) Schematic of the proposed role of the polysaccharide binder to counteract volume expansion of sulfur during sodium-ion insertion. Reproduced with permission.[89] Copyright 2019, American Chemical Society.

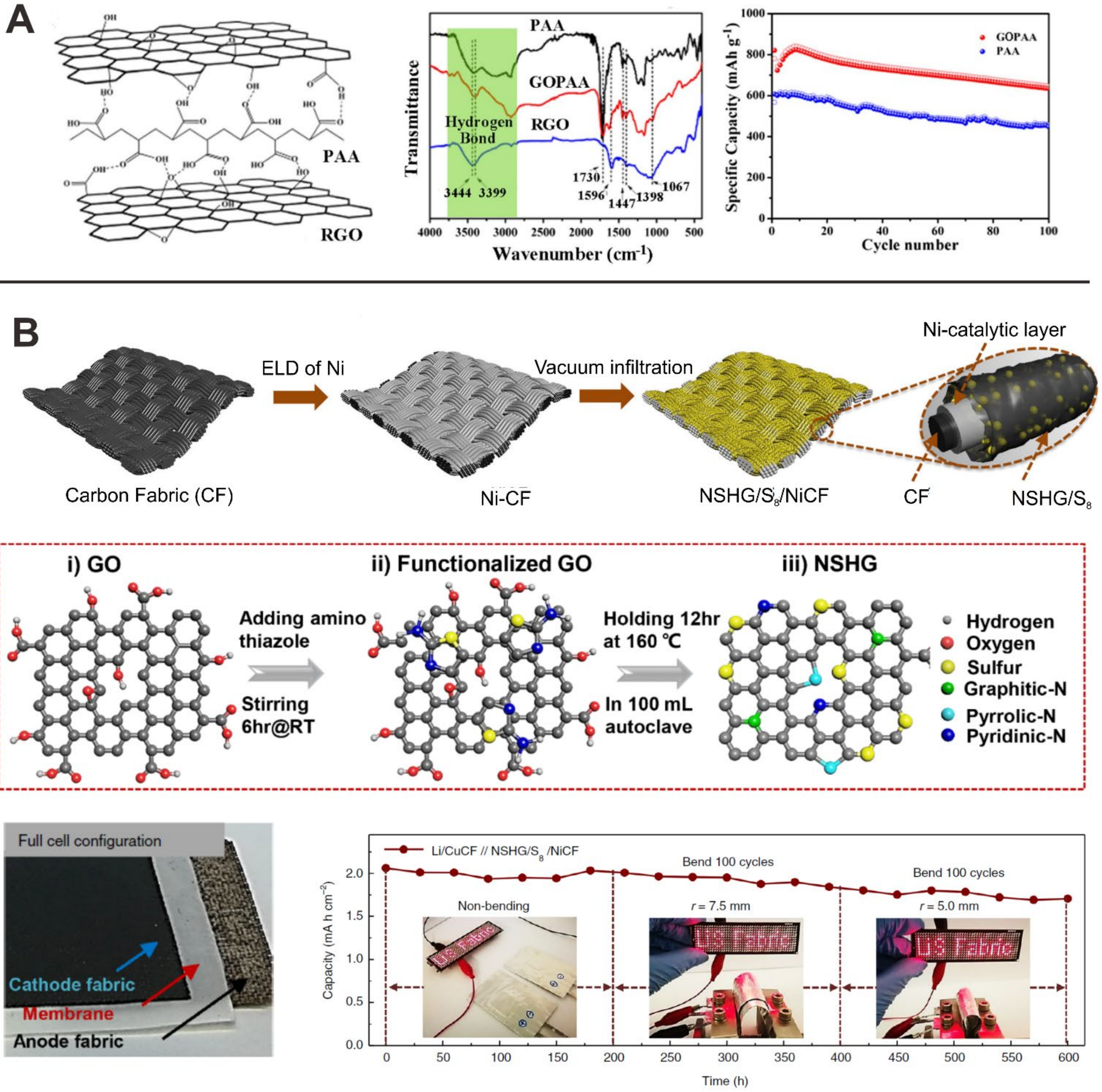


Figure 6. A) Schematic illustration for the formation of hydrogen bonding between the reduced graphene oxide (rGO) and polyacrylic acid (PAA), which was evidenced by the FT-IR spectra of PAA, rGO and rGO/PAA. Cycling performance of Li-S batteries with rGO/PAA and PVDF at 0.5 C. Reproduced with permission.[90] Copyright 2016, Elsevier. B) Schematic of the fabrication process and design principle of NSHG/S_8/NiCF cathode and the NiCF binder. The cell configuration in full-cell Li-S batteries and the corresponding areal capacities recorded during repeating bents at various radius (1 mA cm^{-2}, 150 cycles). Reproduced with permission.[97] Copyright 2018, Springer Nature.

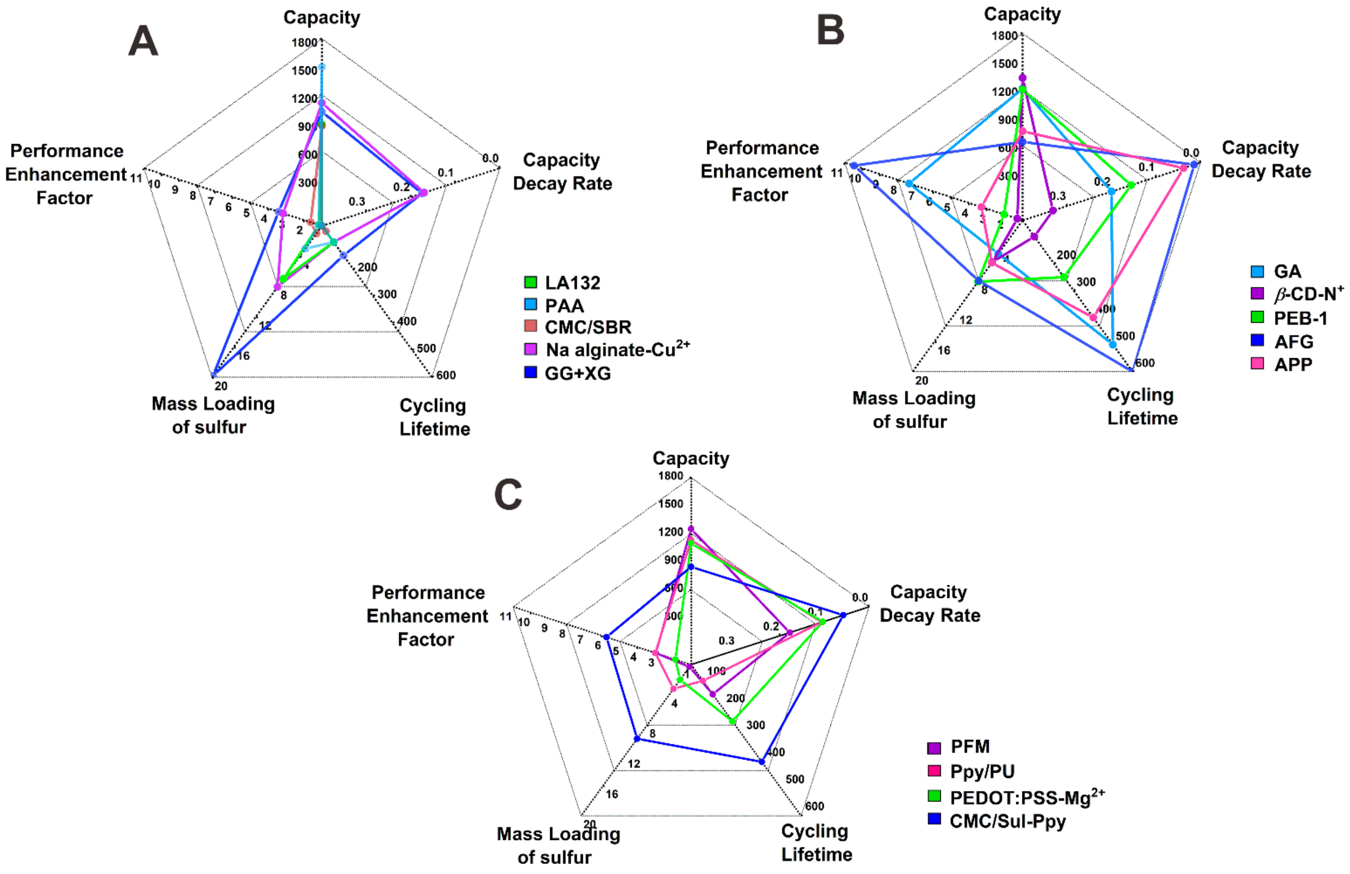


Figure 7. Performance comparisons of representative binder with specific function of A) structural and mechanical stabilizer (LA132 ($–[–R_1–R_2–CH_2–CH(CN)]_n$),[36] PAA,[100] CMC/styrene butadiene rubber (CMC/SBR),[38] Na alginate-Cu^{2+},[48] GG+XG[49]), B) polysulfide immobilization (gum arabic (GA),[55] *β*-CDp-N^+,[67] PEB-1,[72] AFG,[64] APP[63]) and C) facilitation of electron transport (poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM),[83] polypyrrole/polyurethane (Ppy/PU),[84] PEDOT:PSS-Mg^{2+},[86] CMC/4,4'-biphenyldisulfonic acid connected polypyrrole (CMC/Sul-Ppy) [85]). They are compared in terms of initial specific capacity (mAh g^{-1}), cycling decay rate (%), cycling lifetime, mass loading of sulfur (mg cm^{-2}) and cycling performance enhancement factor compared with PVDF basing on the decay rate.