

Recent Progress in Advanced Organic Electrode Materials for Sodium-Ion Batteries: Synthesis, Mechanisms, Challenges and Perspectives

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Rechargeable sodium-ion batteries (SIBs) are considered attractive alternatives to lithium-ion batteries for next-generation sustainable and large-scale electrochemical energy storage. Organic sodium-ion batteries (OSIBs) using environmentally benign organic materials as electrodes, which demonstrate high energy/power density and good structural designability, have recently attracted great attention. Nevertheless, the practical applications and popularization of OSIBs are generally restricted by the intrinsic disadvantages related to organic electrodes, such as their low conductivity, poor stability, and high solubility in electrolytes. Here, the latest research progress with regard to electrode materials of OSIBs, ranging from small molecules to organic polymers, is systematically reviewed, with the main focus on the molecular structure design/modification, the electrochemical behavior, and the corresponding charge-storage mechanism. Particularly, the challenges faced by OSIBs and the effective design strategies are comprehensively summarized from three aspects: function-oriented molecular design, micromorphology regulation, and construction of organic–inorganic composites. Finally, the perspectives and opportunities in the research of organic electrode materials are discussed.

1. Introduction


As the advanced electrochemical charge storage devices, lithium-ion batteries (LIBs) have been widely used in small electronic appliances and electric vehicles, and is likely to be the power supply equipment for the future large-scale energy storage projects.^[1,2] However, the high cost and the safety problems caused by exothermic side effects are important factors that limit the wide use of LIBs. Sodium-ion batteries (SIBs) have been extensively studied in recent years, attributed to the following reasons:^[3–10] 1) The advantages of rich Na resources, easy exploitation and low cost, makes it a good candidate in large-scale energy storage; 2) the half-cell potential of sodium is about 0.3 V higher than that of lithium. Consequently, the operating voltage of Na-ion batteries is lower than that of Li-ion batteries,

so electrolytes with lower decomposition potentials can be used, resulting in the better safety; 3) unlike LIBs, SIBs have no overdischarge characteristics, therefore they are allowed to discharge to zero volts, and maximize their energy density.

A large number of materials including both organic and inorganic materials have been applied as SIB electrodes. Compared with inorganic materials, organic electrode materials display the following merits:^[10] i) organic materials are usually composed of four elements (C, H, O, N), for which the synthesis steps are simple, the raw materials are easily available and environmentally benign; ii) the designability of organic molecules facilitate the targeted design and functionalization of organic electrodes; iii) the good flexibility of organic materials allow them to accommodate large Na⁺ ions without space constraints, thus favoring the rapid intercalation/deintercalation of sodium ions.

To date, a great amount of organic electrode materials has been designed and reported in SIBs.^[11–16] Organic sodium-ion batteries (OSIBs) have been rapidly developed and have shown great development prospects. Therefore, it is of great urgency and importance to summarize the progress and possibly draw general conclusions that could benefit the future advancement of this field. In this review, the organic electrode materials are classified into two main categories, i.e., organic small molecules and macromolecular polymers according to their molecular weights as shown in **Scheme 1**. Particularly the application of new azo compounds and MOFs as OSIB materials are also included in this review. Among them, organic small-molecular materials include mainly three different classes: carbonyl compounds (C=O),^[17–55] Schiff and pteridine derivatives (C=N),^[56–61] and azo derivatives (N=N).^[62] In carbonyl (C=O) compounds, quinones and ketones demonstrate higher redox potential, carboxylic acids however possess lower Na insertion voltage, while the anhydride compounds are recognized by their high specific capacity and long cycle life. Particularly, Schiff and pteridine derivatives based on the C=N bond show adjustable electrochemical activity. Azo derivatives based on the N=N bond on the other hand, could provide an opportunity for the development of OSIBs with both of high capacity and high rate, through the modification on the molecular structure. The macromolecular polymers used in OSIBs

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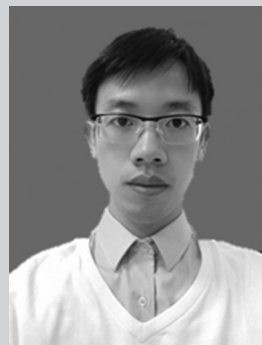
include mainly nitroxyl radical polymers, conductive polymers, organometallic polymers, conjugated microporous polymers, and metal–organic frameworks. The organic radical polymers, organometallic polymers usually exhibit faster kinetic properties, but their capacity is very low. COF (covalent organic framework) and MOF (metal organic framework) derived materials show structural advantages with good stability, of which the nanostructures and morphology can be readily manipulated to accommodate more Na^+ ions.^[64–100]

Nevertheless, the small-molecular organic electrode materials generally have the shortcomings of high solubility and poor stability, while organic polymer materials often have a low theoretical specific capacity and low electric conductivity. The effective strategy to solve these problems is summarized in the following three aspects: i) function-oriented molecular design, ii) morphology control, and iii) compositing organic materials with inorganic materials. For example, the introduction of electron absorbing group can increase the working voltage,^[17–19,40,42,62,77] and increasing π conjugated degree can improve the rate performance,^[43,44,54] while salinization and polymerization can effectively reduce the dissolution of organic electrode materials in electrolyte.^[20,25,30–33,37,49–52] In addition, proper morphology control can improve the stability of organic materials and the electrochemical performance for SIBs.^[21,22,30,35,46,96–100] The compositing of organic material with conductive material not only improves the stability, but also enhances the electric conductivity, so that the properties of the material can be brought into full play.^[23,24,36,39,41,60,61] It is worth to mention that, these strategies are universal and can provide the basic guideline for the design and development of the organic electrode materials of other metal ion rechargeable batteries in the future.^[126,127]

2. Research Progress of Organic Electrode Materials

2.1. Organic Small Molecules

Up to now, organic small molecules with different groups, including C=O (quinones and ketones, carboxylates, anhydrides, and imides derivatives), C=N (Schiff, pteridine derivatives), and N=N (azo derivatives) bond compounds, have been proved to be electroactive electrode materials for SIBs. Among them, the carbonyl compounds containing C=O bond is the most widely studied organic electrode materials, because of their unique multielectron reaction, high theoretical capacity and a wide structural diversity.^[17–55] Schiff and pteridine derivatives containing C=N bond has an adjustable electrochemical activity, in which plane structure and conjugated structure play an important role in stabilizing their electrochemical activity.^[56–61] Azo compounds containing N=N bonds are newly recognized as electrode materials for OSIBs; the experimental results show that the N=N bond acts as an electrochemical activity groups to reversibly bond with Na ions.^[62] Through reasonable design of their structures, there is great room for further development. Although electrode materials based on organic small molecules have shown interesting advantages, there are still some problems to be solved. For example, the poor conductivity of most C=O bond compounds limits the



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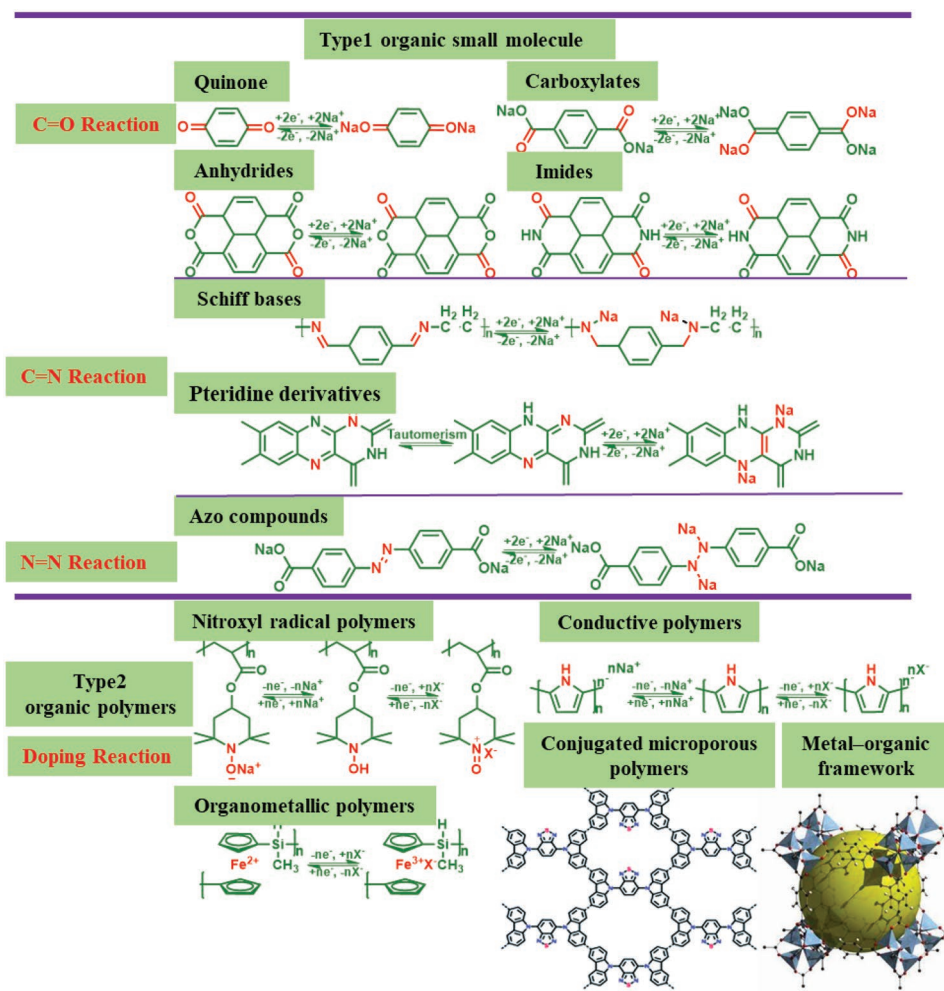
University Marburg, Germany (2008–2009) as a research scientist. She was also a visiting professor at Northwestern University (2014–2015). Her research mainly focuses on energy-storage materials and devices, such as nanocarbon materials, supercapacitors, and electrocatalysts.



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full play of their high theoretical capacity; the compounds with the C=N bond have the problem of low theoretical capacity and poor cycle stability;^[56–61] and the N=N bond azo compound exhibits high solubility in the electrolyte.^[62] Below, these three types of small organic molecules are discussed in detail as active electrode materials for SIBs.



Scheme 1. Proposed working principles of organic electrodes in SIBs with two types (organic small molecules and organic polymers).

2.1.1. C=O Bonded Compounds

At present, carbonyl compounds are the most widely applied organic materials in OSIBs. According to the type of functional groups, carbonyl materials can be generally categorized into three types, namely quinones and ketones,^[17–38] carboxylates,^[39–47] anhydrides,^[48–53] and imides^[48–53] (Scheme 1). Taking advantage of the structural diversity of carbonyl compounds, the redox behavior of carbonyl compounds can be controlled by regulating the inductive and resonance effect in molecules. However, this type of material also shows disadvantages such as low redox potential, high solubility, and low conductivity. Increasing the degree of π -conjugation or introducing electron-withdrawing groups, nanostructure design, and compositing with inorganic conductive material are recognized as effective strategies to overcome the above issues.^[17–19,40,42] The research progress and corresponding improvement methods of these four kinds of materials are introduced in detail below.^[17–51]

1) *Quinones and Ketones* (Its structure is shown in **Figure 1**): Quinones are a class of organic compounds with two double bonds of hexagonal cyclic diketone (containing two carbonyl groups)

in the structure. Recently, quinone-based electrode materials and their derivatives have attracted widespread attention owing to their higher redox potential compared with other organic materials.^[17] Kim et al.^[18] have confirmed by density function theory (DFT) that the introduction of electronegative groups into the quinone structure can significantly increase the storage potential of sodium. Their charge storage potential (vs Na^+/Na) follows such sequence: $\text{C}_6\text{F}_4\text{O}_2 > \text{C}_6\text{Cl}_4\text{O}_2 > \text{C}_6\text{Br}_4\text{O}_2 > \text{C}_6\text{H}_4\text{O}_2$. However, the high solubility of quinone-based materials in aprotic electrolyte is an urgent problem to be solved. Further study reveals that salinization, i.e., forming or introducing salt into the quinone-based compound is one effective strategy to increase the molecular polarity.^[19] Tarascon et al.^[20] reported a quinone salt (lithiated oxocarbon salt ($\text{Li}_2\text{C}_6\text{O}_6$)): the introduction of salt could increase the molecular polarity, and also the strong coordination bond of LiO/NaO partially hinders the dissolution of organic electrode material. At present, salinization is the most widely used approach to reduce the solubility of quinone-based materials. However, it is worth noting that the quinone salts usually undergo phase transformation during charge and discharge process, which normally leads to the pulverization of electrode materials, and causes serious capacity fading.

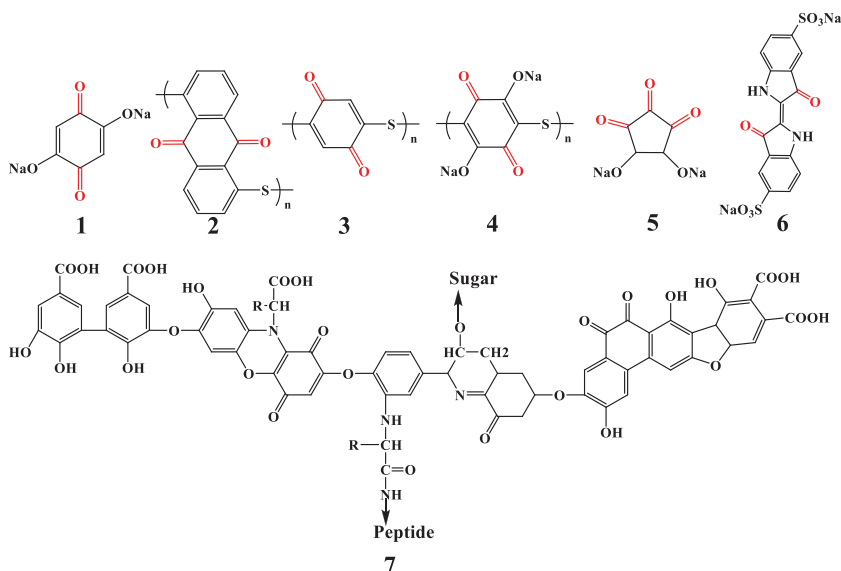


Figure 1. Structures of quinones (1–4) and ketones (5–7) as electrode materials.

In order to enhance electrochemical performance, various modification methods have been proposed, which mainly include design of the molecular structure and nanostructure of electrode materials, modification of the electrolyte viscosity and incorporation of the quinone structures into a polymeric moiety.^[21] For example, Zhu et al.^[21] prepared disodium salt of 2,5-dihydroxy-1,4-benzoquinone (Na_2DBQ , No. 1) for the first time which was applied as the anode electrode material for SIBs. The Na_2DBQ delivered a high capacity (265 mAh g^{-1} , 29.1 mAg^{-1}), long cycle life (181 mAh g^{-1} after 300 cycles), and good rate capability (160 mAh g^{-1} at 1.45 mA g^{-1}). The electrochemical reaction kinetics of organic compounds was greatly improved by controlling their morphology and size effect. The nanostructure construction can effectively improve the sodium-storage performance of quinone-based organic electrode materials. Wang et al.^[22] found that a nanorod structure could deliver a high capacity of 190 mAh g^{-1} and 90% retention over 100 cycles. Another way to solve the solubility problem of quinones is to composite them with other material.^[23–29] For example, an Al_2O_3 layer (2 nm) was successfully deposited on Na_2DBQ electrode surface to suppress the dissolution of Na_2DBQ , which showed significant enhancement on the SIB performance (reversible capacity of 212 mAh g^{-1} over 300 cycles).^[23] Wu et al.^[24] immobilized CNTs onto Na_2DBQ by a spray drying method, and the as obtained nanocomposite delivered a high reversible capacity (259 mAh g^{-1}) and excellent rate performance (142 mAh g^{-1} at 7 C). Chen et al.^[25] found that 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) with 60% carbon black exhibited high reversible capacity of 456 mAh g^{-1} at 0.1 A g^{-1} and cycling life with 436.5 mAh g^{-1} over 100 cycles for SIBs. Recently, Huang et al.^[26–29] investigated the effect of carbon materials on the organic electrode materials performance. The dissolution of C4Q can be effectively restricted by encapsulating it in CMK-3, and the stability and electronic conductivity of C4Q/CMK-3/SWCNTs are intensified by the 3D conductive network.^[26,27] Such structure can not only improve the conductivity and decrease the solubility of

organic materials, but also effectively buffer the volume change of and improve the long cycle stability of the batteries.

Second, the material morphology demonstrates significant effect on the cyclability and rate performance of organic electrodes. For example, Wang et al.^[30] revealed that the ion-diffusion can be significantly improved by forming a flake-like structure, which results in a high capacity and long-term cycle life. In addition, introducing quinonyl into polymerization unit is an effective method to improve the properties of electrode materials. For example, the poly(anthraquinonyl sulfide) (PAQS, No. 2) exhibited a capacity of 220 mAh g^{-1} , with an excellent rate performance of 160 mAh g^{-1} @ 6 A g^{-1} , and 85% retention after 500 cycles at 1.6 A g^{-1} , representing one of the best rate capabilities of quinones (Figure 2).^[31] Similarly, poly(benzoquinonyl sulfide) (PBQS, No. 3)^[32] and sodium salt of poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide) (Na_2PDS , No. 4)^[33] also exhibited an initial capacity of 247 mAh g^{-1} and 309 mAh g^{-1} at 50 mA g^{-1} and 100 mA g^{-1} , respectively. Ionizable sodium sulfonate functional groups lead to a significant enhancement of the structural stability of $\text{C}_{14}\text{H}_8\text{O}_2$, yielding excellent cycle and rate performance. In practical tests, the $\text{C}_{14}\text{H}_6\text{Na}_2\text{O}_8\text{S}_2$ and $\text{C}_{14}\text{H}_7\text{NaO}_5\text{S}$ as anode materials in SIBs exhibit high initial discharge capacities of 195 and 209 mAh g^{-1} , which are maintained at 131 and 93 mAh g^{-1} at 30 mA g^{-1} after 100 cycles, respectively.^[34]

Ketones with a high potential of $\approx 2\text{--}3 \text{ V}$ (vs Na/Na^+) are recognized as good candidates for cathode materials of OSIBs. This kind of materials can be reduced to the corresponding alcohols and then reoxidized to the original state in the electrochemical process, thus realizing the single-electron redox reaction. In 2013, Okada et al.^[35] first used disodium salt of rhodizonate (DSR, theoretical capacity of 500 mAh g^{-1}) in OSIBs, which delivered a capacity of about 150 mAh g^{-1} at 18 mAg^{-1} after 40 cycles. Wang et al.^[30] further revealed that, a pre-activation can cause cracks on the surface of DSR thus forming a flaky morphology, which could promote Na^+ diffusion in between the adjacent layers. Consequently, the as produced materials exhibited a high reversible capacity of 173.5 mAh g^{-1} @ 50 mA g^{-1} , which holds 115 mAh g^{-1} @ 5 A g^{-1} . Especially, excellent cycling stability was obtained with a reversible capacity of 110 mAh g^{-1} @ 1 A g^{-1} after 1500 cycles. Unfortunately, ketones always show a serious capacity loss due to their large volume change during the initial cycle. Croconic acid disodium salt (CADS, No. 5) has the same problem, which has a similar structure with DSR. To address this problem, Luo et al.^[36] used graphene oxides (GO) encapsulated CADS and minimizing by ultrasonic spray pyrolysis, which are two effective methods to reduce volume changes and suppression of pulverization (Figure 3). The as constructed composite material delivered a superior reversible capacity of 293 mAh g^{-1} . Benefiting from salinization, $\text{p-Na}_2\text{C}_6\text{H}_2\text{O}_6$ delivers a high capacity of 121 mA h g^{-1} after 50 cycles at 0.1 C and superior rate with 99.5 mA h g^{-1} at 20 C and long-cycling life for SIBs.^[25]

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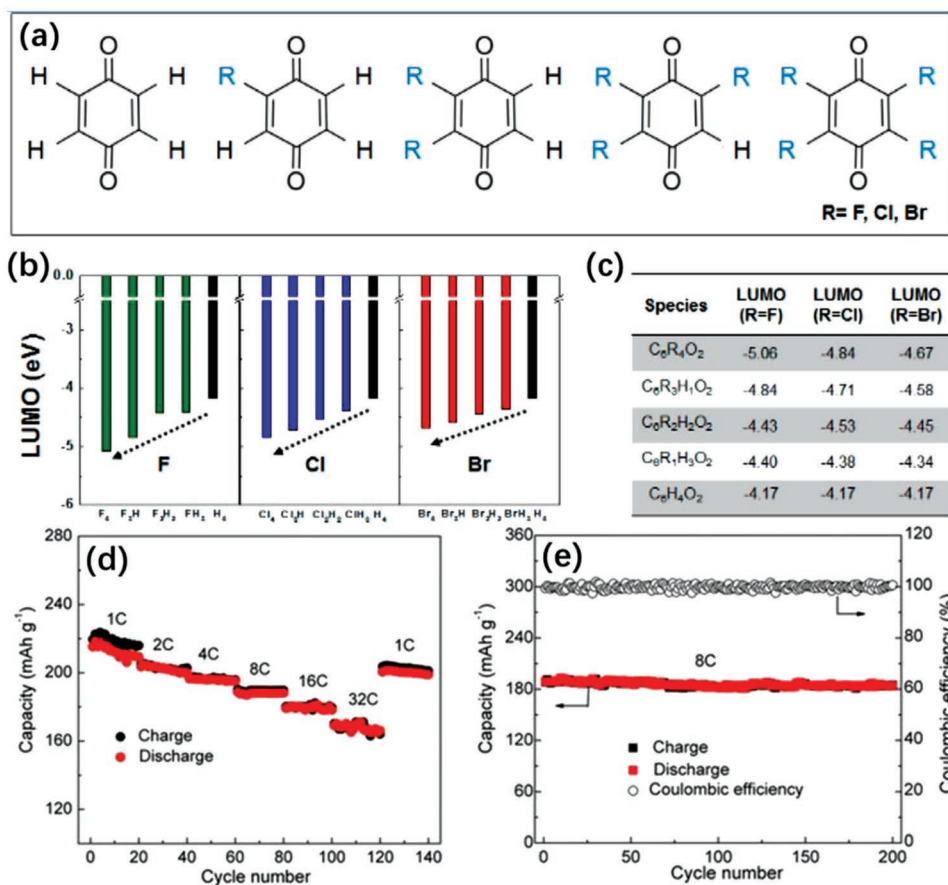


Figure 2. a) Chemical structure of $C_6R_4O_2$ molecules ($R = F, Cl, Br$). b,c) LUMO energies of $C_6R_4O_2$ molecules using DFT calculations. a–c) Reproduced with permission.^[18] Copyright 2015, American Chemical Society. d) Rate capability of PAQS at different C-rates; (1C = 200 mA g⁻¹). e) Cycling performance of PAQS at 8C rate (1600 mA g⁻¹). d,e) Reproduced with permission.^[31] Copyright 2015, Springer Nature.

In addition, the design and optimization of molecular structure can reduce the solubility of the organic electrode material and improve the battery performance. For example, introduction of other groups or polymerization can effectively prevent the dissolution of organic electrode materials in electrolytes. Indigo carmine (IC, No. 6) with polar sulfonate groups deliver a discharge capacity of 106 mAh g⁻¹ with a good cycling stability. This material exhibited an average voltage of 1.8 V versus Na⁺/Na and dropped only 20 mAh g⁻¹ after 40 cycles with an almost 100% coulombic efficiency (CE).^[37] On the other hand, a natural polymer humic acid (HA, No. 7) exhibited a comparably large initial discharge capacity of 244 mAh g⁻¹, but low capacity retention was observed at high rates owing to rapid capacity decay of organic material.^[38]

II) **Carboxylates:** Sodium-carboxylate-based material including aromatic ring connected with multi sodium carboxylates have been extensively investigated in OSIBs. Due to the effect of electron donor groups connected to carbonyl groups, sodium carboxylate derivatives usually have a low Na-insertion voltage (at a voltage below 1 V), which is ideal for anode material application from the viewpoint of high energy density and safety. Disodium terephthalate (Na₂TP, No. 8, Figure 4) was the first example of carboxylate material in

SIBs, which was simultaneously reported by two groups.^[39,40] Two Na⁺ ions per Na₂TP are stored in the electrode during the discharge, corresponding to a high capacity of 255 mAh g⁻¹. Particularly, this type of materials gives rise to the lowest discharge voltages in OSIBs which deliver a discharge platform of 0.3 V.

The atomic layer deposition (ALD) technology was used to coat thin layer of Al₂O₃ (2 and 5 nm) on the carboxylate-based electrode material surface, targeting to optimize the cycle stability (82.7% after 60 cycles), rate capacity (≈150 mAh g⁻¹ at 510 mA g⁻¹), and initial Coulombic efficiency.^[39] Significantly, most of the anode electrode materials in SIBs are conjugated systems, and the nonconjugated dicarboxylate are rarely studied. Ma and Wu did excellent work on nonconjugated dicarboxylate anode materials for SIBs. The 1,4-cyclohexanedicarboxylic acid (C₈H₁₂O₄, CHDA) and sodium humate (Na₂HA) exhibited high capacities of 284 mAh g⁻¹.^[41] Wu et al.^[42] reported that, green sodium huamate (Na₂HA) with nonconjugated carboxylate groups and functionalized by reduced graphene oxide (rGO), can procure a highly reversible anode material in SIBs. The composite material exhibited a highly reversible discharge capacity of 133 mAh g⁻¹ at 500 mA g⁻¹, and highly retention of 91.6% after 2000 cycles.

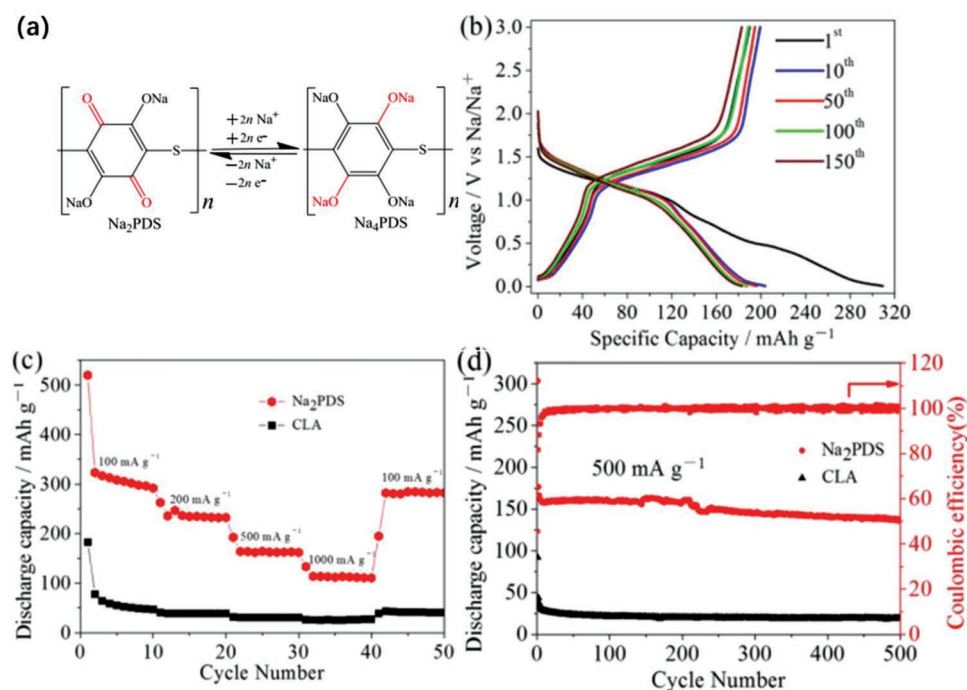


Figure 3. a), Schematic representation of the electrochemical reaction of Na₂PDS. b) Discharge and charge curves of the Na₂PDS electrode at a current density of 100 mA g⁻¹ between 0.01 and 3.0 V versus Na/Na⁺. c) Rate performances for the electrodes made of CLA and Na₂PDS at different current densities of 100, 200, 500, and 1000 mA g⁻¹. d) Cycling performances the electrodes made of CLA and Na₂PDS at a current densities of 500 mA g⁻¹. a–d) Reproduced with permission.^[33] Copyright 2016, The Royal Society of Chemistry.

In addition, some researchers found that the operational voltage of carboxylate-based materials has been tuned by linking different substituents in the molecular structure.^[40,43] Lee's et al.^[40] research results indicate that substitutes with

strong electronegativity could withdraw electron density from the conjugated carbon scaffold leading to a boosted discharge voltage. According to the relevant articles, we know that the order of discharge voltage is F-Na₂TP (No. 12) > NO₂-Na₂TP

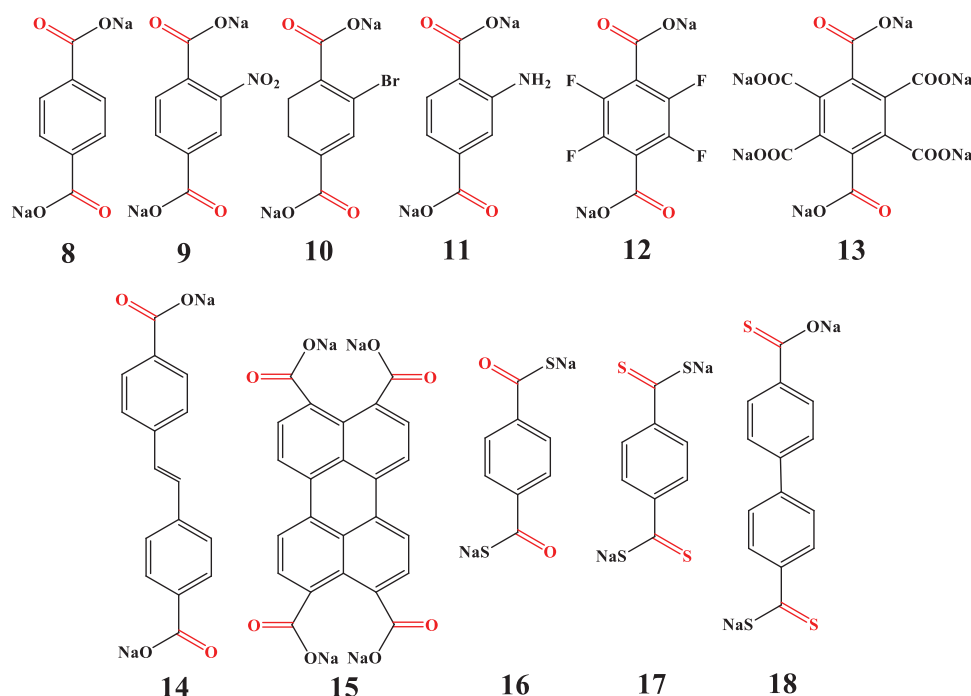


Figure 4. Structures of carboxylates as electrode materials.

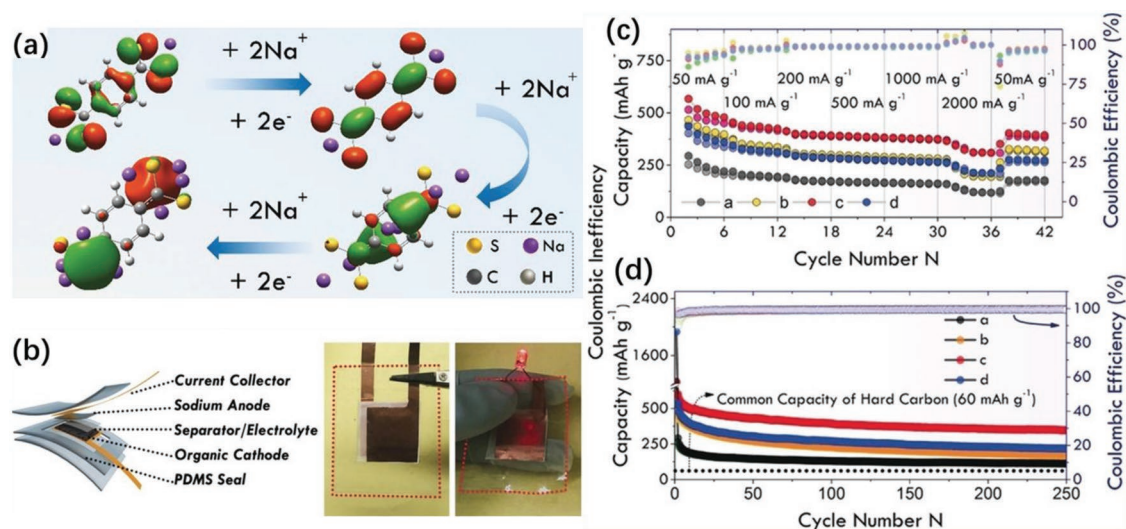


Figure 5. a) Calculated HOMO plots of molecule 17 with different uptake amounts of sodium. b) Prototype of a flexible organic battery. c) Rate capability and d) cycle stability at 500 mA g⁻¹. a-d) Reproduced with permission.^[47] Copyright 2017, Wiley-VCH.

(No. 9) > (COONa)-Na₂TP (No. 13) > Br-Na₂TP (No. 10) > NH₂-Na₂TP (No. 11) > Na₂TP. It is worth noting that the F-Na₂TP and NO₂-Na₂TP exhibited a higher capacity, but rapid capacity decay due to the irreversible formation of NaF and NaNO₂ limit their applications. Meanwhile, although the amino group is electronegative, it can result in a lower discharge voltage than the nonsubstituted compound owing to the dominant π donor effect. Furthermore, extending the π -conjugated system can effectively improve the chemical stability, conductivity and decrease the solubility of carboxylate-based materials.^[44–49] For example, the 4,4'-biphenyldicarboxylate sodium delivers 100 mAh g⁻¹ discharge capacity at 3740 mA g⁻¹,^[44] and Wang et al.^[45] demonstrated an extended π -conjugated sodium 4,4'-stilbene-dicarboxylate (SSDC, No. 14) showing an excellent rate performance of 110, 90, 72 mAh g⁻¹ at a high current density of 2, 5, 10 A g⁻¹ respectively, and kept 70% of capacity at 1 A g⁻¹ after 400 cycles. The anhydrides-derived multicarboxylate sodium salt of 3,4,9,10-perylene-tetra-carboxylic acid (NaPTCDA, No. 15) was also used as anode material in SIBs, and exhibited stable cycle life over 300 cycles due to the extended conjugated structure.^[46]

In addition, the introduction of sulfur atoms with larger atom radius and electron density compared to oxygen atom is another efficient way to increase the electrical conductivity, thus leading to the higher cycle stability and rate performance (No. 16–18).^[47,48] Surprisingly, the substitution of oxygen in carboxylate group with sulfur can also improve the capacity of SIBs. When two and four sulfur atoms are incorporated in Na₂TP, the material delivers a larger capacity of 466 mAh g⁻¹ and 567 mAh g⁻¹ at 50 mA g⁻¹. The electron-rich sulfur substituted molecules can store additional sodium ions by DFT calculations, which thus benefit the improvement of battery capacity and stability compared to the traditional carboxylic acid based organic electrode.^[47] Besides, this type of materials demonstrate good flexibility, a flexible battery model was also developed to show their potential applications in flexible bioelectronics (Figure 5).

Finally, nanostructure engineering of the organic materials demonstrates another way for the improvement of their electrochemical performance. For instance, Wan et al.^[48] disclosed the main role of nanoeffects on the electrochemical performance of sodium terephthalate. The experimental results show that the nanosheet-like sodium terephthalate has an improved capacity (248 vs 199 mAh g⁻¹), higher rate capability (59 vs 38 mAh g⁻¹ at 1250 mA g⁻¹) and superior cycling stability (105 vs 60 mAh g⁻¹ after 100 cycles at 250 mA g⁻¹) compared with the bulk counterpart.

III) *Anhydrides and Imides*: Anhydride-based materials commonly have an aromatic and two anhydride groups, and have high specific capacity and long cycle performance due to the large conjugated structures and multielectron reaction. Up to now, among the organic anhydride electrode materials, pyromellitic dianhydride (PMDA, No. 19, Figure 6), 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA, No. 20), and perylene 3,4,9,10 tetracarboxylic dianhydride (PTCDA, No. 21) have been widely applied in SIBs.^[49–52] In particular, the anhydrides could accommodate adjustable amounts of Na⁺ ions with manipulated discharge voltages. For instance, PTCDA can generally store two Na⁺ within the potential window of 1.0–3.0 V, and exhibited a reversible capacity of 145 mAh g⁻¹ @ 91 mAh g⁻¹.^[48] But when it is deeply discharged to 0.01 V, PTCDA can uptake 15 Na⁺ and delivered extremely high capacity of 1017 mAh g⁻¹ in the initial cycle.^[50]

The structural formula of imide is R–C(O)–N(R)–C(O)–R, in which N atoms are connected to two carbonyl groups and connected directly to aromatic nucleus. Usually, small-molecule imides have high solubility in electrolyte, so it is difficult to be directly used in electrode materials. Based on this, salinization and polymerization are often used to reduce their solubility. Dimide disodium salt and polyimide are often used in SIBs.^[51–55] Due to the strong electronic properties of Na, diimide salts (No. 22) as anode material show lower discharge

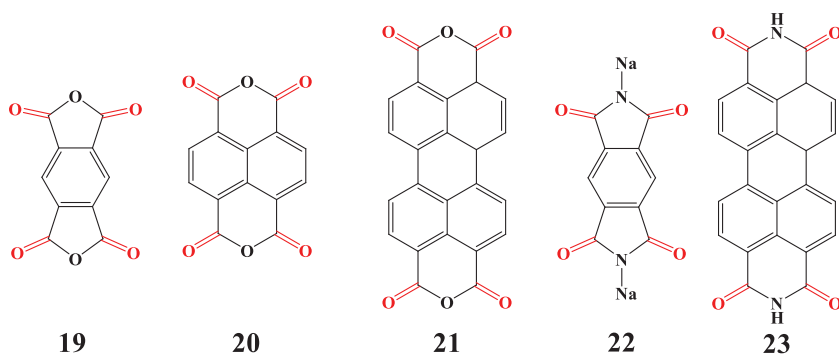


Figure 6. Structures of anhydrides (19–21) and imides (22, 23) as electrode materials.

voltage in both electrolyte and aprotic electrolytes.^[51] Besides, this material demonstrated a good cycle stability (90 mAh g⁻¹ after 100 cycles), making it a competitive electrode material in OSIBs. Another approach to eliminate the electrode dissolution is to increase the degree of conjugated molecules. For example, the 3,4,9,10-perylene-bis(dicarboximide) (PTCDI, No. 23) of the large π -conjugated structure with strong hydrogen bond between components, which delivered a high reversible specific capacity of 140 mAh g⁻¹ @ 20 mA g⁻¹ and good rate performance (103 mAh g⁻¹ @ 600 mA g⁻¹).^[52] In particular, this PTCDI shows the advantages of commercialization with low cost, nontoxicity, representing a new alternative cathode for OSIBs. Zhao et al.^[53] synthesized pyromellitic

dianhydride-based polyimides [C₁₆H₆O₄N₂]_n by simple one-step hydrothermal method. It delivered a capacity of 125 mAh g⁻¹ at 25 mA g⁻¹ over 100 cycles and 43 mAh g⁻¹ at 2 A g⁻¹.

2.1.2. C=N Bonded Compounds

To improve the capacity of Schiff base electrode material, some Schiff bases with carboxylate end groups (No. 30–36, Figure 7) are reported. The results indicate the operation voltage of carboxylate (No. 31), Schiff base (No. 32, 33), and carboxylate-Schiff base (No. 34) can be efficiently controlled by introducing carboxylate group. The DFT calculations confirmed that the active Hückel co-planar groups (–OOC–Ar–C=N– and –N=C–Ar–C=N–) provides storage location of Na-ion, and the isoelectronic groups (–OOC–Ar–N=C– and –C=N–Ar–N=C–) do not serve as active centers, but they can stabilize the discharge/charge process owing to favoring the π – π interaction or the loss of planarity and attenuate N–N repulsions. Similarly, the non-active Ar group also plays an important role for stabilizing the Schiff bases structure. For instance, the compounds (No. 35, 36) lacking of Ar-group show poor stability and capacity. Therefore, introduction the conjugated and planar structures is an efficient way to improve the electrochemical activity of the oligomeric

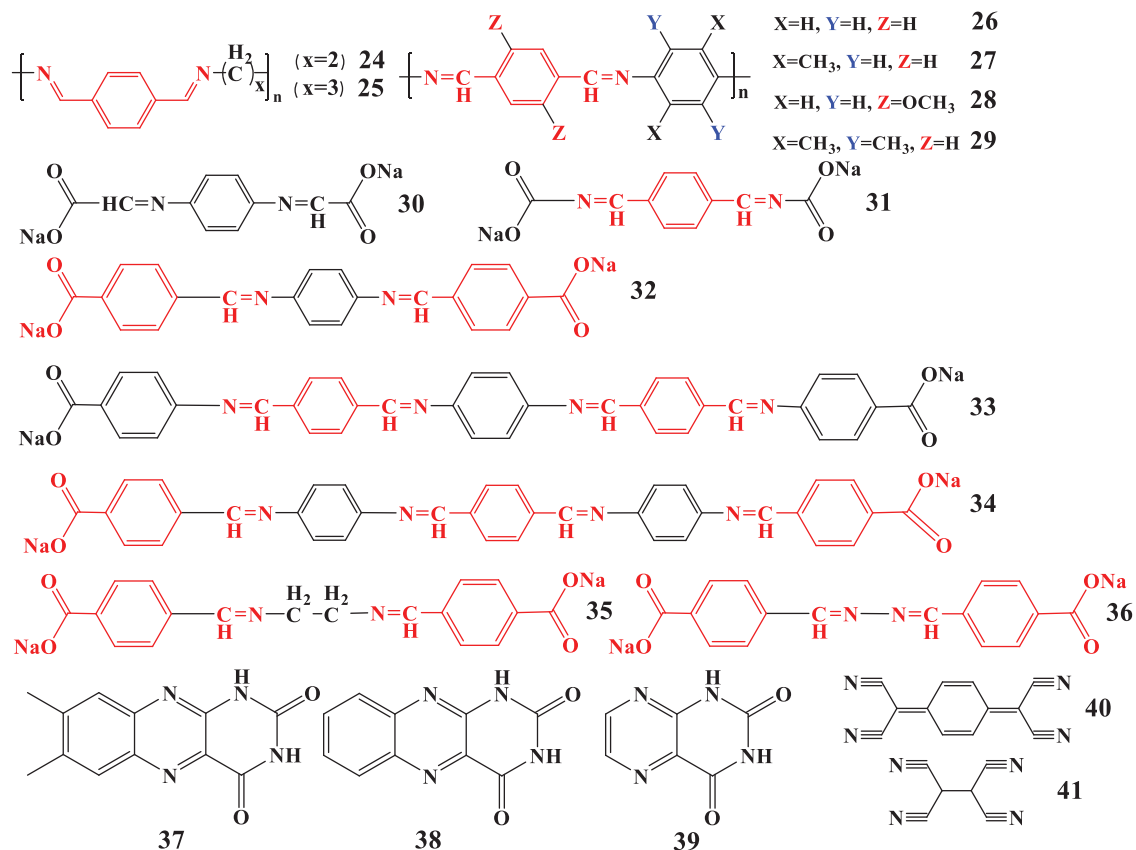


Figure 7. Structures of Schiff bases (24–36) and pteridine derivatives (37–41) as electrode materials.

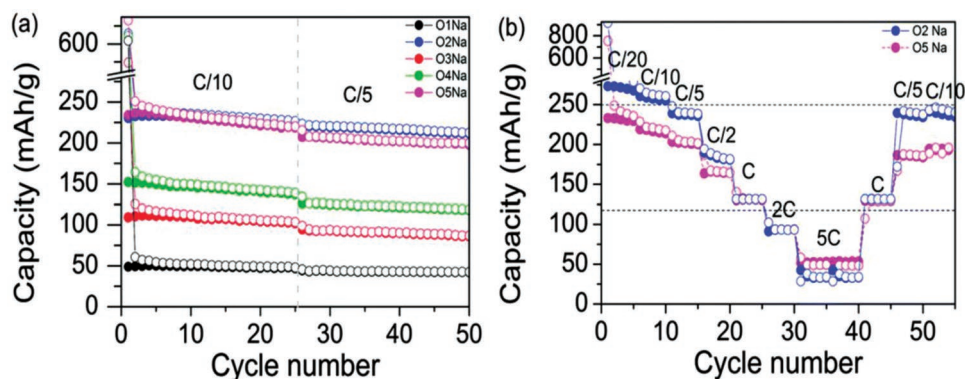


Figure 8. a) Cyclability for oligomers O1–O5 (30–34) in their sodiated forms, and b) rate capability for five cycles at C/20, C/10, C/5, C/2, C, 2C, 5C, C, and C/5 for O2Na (blue) and O5Na (pink). a,b) Reproduced with permission.^[56] Copyright 2015, The Royal Society of Chemistry.

Schiff bases materials. From the results of these studies, the oligomeric Schiff base compounds exhibited high capacities (up to 340 mAh g⁻¹), > 98% CE after a few cycles at a low discharge voltage (<1.2 V) (Figure 8).^[56]

In addition to Schiff bases, the most common C=N bond compounds are pteridine derivatives. The use of pteridine derivatives with biologically occurring redox centers has great potential in OSIBs electrode materials.^[57] Inspired by the heterocyclic with contain pteridine (1,3,5,8-tetraazanzphtalene) nucleus, Kang et al.^[58] designed and synthesized a series of derivatives as cathodes of OSIBs. The XPS, FT-IR and DFT calculations confirm that the conjugated diazabutadiene region acts as a redox activity center, which is beneficial to the electron transfer reaction after reduction of nitrogen. The derivatives of lumichrome, alloxazine and lumazine were also tested in SIBs, and exhibited capacities of 138, 168 and 70 mAh g⁻¹ at 20 mA g⁻¹, respectively. When these materials are combined with conductive carbon materials, their capacities could be improved to 225 (lumichrome, No. 37), 255 (alloxazine, No. 38) and 220 (lumazine, No. 39) mAhg⁻¹. Furthermore, tetracyanoethylene (TCNE, No. 41) and tetracyanoquinodimethane (TCNQ, No. 40) with C≡N bonds were investigated for OSIB.^[59–61]

2.1.3. N=N Bonded Compounds

The azo compounds based on azo group (N=N) are a new type of organic electrode material. The azo group can be used as redox center for reversible electrochemical reaction with Na⁺. The reversible redox chemistry between azo compounds and Na⁺ provides an opportunity for the development of long cycle and high rate SIBs. For instance, Luo et al.^[62] studied the electrochemical behavior and reaction mechanism of azo compounds (azobenzene (AB, No. 42, Figure 9), 4-(phenylazo) benzoic acid sodium salt (PBASS, No. 43), and azobenzene-4,4'-dicarboxylic acid sodium salt (ADASS, No. 44)) in SIBs. B is the basic model of aromatic azo compounds which contains only one azo group with electrochemical activity. The cycle stability of this material is very poor owing to its high solubility in organic electrolytes. In order to overcome this disadvantage, PBASS and ADASS were formed by introducing carboxyl groups at both ends of AB. The as prepared ADASS

demonstrated a high specific capacity (170 mAh g⁻¹ at 0.2 C), high rate capacity (113 mAh g⁻¹ at 10 C and 98 mAh g⁻¹ at 20 C), and long cyclic stability (a reversible capacity of 98 mAh g⁻¹ after 2000 cycles at 20 C).

2.2. Organic Polymers

2.2.1. Conjugated Conductive Polymers

Conjugated conductive polymers (CPs) are recognized as the first kind of organic polymer applied in OSIBs. Research on CPs began in 1985 with the polyacetylene (PAC, No. 45, Figure 10) and polyparaphenylene (PPP, No. 46).^[63] So far, polypyrrole (PPy, No. 47)^[64–67] and polyaniline (PAN, No. 48)^[68–70] are two traditional CPs that have been widely studied. CPs were usually synthesized in the p-doped state and can undergo n-doping or p-doping electrochemical reactions in different controlled voltage regions. There are two main factors that affect the performance of conductive polymers: low doping degree and low capacity utilization of polymer; followed by p-doped polymer are not the main body of sodium storage. Deng et al.^[71] reported an all-organic SIB by polytriphenylamine (PTPAN, No. 49) as the cathode and polyanthraquinonyl sulphide (PAQS) as the anode. The battery delivered a considerable high specific energy of 92 Wh kg⁻¹. PTPAN materials are reported to display a high reversible capacity of 98 mAh g⁻¹ (90% of theoretical capacity) at a quite high voltage of 3.6 V, and a surprisingly high rate capability (96 mAh g⁻¹ @ 2 C, 88 mAh g⁻¹ @ 20 C), and a stable cycle life with 97% capacity retention over 200 cycles at 5 C rate.^[31] In addition, noncrystalline oligopyrene (OPr, No. 50) was synthesized by interfacial polymerization also exhibited a voltage plateau at 3.5 V during discharge and a high energy density of 423 Wh kg⁻¹.^[72,73]

Conducting polymers show general advantages with intrinsic high electronic conductivity and high redox potentials. However, their discharge platforms are not obvious because of the low density of active center in polymer skeleton, which leads to the relatively low specific capacity of energy density. An effective strategy is to introduce redox-active groups into polymer chains, thereby enhance electrochemical activity of the material, and at the same time, these groups can provide a certain

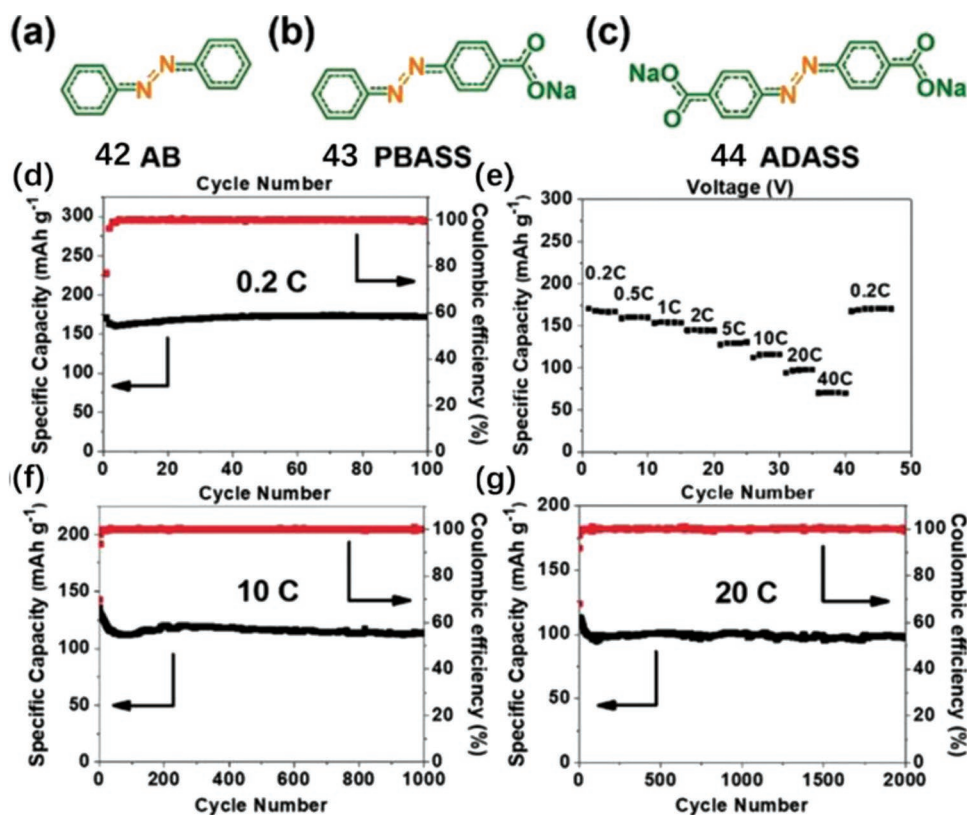


Figure 9. Molecular structure of a) AB, b) PBASS, and c) ADASS. The electrochemical performance of ADASS in Na-ion batteries: d) de-sodiation capacity and Coulombic efficiency versus cycle number at the current density of 0.2C; e) rate performance at various C-rates; de-sodiation capacity and Coulombic efficiency versus cycle number at f) 10C and g) 20C. a–g) Reproduced with permission.^[62] Copyright 2017, Wiley-VCH.

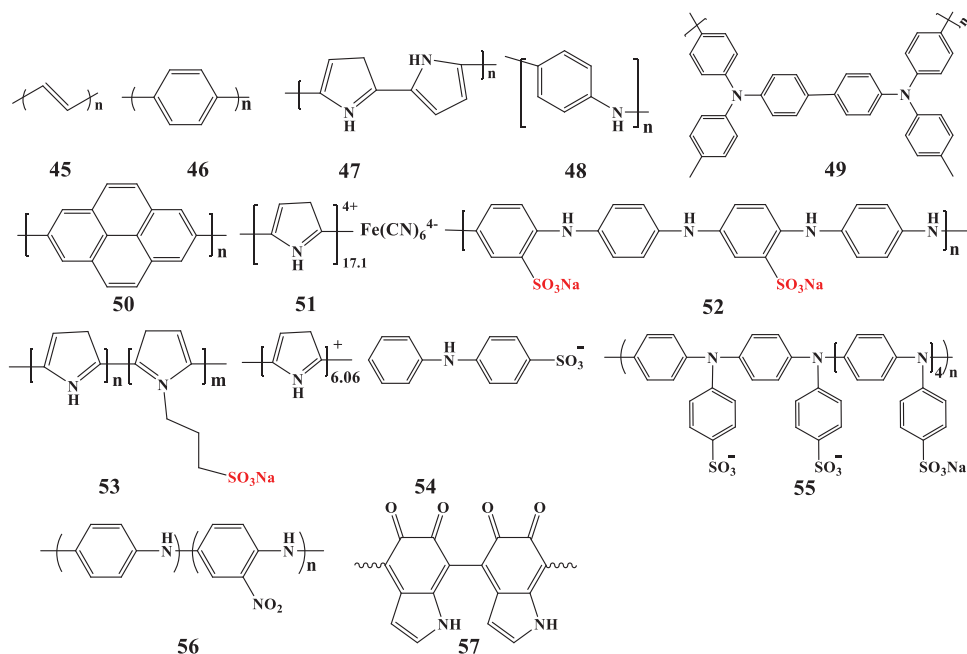


Figure 10. Structures of conductive polymers (Nos. 45–57) as electrode materials.

contribution to the redox capacity of the material. For example, the PPy/FC (No. 51) with the introduction of inorganic redoxactive ferricyanide anions deliver a high capacity of 135 mAh g⁻¹ with 85% retention after 100 cycles.^[74]

Polyaniline-co-aminobenzenesulfonic sodium (PANS, No. 52) synthesized by grafting the electron-withdrawing -SO₃Na group on polyaniline chains exhibited a high capacity (133 mAh g⁻¹) and excellent cyclical stability with 96.7% retention after 200 cycles owing to the immobile doping and effective activation of the sulfonate group.^[75] Poly(pyrrole-co-(sodium-3-(pyrrol-yl) propanesulphonate)) (PPy-PS, No. 53),^[76] diphenylamine-4-sulfonate-doped PPy (PPy/DS, No. 54),^[74] and poly(diphenylaminesulfonic acid sodium) (PDS, No. 55)^[77] were obtained by the same strategy. The PPy-PS copolymer exhibited effective Na storage with considerably high voltage (3.4 V), reversible capacity (85 mAh g⁻¹) and kept quite steady after 100 cycles. PPy/DS composite showed a quite high reversible capacity of 115 mAh g⁻¹, excellent rate capability and cycling stability. PDS can deliver a high voltage (3.6 V), a stable cycle life (85% retention after 65 cycles), and a reversible capacity of 100, 92, and 75 mAh g⁻¹ at 30, 100, 200 mA g⁻¹, respectively. Copolymer of aniline/*o*-nitroaniline (PANNA, No. 56) was synthesized by grafting electron-withdrawing *o*-nitroaniline groups onto polyaniline chains, which displayed an enhanced capacity of 180 mAh g⁻¹ at an average potential of ≈3.2 V (vs Na⁺/Na) and a strong capacity retention (remain 173 mAh g⁻¹ over 50 cycles).^[78]

In recent years, polydopamine (PDA, No. 57, Figure 10) has been studied for its interesting molecular structure, in which carbonyl groups exhibit *n*-type behavior while secondary amines (RNH-R) exhibit *p*-doping/*de*-doping properties. Among all the reported CPs, PDA exhibits the best electrochemical performance, retains stable capacity of 500 mAh g⁻¹ over 1024 cycles at 50 mA g⁻¹.^[78]

Another effective strategy for improving the electrochemical properties of materials is to increase surface area by nanostructure engineering. For example, 2D mesoporous PPy nanosheets have pore size of 6.8–13.6 nm, ultrathin thickness of 25–30 nm and high specific surface area of 96 m² g⁻¹.^[79] They exhibited a high capacity of 123 mAh g⁻¹ at 50 mA g⁻¹, suggesting that high surface area can provide more electrochemical active sites and improve the specific capacity. Significantly high rate capability was achieved in submicron PPy particles that kept a capacity of 84 mAh g⁻¹ over 500 cycles at 14.4 A g⁻¹.

2.2.2. Covalent Organic Frameworks

Conjugated microporous polymers with covalent organic frameworks (COFs), which are based on dynamic polymerization of covalent bonds, is a kind of structured crystalline organic porous polymer. COF materials have the characteristics of uniform pore size, low density, large specific surface area, and adjustable pore size.^[80] By introducing functional groups into monomers or COF polymers, COF materials can be endowed with many unique properties and have great application potential in energy storage, separation, optoelectronic materials, adsorption, catalysis, functional devices, and so on. Meanwhile,

high specific surface area and microporous structure promote the rapid migration of Na⁺ ions; the polymer structure reduces its solubility; the large amount of redox active centers provides higher theoretical capacity. Therefore, COFs are also used as a new kind of organic electrode materials for LIBs, SIBs, and lithium-sulfur batteries, etc.^[81–86]

For instance, Sakaushi et al.^[81,82] reported a bipolar porous organic electrode (BPOE, No. 58) fabricated in OSIBs. BPOE is comprised of noncoplanar 2D organic frameworks made up of aromatic rings like hard carbon. It delivered a high capacity of 200 mAh g⁻¹, long cycle life after 7000 cycles at the current density of 1.0 A g⁻¹ and excellent rate capacity of 50 mAh g⁻¹ at 5 A g⁻¹.^[81] After that, they used BPOE as the anode and cathode materials of the all-organic energy storage device, which showed a high power density of 1 kW kg⁻¹ based on the total mass of the BPOE and the cycle life was more than 1000 times.^[82] Furthermore, 4, 7-dicarbazyl-[2,1,3]-benzothiadiazole (PDCzBT, No. 59) with high surface area of 1166 m² g⁻¹ and micropores of 0.52 and 0.86 nm exhibited a high capacity of 145 mAh g⁻¹ over 100 cycles at 20 mA g⁻¹.^[83]

Note that, the self-assembly form, specific surface area and molecular smoothness of COFs depended on the combination of monomers and the preparation conditions of the experiment. By enhancing the flatness of the polymer skeleton or increasing its specific surface area while maintaining the skeleton structure, the sodium ion storage capacity of the COFs can be significantly improved. Kim et al.^[84] prepared CONs with three new network structures (macromolecular ring diameters of ~2.8, 3.3, and 4.2 nm) by the Stille cross-coupling method of two monomers (Figure 11e,f). The specific surface area of COFs can be controlled by changing the reaction conditions such as solvothermal or condensation reflux. The CON-16 (No. 60) showed a high-rate capability with 124 mAh g⁻¹ at 1000 mA g⁻¹ and the best cycling stability with reversible capacity of 250 mAh g⁻¹ after 30 cycles at 100 mA g⁻¹. Therefore, the results suggest that a wider range of synthetic methods and monomer structures may be needed to obtain more COFs with the desired performance.

2.2.3. Nitroxyl Radical Polymers

Organic radical polymers (ORPs) are composed of flexible unconjugated skeletons and functional side groups with stable organic radicals which carry highly localized electrons. Although ORPs have been widely studied in OLIBs, only poly[norbornene-2,3-endo,exo-(COO-4-TEMPO)₂] (No. 63) and poly(2,2,6,6-tetra methylpiperidinyloxy-4-vinylmethacrylate) (PTMA, No. 64) were investigated on OSIBs in the past decades.^[87,88] Their structural units all contain nitroxyl radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). TEMPO has bipolar properties and can be oxidized to ammonium oxide cations or reduced to amino anion. The exo-(COO-4-TEMPO)₂ exhibited a high irreversibility discharge capacity of 75 mAh g⁻¹ at the first cycle and a capacity retention of 64.5% (48 mAh g⁻¹) after 50 cycles.^[87] However, the ORP materials suffer from serious self-discharge and low practical capacity because the polymer electrode easily dissolves in organic electrolyte and forms an insulating layer. Therefore, Kim et al.^[88] have designed

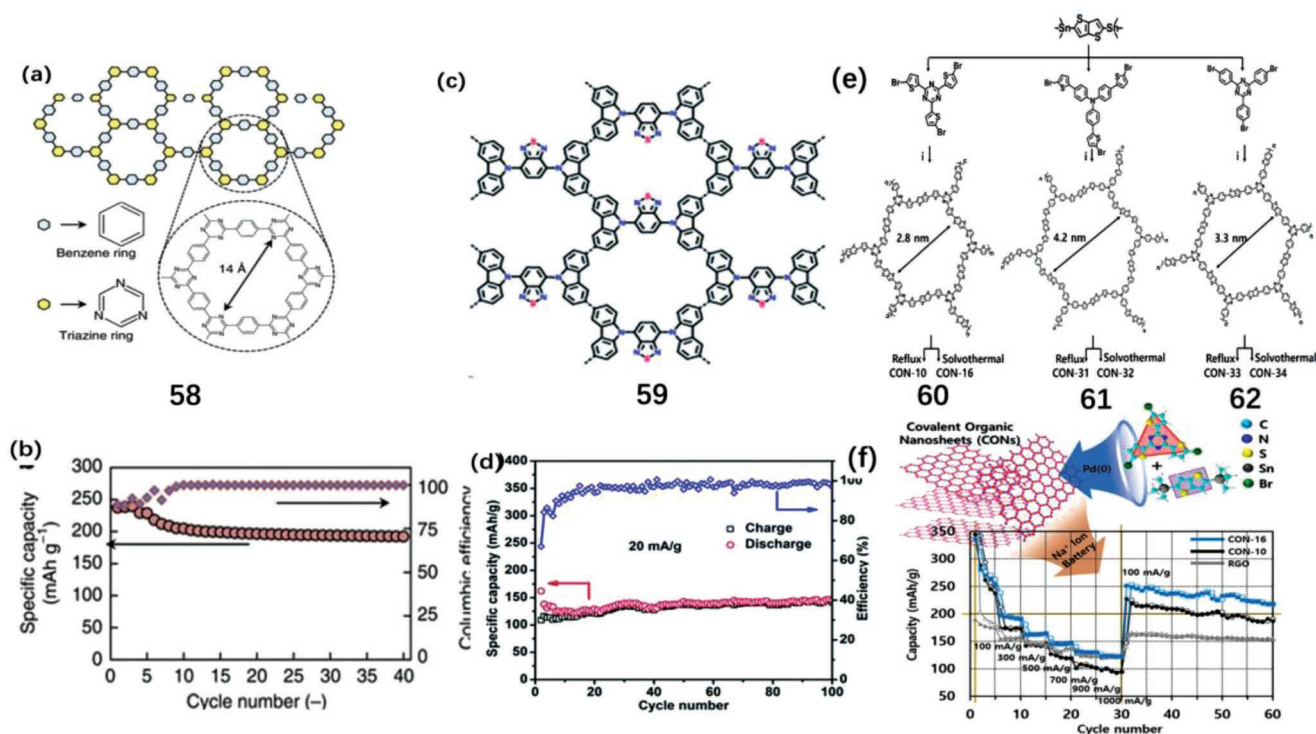


Figure 11. a) Structures of BPOE. b) Cycle performance of a sodium organic energy-storage device at a current density of 0.01 Ag⁻¹. c) Structures of PDCzBT. d) Cycle performance at a current density of 20 mA g⁻¹. a-d) Reproduced with permission.^[82] Copyright 2015, The Royal Society of Chemistry. e) General synthesis procedure and molecular structures of CONs along with precursor monomers. f) Cyclic performance of CON-10 and CON-16 electrodes under various current densities. e,f) Reproduced with permission.^[83] Copyright 2018, American Chemical Society.

a unique organic electrode in which poly(2,2,6,6-tetra methyl-piperidinyloxy-4-vinylmethacrylate) (PTMA) is encapsulated into the carbon nanotubes (CNTs). This PTMA composite shows

a high capacity (222 mAh g⁻¹ at 0.1 C rate), a great rate capacity (190 mAh g⁻¹ at 5 C rate), and a stable cycle life (93% retention over 100 cycles) (Figure 12). If we can reasonably solve the

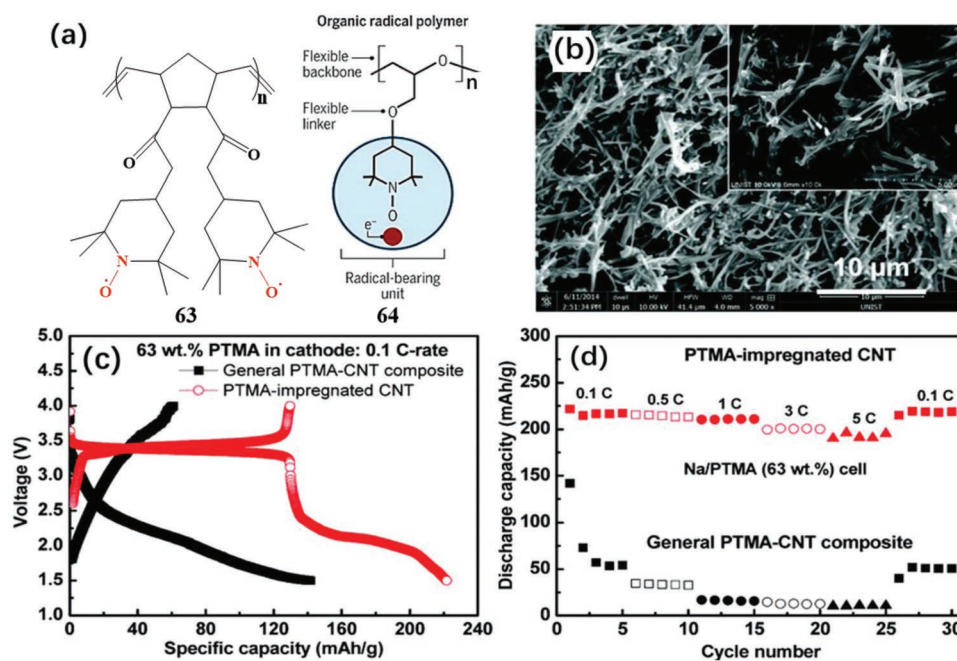


Figure 12. a) Structures of nitroxyl radical polymers. b) SEM image of PTMA-impregnated CNT. Rate performance of c) PTMA-CNT composite and d) PTMA-impregnated CNT electrodes. a-d) Reproduced with permission.^[88] Copyright 2016, The Royal Society of Chemistry.

solubility, conductivity and self-discharge issue, organic radical polymers will have great potential in the application of flexible battery devices.

2.2.4. Organometallic Polymers

Organometallic compounds are a kind of material formed by the direct bonding between metal and organic groups. It has excellent electrochemical activity due to their electrochemically redox active groups. Ferrocene has become the most studied metal organic polymer in SIBs, benefiting from its excellent electrochemical activity and air stability.^[89] By increasing the molecular weight of organometallic polymers to reduce their solubility in electrolyte solutions, they have the potential as a cathode material in SIBs. However, the capacity of ferrocene-based polymer is only about 100 mAh g⁻¹, due to the limitation of its high molecular weight. For example, an n-type poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo [1,2-c:4,5-c']-dipyrrole-2,6(1H,3H)-diyl-1,4-phenylene] (PMDA) material exhibited a capacity of 85 mAh g⁻¹ at 5 C rate with 74% retention over 200 cycles.^[90]

2.2.5. Metal–Organic Frameworks

Metal–organic frameworks are a novel class of crystalline porous materials which are composed of coordinated metal ions (or clusters) and organic ligands.^[91,92] In recent years, MOFs-derived materials, which are prepared via appropriate treatment of MOFs, have attracted wide attention in the field of nanoelectrode materials for SIBs.^[93–110] As anode materials for SIBs, MOF-derivative electrode materials display several inherent advantages (Figure 13). First, these materials have porous structures, due to the pores of MOFs itself and the gas release and

skeleton collapse during heat treatment. Second, for the carbon composites derived from MOFs, the carbon distribution of the materials is more uniform and the graphitization degree of carbon is high because of the catalysis of metal elements during heat treatment. Third, the synthesis strategy of MOFs is easy, and MOFs usually possess uniform and stable nanostructures. Finally, by simple ligand and metal element adjustment, the morphology and structure of the synthesized materials and the kinds of polymetallic doping can be regulated.

At present, the research of MOF materials in the direction of SIBs mainly includes the following two aspects: 1) MOF materials are used as direct electrode material in SIBs; 2) MOF materials are used as precursor and template to prepare a series of metal oxides (MOs), MOs/carbon composites, metal sulfides (MSs)/carbon composites, metal phosphides (MPs)/carbon composites, non-M oxides/carbon composites, and carbon materials.

At present, MOF materials still have the challenges of low specific capacity, low CE of first cycle, and poor conductivity as electrode materials. Therefore, there are few reports of electrode materials for application of MOF materials to SIBs.^[93–95] Ning et al.^[95] synthesized a mesoporous flower-like Co-MOF by solvothermal method and used as anode electrode material for the first time in SIBs. Co-MOF exhibited an outstanding charge capacities of 396.9 mAh g⁻¹ at 50 mA g⁻¹ and a stable cycle life (328 mAh g⁻¹ after 100 cycles). It was the first time that MOFs was applied as anode materials in SIBs, and it outperforms many of the carbon-based materials for SIBs. Liu et al.^[96] have established the Na⁺-ion storage mechanism of sp²-hybridized carbons in aromatic rings by constructing a stable 3D open-framework structure to make Na⁺ ions accessible to the aromatic rings (Figure 14). In the experiment, Zn-PTCA was constructed by coordination of 3,4,9,10-perylenetetracarboxylate and Zn²⁺ ions. The unpaired electrons added in aromatic rings are mainly stabilized by

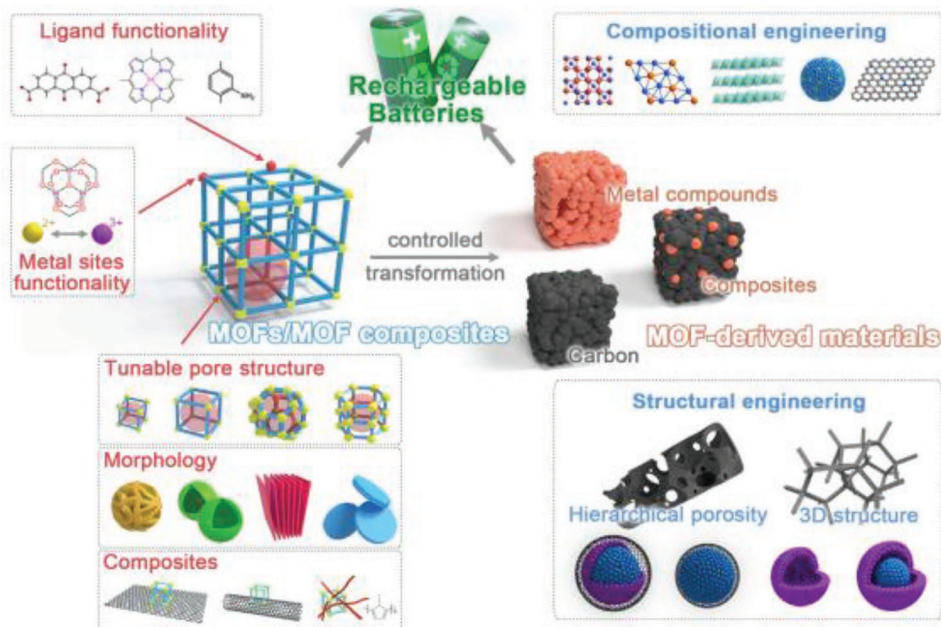


Figure 13. Schematic illustration of MOF-related materials for SIBs. Reproduced with permission.^[110] Copyright 2018, The Cell Press.

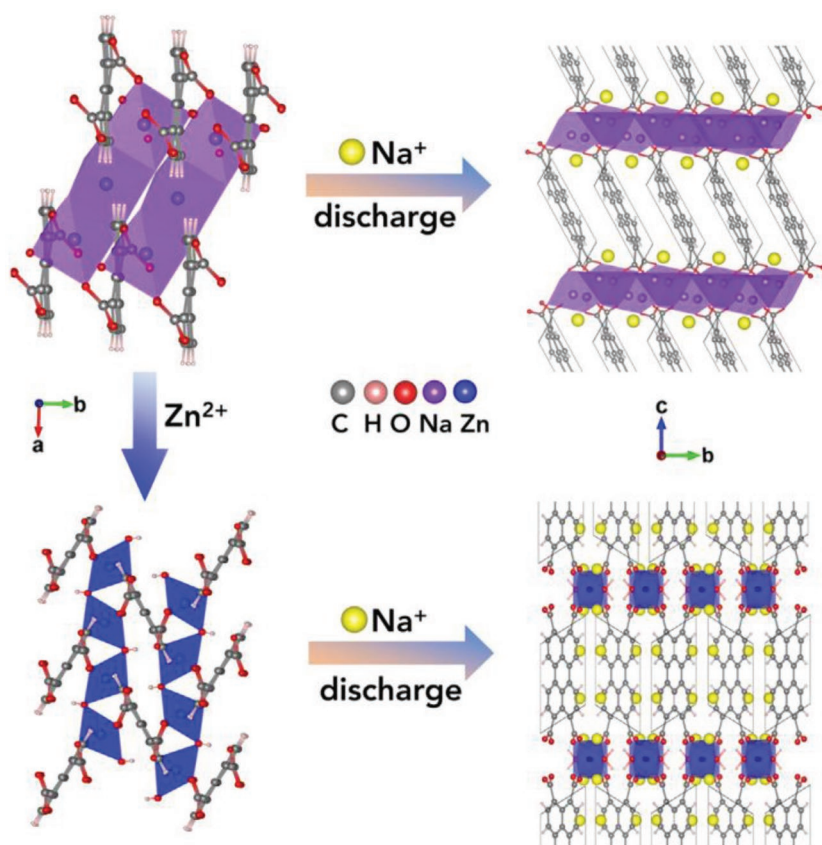


Figure 14. The Na-storage schematic diagram of Na-PTCA and Zn-PTCA.^[96] Copyright 2018, The Cell Press.

the p - π conjugation effect. This strategy greatly improved the electrochemical activity of the conjugated aromatic rings, and increasing the capacity of sodium storage. Zn-PTCA exhibited a high specific capacity of 357 mAh g^{-1} at 50 mA g^{-1} and good cycle stability. Theoretical calculations and experimental characterizations confirmed that the Zn-PTCA with 3d open-framework structure shows two storage sites of $\text{C}=\text{O}$ in carboxylate groups and sp^2 -hybridized carbons in aromatic rings. The present study can open up a new avenue for developing high specific capacity electrode materials with enhanced electrochemical activity for energy storage.

MOF materials have been rarely used as electrode material directly, because the electrochemical performance was not ideal, many researchers turned their attention to the synthesis of more mature metal compounds materials using MOF materials as precursors or template. The MOFs template is an efficient way to construct ideal nanostructures, such as nanoporous structures, polyhedral structures, and core-shell structures. Metal compounds derived from MOFs can prodigiously maintain the inherent morphology of MOFs, and thus have the advantages of porous structure and layered morphology of MOFs.^[97,98] For instance, Zhang et al.^[97] synthesized porous $\text{CuO}/\text{Cu}_2\text{O}$ mixed hollow octahedron using copper-base MOFs as template. The synergistic effect between CuO and Cu_2O , as well as their porous hollow structure, make the material ideal for electrode fabrication of SIBs. The device

showed a high cyclic capacity of 415 mAh g^{-1} at the current density of 50 mA g^{-1} , good cycle performance and rate performance ($440, 349.3, 217.2,$ and $153.8 \text{ mA h g}^{-1}$ at $50, 250, 1000,$ and 2500 mA g^{-1} , respectively (Figure 10)) A highly efficient method for improving the cyclic and rate properties of conversion materials is to coat carbon materials (mesoporous carbon, CNTs, graphene) on the surface of metal oxides, which can effectively adapt to the change of volume and improve the conductivity of the materials. For example, through the successive heat treatment of Ni-MOF, Zou et al.^[98] obtained graphene coated NiO/Ni nanocrystals and kept the original layered hollow sphere structure intact. The NiO/Ni/Graphene anode materials exhibited a good cycle stability with a fading rate of 0.2% per cycle and rate capacity with 207 mAh g^{-1} at 2 A g^{-1} . Based on the advantages of safety, high specific capacity, high natural abundance and low cost of vanadium oxide with layered structure, Cai et al.^[99] synthesized porous shuttle-like vanadium oxides ($\text{V}_2\text{O}_5, \text{V}_2\text{O}_3/\text{C}$) by using MIL-88 (V-MOFs) as precursor. Due to the inherent layered structure and metal behavior of V_2O_3 , as well as the porous fusiform morphology and conductivity of uniform C coating, the material exhibited excellent electrochemical properties.

3. Challenges and Strategy to Improve the Organic Electrode Material

3.1. Challenges

Nowadays, although a large number of organic electrode materials have been developed, it is still challenging to find satisfactory materials after considering complex requirements of SIBs. The current organic electrode materials for SIBs, face several problems that need to be solved urgently:

- 1) *Poor Chemical Stability of Organic Compounds*: The chemical stability of organic compounds mainly depends on the strength of chemical bonds in molecules. Most of the organic compounds are covalent compounds, while covalent bonds tend to form free radicals during the charge/discharge process, and are also susceptible to action with active groups on the main chain. Therefore, the occurrence of side reactions leads to the inactivation of organic electrode materials. In addition, the large volume expansion of organic material causes the serious particle pulverization and easily fall off the current collector, leading to the poor stability.^[30,36,113] This requires that we optimize both the molecular structure and the morphology of the organic material, so as to improve the stability of the electrode material.^[113–116]

- II) *High Solubility in Organic Electrolytes*: Organic materials, especially small organic molecules, show generally high inherent solubility in organic electrolytes. The high solubility leads to the rapid capacity attenuation and poor cyclic stability of organic electrode materials.^[19,20] The solubility problem is the main obstacle to the application of organic materials in SIBs, but it promotes the electrochemical reactions in solution phases. This problem can be relieved through proper molecular design or compositing them with inorganic materials. Using aqueous electrolyte may also be considered as a good choice.^[129–131]
- III) *Low Electric Conductivity*: Most of the organic compounds are covalent compounds with no free electrons or ions, which demonstrate slow charge transfer rate and thus forth poor electric conductivity. Therefore, a large portion of carbon is required as the conductive additives when preparing the electrodes, resulting in the loss of total energy density of OSIBs.^[78,118–120] The conductivity of organic electrode materials can be improved by molecular design,^[111] doping,^[74] and the composite of conductive polymers or inorganic conductive materials,^[78,118–124] so as to improve the performance of OSIBs.

3.2. Design Strategies of the Organic Electrode Materials

The above challenges faced organic electrode materials can be addressed through careful design and modification of organic molecules. Mainly, there are three general strategies: function-oriented molecular design, the morphology control, and compositing organic materials with inorganic materials. Through these strategies, the conductivity, solubility, working voltage and theoretical capacity of organic molecules can be adjusted reasonably, so as to improve the capacity, rate performance and cycle stability of organic materials in SIBs.

3.2.1. Function-Oriented Molecular Design

One of the outstanding features for organic materials is the designability of their molecular structures. Thus forth, targeting designs of organic molecules can be realized through a careful molecular engineering. Specifically, the following points can be reasonably adjusted:

- 1) By introducing the electron-withdrawing ($-\text{NO}_2$, $-\text{CN}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{SO}_3\text{Na}$, $-\text{OCH}_3$)/electron-donating groups ($-\text{NR}_2$, $-\text{NHR}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OR}$, $-\text{OCOR}$, $-\text{R}$, $-\text{Ph}$, $\text{R} = \text{alkyl}$), the lowest unoccupied molecular orbital (LUMO) energies can be effectively reduced/enhanced, which leads to the enhanced/decreased working voltage in SIBs. For example, doping halogen atoms such as fluorochlorine, chlorine and bromine can increase the redox potential of benzoquinone derivatives without increasing their molecular weight.^[18]
- 2) Increase the degree of π -conjugation of electrochemical active center unit can improve the rate performance of organic material. The extension of the π -conjugation system is beneficial to the rapid transfer and collection of charge, and to improve the tolerance to the rapid insertion/extraction of Na^+

ion in the fast charge and discharge process. At the same time, the extended π -conjugation system also helps to strengthen the interaction between molecules (such as π or $\text{C}-\text{H} \cdots \pi$ interactions), which may lead to a layer of molecular arrangement. This layer-by-layer molecules are arranged to form a fast route for Na -ion diffusion between the two layers. Wang et al.^[45] modified the π conjugated system SBDC using $\text{C}-\text{C}$, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$ to form extended π -conjugation molecules **1**, **SSDC**, and **2**, respectively. Among them, the SSDC with the highest degree of π -conjugation showed excellent rate capacity (105 mAh g^{-1} at 2 A g^{-1} , 72 mAh g^{-1} at 10 A g^{-1}) and a high reversible capacity of 220 mAh g^{-1} at 50 mA g^{-1} . Liu et al.^[111] studied the properties of cyclo-octatetraene-based (C_8H_8) organic molecules thickened with different C_4/C_8 ratios through molecular models, and developed a high capacity/high voltage organic cathode with conjugated ring as electrochemical active center (**Figure 15**). The DFT calculations predict that fused molecules of $\text{C}_8-\text{C}_4-\text{C}_8$ ($\text{C}_{16}\text{H}_{12}$) and $\text{C}_8-\text{C}_4-\text{C}_8-\text{C}_4-\text{C}_8$ ($\text{C}_{24}\text{H}_{16}$) exhibit high specific capacities of 525.3 and $357.2 \text{ mA h g}^{-1}$ at the voltage change from $3.5-1.0 \text{ V}$ and $3.7-1.3 \text{ V}$ versus Na^+/Na , respectively.

- 3) The formation of high polarity salt to reduce solubility in electrolyte.^[19,20] On the one hand, the salinization of organic molecules can increase their molecular polarity, which can prevent the dissolution of organic electrode materials in aprotic electrolytes. On the other hand, strong hydrophilic groups of organic salt can form coordination bonds such as $\text{Na} \cdots \text{O}/\text{K} \cdots \text{O}/\text{Ca} \cdots \text{O}$, which may partially hinder the dissolution of organic electrode materials. The organic salt (Ca_2BTEC) formed by Ca^{2+} and H_4BTEC (1,2,4,5-benzenetetracarboxylic acid) showed a reversible capacity of 140 mA h g^{-1} even after 300 cycles as anode material in SIBs.^[112]
- 4) The polymerization is also an effective way to improve the performance of the organic material in SIBs. First, the rapidly increasing molecular weight (M_w) of the polymer can greatly reduce the dissolution of the organic material, and second, the copolymer with other electrochemical active units and 3D porous polymer can also improve the theoretical capacity.

3.2.2. Micromorphology Regulation

The morphology of materials is the key to determine the electron and ion transfer path, so the regulation of micromorphology of battery materials is particularly important. Generally speaking, the nanomerization of electrode materials is an effective strategy to improve the capacity performance. The synthesis of nanostructured electrode materials not only controls the particle size of electrode materials, but also requires controllable synthesis of the morphology, crystal structure and crystallinity of electrode materials. As the electrode materials for SIBs, nanostructured materials not only give full play to the advantages of nanomaterials, but also their unique structure can weaken and overcome the shortcomings of nanomaterials, so as to improve the performance of SIBs. Due to the characteristics of small size, short insertion/detachment distance of sodium ions, excellent kinetic performance, large specific surface area, more active sites of sodium insertion, and low polarization and high reversible capacity of the electrode during charging and discharging

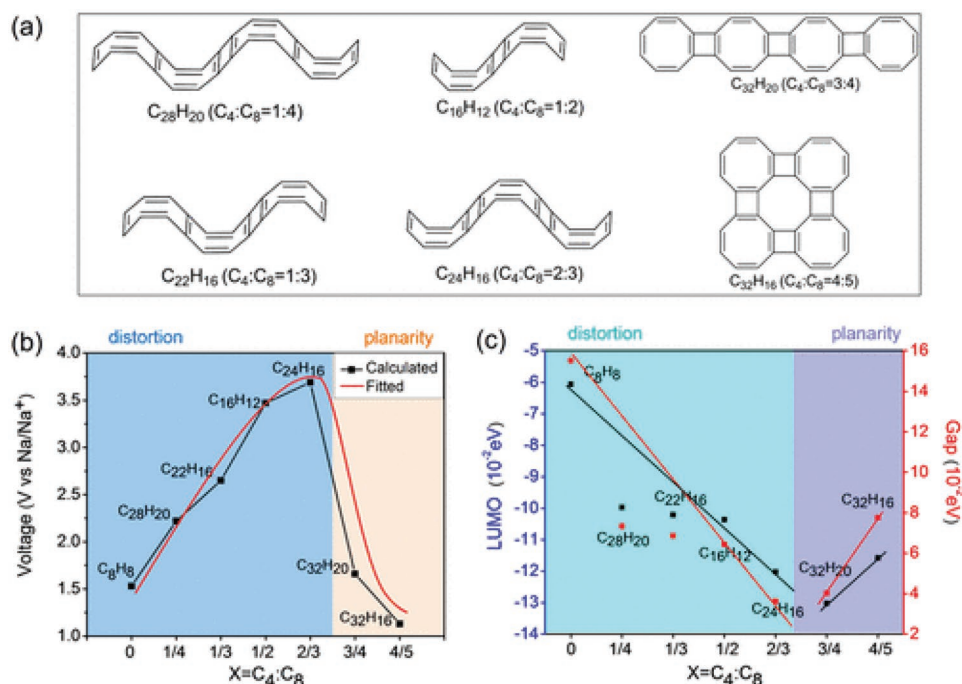


Figure 15. a) The calculated fusion molecules based on C₈ and C₄ rings. b) B3LYP-calculated voltages; c) highest occupied molecular orbital (HOMO)–LUMO gaps and LUMO energy levels of different fused structures with different ratios of C₄ and C₈ rings. a–c) Reproduced with permission.^[111] Copyright 2017, American Chemical Society.

at high current, nanoelectrode materials for SIBs have attracted wide attention among the research community. The kinds of nanoelectrode materials and their preparation methods are also diverse.

For instance, DSR^[30,113] and CADs^[36] with nanostructures encountered less cracks and morphological deformation in battery cycle, which nanostructures could promote to release the stress/strain and inhibit pulverization. The nanorod structure reduces the interfacial resistance and has a high sodium ion diffusion coefficient, the nanorod structure of DSR deliver a high reversible capacity of 190 mAh g⁻¹ at 0.1 C and excellent rate capacity of 95 mAh g⁻¹ than the microrod and microbulk (Figure 16a–d).^[112] Liu et al.^[66] synthesized 2D mesoporous nanoparticles mppy-1 (specific surface area and pore volume: 96 m² g⁻¹ and 0.21 cm³ g⁻¹ respectively) with controllable pore size (6.8–13.6 nm) by synergistic self-assembly of amphiphilic aliphatic amine (octadecylamine, OTA) and polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) block copolymer (BCP) (Figure 16e,f). The mppy1 showed a reversible discharge capacity of 123 mAh g⁻¹ at 50 mA g⁻¹. Chen et al.^[114] successfully synthesized polypyrrole with submicrostructure by simple chemical oxidation polymerization. It showed an excellent rate capacity of 84 mAh g⁻¹ at 14.4 A g⁻¹ over 500 cycles, which is superior to the ppy-based cathode electrode materials (such as nanoparticles and hollow spheres).^[115,116] In addition, the improvement of electrochemical properties due to the nanostructure of organic compounds can be attributed to not only the size effect, but also the new mechanism that the new desodization mechanism and the optimized ion/electronic transfer pathway in nanomaterials.^[117]

3.2.3. Compositing Organic Materials with Conductive Inorganic Materials

It is well known that most organic compounds, whether small-molecular compounds or high-molecular-weight polymers, show poor stability and electrical conductivity, leading to the great sacrifice of battery capacity and rate performance. To overcome these obstacles, an effective strategy is to disperse organic compounds in a conductive matrix, which can provide rich electron and ion channels for electron transfer reactions. Also, on the other hand, by coating a layer of inorganic materials such as metal oxides (Al₂O₃)^[24,39] and various carbon materials (carbon nanofibers,^[118] CNTs,^[78,119] graphene,^[120] GO,^[121] rGO,^[122] microporous and mesoporous carbon^[123]) etc. onto the surface, the dissolution and pulverization of organic materials in charge-discharge cycles can be successfully suppressed. For instance, by coating a 2 nm Al₂O₃ thin layer on 2,5-dihydroxy-1,4-benzoquinone disodium salt (DHDQBS) surface, the dissolution of the DHDQBS nanorods can be obviously inhibited and the cycle stability can be improved (212 mA h g⁻¹ at 50 mA g⁻¹ after 300 cycles). Nevertheless, the poor conductivity of Al₂O₃ limits the full play of the properties of organic materials, so researchers find carbon materials with good electrical and mechanical properties as the conductive matrix, which can not only improve the conductivity but also improve the stability of the organic materials. Deng et al.^[124] embed the porous Na₂NC nanoparticles into a highly conductive graphene nanosheet. The Na₂NC/G composites material exhibits a high reversible capacity (>220 mAh g⁻¹, even higher than the theoretical 2e⁻ redox capacity: 206 mAh g⁻¹) and excellent rate performance (88 mAh g⁻¹ at 10 C rate) due to its high interfacial

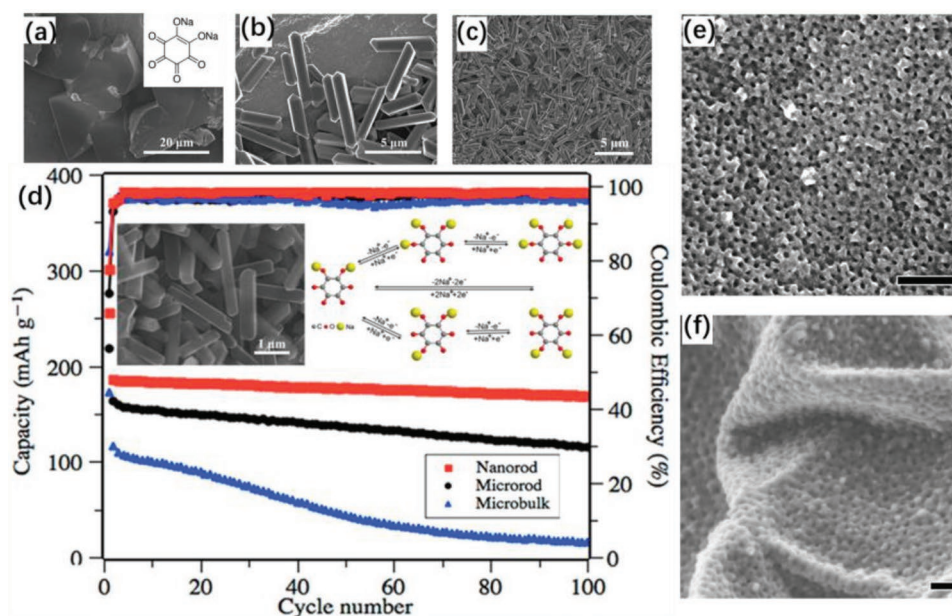


Figure 16. SEM images of a) DSR microbulk, b) microrod, and c) nanorod structured samples (inset, molecular structure of the $\text{Na}_2\text{C}_6\text{O}_6$). d) Cycling test. a–d) Reproduced with permission.^[112] Copyright 2014, The Royal Society of Chemistry. e) SEM images of the mPPy-1 nanosheets synthesized using PS_{33} -*b*- PEO_{114} and OTA as the templates. f) SEM images of the mPPy-2 nanosheets synthesized with PS_{117} -*b*- PEO_{114} and OTA as the templates. e, f) Reproduced with permission.^[66] Copyright 2016, Wiley-VCH.

surface area, rich electron and ion transport channels (Figure 17a,b). Liu et al.^[119] coated polydopamine on FWNTs (few-walled carbon nanotubes) surface, and then prepared flexible hybrid film by a vacuum-filtration method (Figure 17c,d). The flexible hybrid electrodes deliver a high gravimetric capacity of $\sim 213 \text{ mAh g}^{-1}$ and excellent cycling stability in Na-cells. By the same method, Yuan et al.^[125] prepared a flexible composite of aromatic carbonyl compounds/carbon nanotubes, which

showed excellent cyclic stability (over 300 cycles) and good rate capability (48 mAh g^{-1} at 1000 mA g^{-1}) in SIBs.

Despite the obvious progress achieved, the simultaneously acquisition of high capacity, excellent cycle stability and rate performance is still a challenging task. Further improvement on OSIBs may require the combination of the above strategies, or some revolutionary technologies for the fabrication of OSIBs.

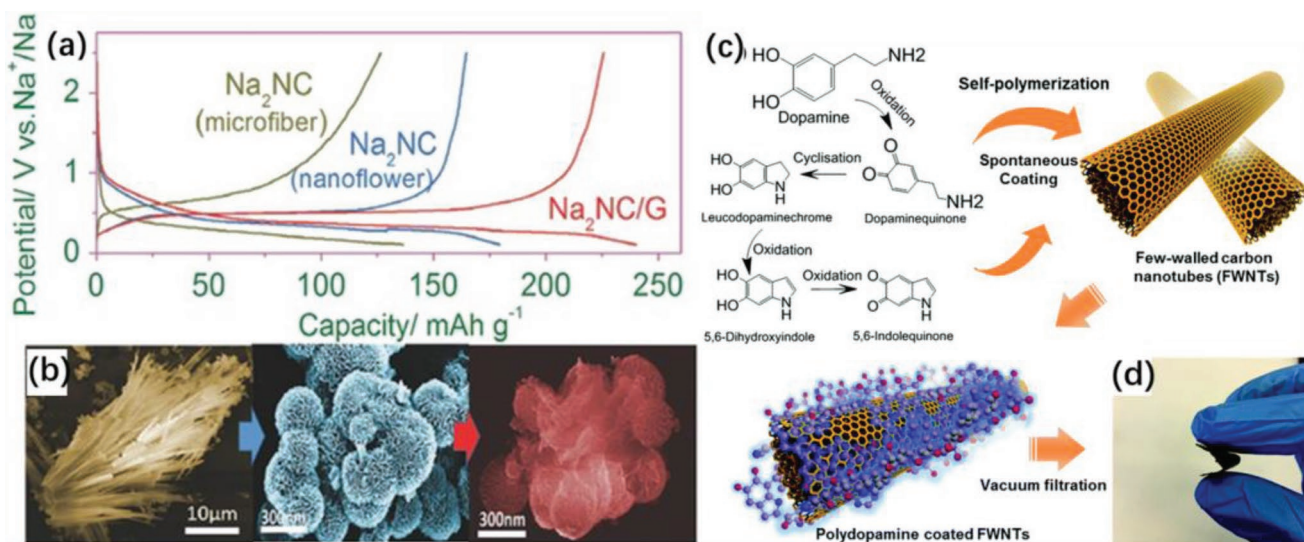


Figure 17. a) Charge/discharge profiles at a constant current of 10 mA g^{-1} . b) SEM images of the three types of Na_2NC anodes (MF- Na_2NC , NF- Na_2NC , and $\text{Na}_2\text{NC}/\text{G}$). a, b) Reproduced with permission.^[124] Copyright 2016, Wiley-VCH. c) Oxidative self-polymerization reactions of dopamine in weak alkaline solution and a continuous coating process of polydopamine on the surface of few-walled carbon nanotubes (FWNTs). d) Digital image of a flexible hybrid film consisting of polydopamine coated FWNTs. c, d) Reproduced under the terms and conditions of the CC-BY Creative Commons Attribution 3.0 Unported License (<https://creativecommons.org/licenses/by/3.0/>).^[119] Copyright 2017, The Royal Society of Chemistry.

4. Conclusions and Perspectives

4.1. Conclusions

In summary, organic electrode materials and organic electrolytes for SIBs have been greatly developed in recent years, but there are still many problems to be solved. In this review, we summarized the evolution of the structure and component from small organic compounds into polymers. As shown in **Table 1**, we summarize the species, properties, the electrode positions (commonly used in SIBs) and discharge potential of the reported organic electrode materials. For small organic electrode materials, there are three types, including compounds with C=O bond, C=N bonds, and N=N bonds. The carbonyl (C=O) materials, quinones and ketones have higher redox potential (often used as cathode materials), carboxylates acids have lower Na insertion voltage (often used as anode materials), and anhydride compounds have higher specific capacity and long cycle performance. In C=N bond compounds, Schiff and pteridine derivatives has an adjustable electrochemical activity. As a new type of electrode material, azo derivatives based on N=N bonds provide an opportunity for the development of high capacity and rate SIBs. For polymer materials, conductive polymers, organic radical polymers, organometallic polymers usually exhibit faster kinetic properties but their capacity is very low, microporous polymers and MOF-derived materials are easy to obtain in uniform, stable nanostructures and layered morphology.

For organic materials, polymerization, salinization can inhibit the dissolution of organic compounds in nonproton electrolytes, composition with inorganic material can improve stability and conductivity, thus improving the cycle stability and rate performance. The properties of organic materials can be controlled purposefully through functional guidance design. In addition, the size effect of nanomaterials and the composite with inorganic conductive materials can also greatly improve the application of organic materials in electrodes for SIBs. However, to obtain high capacity, excellent cycle stability and

rate performance are still great challenges, which requires the synergy of functional design, micromorphology control and material composite. Furthermore, the optimization of electrolyte formulation and the study of its mechanism will remain the focus of future research. With the synthesis of new electrode materials, our research will shift to full-organic, flexible and solid-state batteries. This requires us to continuously improve and synthesize the corresponding electrode materials and electrolyte systems.

4.2. Perspectives

- I) *Molecular Simulation to Explore the New Reversible Active Groups and Reaction Mechanisms of Electrode Materials*: Due to the lack of guiding theory in electrolyte system, we need to make a lot of composition adjustment in order to find a matching optimal electrolyte. Due to the lack of guidance theory in electrolyte design, the researchers need a large number of component adjustments to find a matching electrolyte for most electrode materials. Therefore, the optimization of electrolyte is the major obstacle to the development of battery system. In addition, organic electrode materials can be expanded and applied to other metal-ion batteries (K, Mg, Zn, etc.), based on the similar energy storage mechanism of metal-ion batteries.^[126,127]
- II) *Development of Aqueous Sodium-Ion Batteries (ASIBs)*: Development of ASIBs provides a possible solution. Aqueous electrolytes have good safety, high ionic conductivity, low price, environment-friendly, and ordinary operating environment etc., compared with other nonaqueous electrolytes. The thermodynamic electrochemical window of H₂O is only 1.23 V. However, in order to avoid the electrolytic reaction of H₂O, the voltage of ASIBs should be higher than 1.5 V, lower than 2 V.^[128] The potential of desodium reactions as the cathode electrode material in ASIBs is lower than the oxygen evolution potential of the H₂O, and the potential of sodium-insertion reactions as the anode electrode material is higher

Table 1. Overview of the species, properties, electrode positions (commonly used in SIBs), and discharge potential of the reported organic electrode materials.

Molecular weight (Working principles)	Species	Properties	Electrode (Discharge potential)
Small molecule C=O reaction	Quinones and ketones	Higher redox potentials	Cathode (≈0.5–2.7 V)
	Carboxylates	Lower Na-insertion voltage	Anode (≈0.2–0.7 V)
	Anhydrides	High specific capacity and long cycle life	Cathode/anode (≈0.5–1.6 V)
	Imides	High solubility in electrolyte	Cathode/anode (≈0.6–2.5 V)
C=N reaction	Schiff bases	Adjustable electrochemical activity	Anode (≈0.2–1 V)
	Pteridine derivatives		Cathode (1.6–1.9 V)
N=N reaction	Azo compounds	Need to be further studied	Anode (≈1.0–1.5 V)
	Conductive polymers	Faster kinetic properties	Cathode (≈2.5–3.4 V)
Macromolecular Doping reaction	Nitroxyl radical polymers		Cathode (≈2.2–3.4 V)
	Organometallic polymers	High electrochemical activity	Cathode (3.1–3.4 V)
	COFs	Good stability, uniform and stable nanostructures	Cathode/anode (1.3–2.7 V)
	MOFs		Cathode/anode (1.3–2.7 V)

than the hydrogen evolution potential of the water, so it limits the application of many materials in ASIBs. Currently, there are few organic materials including the PTVE (cathode electrode),^[129] the PAVQ,^[130] PI- derivative (anode electrode)^[131] and biomolecule alizarin^[132] applied in the ASIBs. However, the adjustable structure of organic materials provides a huge development prospect for the development of ASIBs materials.

III) *Development of Flexible OSIBs*: Compared with the brittle inorganic material, the organic material possesses the characteristics of solubility, film-forming and processing.^[133] Therefore, it is easy to load organic material onto the flexible device by casting, printing, vapor deposition, vacuum filtration and in situ polymerization, thereby facilitating the development of the flexible devices. In addition, both flexible and ordinary battery system, organic materials can contribute to binder, diaphragm, and electrolyte, providing a broad prospect for each unit to develop a suitable battery system.

IV) *Development of All-Solid-State OSIBs*: Due to the usage of the noncombustible, thermally and mechanically stable solid-state electrolytes, meanwhile avoiding the dissolution of organic materials in the electrolyte, all-solid-state sodium organic batteries possess high energy density and excellent cycling stability, so that they are considered as the most promising alternative for a traditional liquid battery.^[134]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

design strategy, electrode material, organic material, progress, sodium-ion battery

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