Energy Materials

Review

Electroactive organics as promising anode materials for rechargeable lithium ion and sodium ion batteries

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Abstract
Electroactive organics have attracted significant attention as electrode materials for next-generation rechargeable batteries because of their structural diversity, molecular adjustability, abundance, flexibility, environmental friendliness and low cost. To date, a large number of organic materials have been applied in a variety of energy storage devices. However, the inherent problems of organic materials, such as their dissolution in electrolytes and low electronic conductivity, have restricted the development of organic electrodes. In order to solve these problems, many groups have carried out research and remarkable progress has been made. Nevertheless, most reviews of organic electrodes have focused on the positive electrode rather than the negative electrode. This review first provides an overview of the recent work on organic anodes for Li- and Na-ion batteries. Six categories of organic anodes are summarized and discussed. Many of the key factors that influence the electrochemical performance of organic anodes are highlighted and their prospects and remaining challenges are evaluated.

INTRODUCTION

Since the concept of rechargeable lithium batteries was first proposed in the 1970s[1], lithium-ion batteries (LIBs) have attracted significant attention because of their notable advantages, such as high energy and power density, efficiency and low cost[2]. After decades of development and advancement, LIBs now dominate the portable electronics market and are now illustrating their considerable potential in large-scale applications, such as electric vehicles and smart grids[3]. Unfortunately, with the widespread application of LIBs in the large-scale energy storage market, some shortcomings of LIBs have gradually become prominent and attracted increasing attention. One of the most important issues is that lithium resources are limited and unevenly distributed[4]. Fortunately, sodium is abundant and has similar electrochemical properties to lithium in many aspects[5]. Therefore, sodium-ion batteries (SIBs) are regarded as ideal substitutes for LIBs[6]. Nevertheless, the ionic radius of sodium is larger than that of lithium, which restricts the range of available electrode materials.

In conventional LIB and SIB systems, both the cathode and anode are inorganic materials. For LIBs, the most common electrode materials are transition metal-based inorganic intercalation compounds on the cathode side and graphite on the anode side[7]. However, the theoretical specific capacity of conventional graphite anodes based on intercalation chemistry is only 372 mA h g^{-1}, which limits the energy density of LIBs and conflicts with the high-energy-density batteries required for large-scale energy storage. To solve this problem, silicon (Si) has been intensively studied as an anode material for LIBs because of its exceptionally high specific capacity of 4200 mA h g^{-1}. Although many efforts have been made, the electrochemical properties of Si anodes are far from reaching application levels because of their huge volume change during charge and discharge processes, which is a challenge yet to be solved[8,9]. In addition, there are other high-capacity anode materials (e.g., tin-based materials, bismuth-based materials and transition metal oxides)[10,11], but they also exhibit poor electrochemical performance due to the well-known large volume effects. Titanium-based compounds have also been extensively studied, including TiO_2, $Li_5Ti_4O_{12}$ and Na_2TinO_{2n+1} (where n = 3-8), but their theoretical capacity is even lower than that of graphite, which limits their widespread application[12]. Therefore, there is an urgent need to find new energy storage materials to provide a broader space for future energy storage applications.

Electroactive organics have received significant attention as electrode materials for lithium and sodium storage and are regarded as promising candidates for next-generation electrochemical energy storage. In contrast to most inorganic electrode materials, the volume change of organic compounds during electrochemical cycling is negligible. In addition, organic compounds further benefit from their structural diversity, flexibility, eco-friendliness, widespread availability, low cost and recyclability. In fact, many organic molecules have been successfully reported as electrode materials for LIBs and SIBs [Figure 1]. The properties and progress of different classes of organic materials as electrodes for LIBs and SIBs have been extensively summarized[13-15]. In particular, several reviews have been devoted to the application of carbonyls[16-19], small molecules and polymers[20-22], covalent organic frameworks (COFs) and metal organic frameworks (MOFs)[23-26]. With the development of organic electrodes, more and more organics are being used in anodes and significant progress has been made, which is of particular importance for the development of energy storage. In this review, we provide an overview of the recent work on organic anodes for LIBs and SIBs. First, the redox mechanism and structure of the organics are briefly introduced. Second, the advantages and disadvantages of organic electrodes are introduced. Six categories of organic anodes are then summarized and discussed, namely, small molecules, organic salts, polymers, COFs, organic-inorganic composites and MOFs. Finally, the prospects and remaining challenges of organic anodes are evaluated.

Figure 1. Schematic diagram of organics used in LIBs and SIBs. LIBs: lithium-ion batteries; SIBs: sodium-ion batteries.

## REDOX MECHANISMS AND STRUCTURES OF ORGANICS

During charging/discharging processes, the electrode materials of a battery undergo reversible redox reactions. Therefore, organic materials used for LIBs and SIBs must be chemically reversible. Generally, electroactive organic materials can be classified into three types, namely, n-, p- and bipolar-types [Figure 2][27]. An n-type material operates by accepting an electron, which results in a negatively charged state. In contrast, a p-type material is electrochemically active with the extraction of an electron from its original neutral state, which results in a positively charged state. Thus, the redox reactions occur between the neutral state and the negatively charged state for n-type or positively charged state for p-type. Bipolar-type materials have properties of both p- and n-types and are thus capable of utilizing both positively and negatively charged states and can be charged or discharged from the neutral state with two different redox potentials[7].

In recent years, many organic electrodes have been reported and their reaction mechanisms can be divided into six types, namely, disulfide, anion insertion, azo, carbonyl, imine and superlithiation reactions. The structures of organic electrode materials can be approximately categorized as conjugated amines, conjugated or non-conjugated thioethers, organodisulfides, conjugated carbonyls, conjugated hydrocarbons and nitroxyl radicals. The former two types are p-type organics, the next two types are n-type organics and the latter two types are bipolar organics. Depending on their redox potentials, p-type organic materials are usually used as cathodes, while n-type organic materials can be used as cathodes or anodes.

ADVANTAGES AND CHALLENGES OF ORGANICS

Advantages of organics

In recent years, many organics have been studied as electrode materials for LIBs and SIBs because of the following advantages.
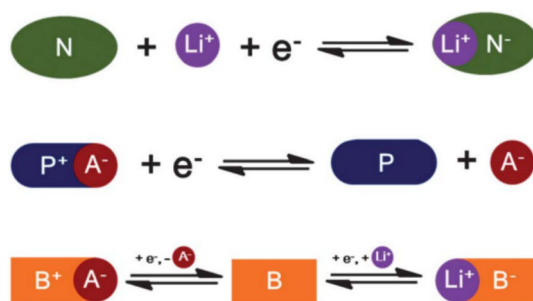
Figure 2. Schematic diagram of the redox reaction of three types of electroactive organics[27]. Reproduced from Ref.[27] with permission from Royal Society of Chemistry.

Sustainability

Current inorganic electrode materials are mainly produced from limited and non-renewable ores rather than renewable resources, with the process of obtaining these electrode materials normally requiring high-temperature processing, which causes various environmental issues. However, organic compounds can be derived from biomass and their common constituents are abundant and light elements, such as carbon, oxygen, nitrogen and hydrogen. In addition, the process of obtaining organics does not require high-temperature annealing, which contributes to a low CO_2 footprint. Thus, organic electrode materials are promising candidates for green and sustainable LIBs and SIBs.

Tunability

In recent decades, substantial progress has been made to optimize inorganic electrode materials through doping, coating and other modification methods. However, the breakthrough of these materials is restricted by their redox potential and theoretical specific capacity. Although the redox potential of inorganic materials can be tuned by regulating the valence of the metal cations, the applicability of this approach is very limited. Unlike inorganics, the redox potential properties of organic materials can be easily regulated through the introduction of electron-donating or electron-withdrawing groups. Therefore, organic materials, characterized by tunable structures, represent abundant electrode candidates for energy storage.

Flexibility

The application of inorganic electrode materials with high specific capacity (e.g., Si and Sn) is restricted by their poor electrochemical performance. Inorganic particles cannot withstand the huge volume changes during alloying and dealloying, and the resulting particle pulverization leads to an increase in electrode polarization and constant electrolyte consumption. In contrast to inorganic materials, which are inherently fragile and rigid, organics are flexible and do not cause structural failure during electrochemical cycling. Therefore, it is expected that the generally flexible properties of organic materials can be advantageous in producing flexible and wearable devices.

Universality

It is well known that many of the inorganic electrode materials that can be used in LIBs cannot be directly applied to SIBs, which is mainly because the ionic radius of sodium is larger than that of lithium. Interestingly, organic electrode materials are not typically restricted by the choice of counter ion and are electroactive toward not only lithium but practically any metal. This means that, to a certain extent, the same organic material can be useful for a wide variety of different energy storage devices, including lithium-, sodium-, multivalent- and dual-ion batteries[28].

Challenges of organics

Although organic materials have several remarkable advantages, as discussed above, and significant success has been achieved for organic electrodes, they still face two main issues, as discussed below.

Low electronic conductivity

It is well known that the electrical conductivity of electrodes influences their charge and discharge rates, and although the electrical conductivity of electrodes can be enhanced by adding conducting carbon additives, too many results in a decrease in the power and energy density of the batteries. As a commercial inorganic anode, the conductivity of graphite is as high as 10^4 S cm^{-1}, meaning that only 3-5 wt.% conductive carbon additives are required. Unfortunately, with the exception of conducting polymers, almost all other organic materials are poor conductors ($< 10^{-10}$ S cm^{-1}). Thus, it is unsurprising that large quantities of conductive carbon additives (previously reported 20-80 wt.%) need to be supplemented in organic electrodes to form a conductive network and ensure a high utilization ratio of electroactive organics, which seriously hinder their application.

High solubility

The dissolution of active materials is one of the main reasons for the capacity degradation of batteries. Unfortunately, although small organic compounds offer high specific theoretical capacities, most of them suffer from severe dissolution in commonly used organic electrolytes, resulting in short cycle life. In order to reduce dissolution, there is significant interest in forming organic salts, optimizing electrolytes, designing composite electrodes and synthesizing macromolecule polymers. The polymerization of small organic molecules with a stable backbone is regarded as the most efficient method to solve this problem, because they become insoluble in organic electrolytes. Nevertheless, there are trade-offs in applying these methods, such as a decrease in theoretical specific capacity and increases in electrochemical polarization and cost.

DEVELOPMENT OF ORGANIC ANODE MATERIALS

In this section, we review the development of organic anode materials, with six types discussed in detail, namely, small molecules, organic salts, polymers, COFs, organic-inorganic composites and MOFs.

Small molecules

Table 1 lists the electrochemical parameters of small molecules as anodes for LIBs and SIBs. Most small molecules have a high capacity, as discussed by many groups. Han *et al.*[29] reported that 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) has a Li-ion insertion capacity of up to nearly 2000 mA h g^{-1}, which was ascribed to the fact that each C_6 ring can reversibly accept six Li ions to form a 1:1 Li/C complex [Figure 3A]. The lithium storage capability of the C_6 ring was also verified by Yang *et al.*[30]. They reported that a 2,9-dimethylquinacridone (2,9-DMQA) anode can deliver a high capacity of 1150 mA h g^{-1} at 0.1 A g^{-1} and suggested that the carbonyl groups in 2,9-DMQA and the intermediate with 20 π-electrons enable reversible store a total of 22 Li ions [Figure 3B]. However, it also has been reported that the C_6 ring in aromatic compounds is inactive. Wang *et al.*[31] found that the first reversible capacity of perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA) is only 436.1 mA h g^{-1} and no Na-ion insertion in condensed aromatic structures is one of the reasons for the low capacity, as also observed in its derivative (NaPTCDA) [Figure 3C]. Thus, it can be summarized that the electroactivity of the C_6 ring is related to the type of stored metal ions, with Li ions capable of being reversibly stored.

Although small molecules usually have high capacities, most of them suffer from poor cyclic stability due to their solubility in organic electrolytes. Many methods have been attempted to suppress the dissolution of organics. Chen *et al.*[32] focused on the co-effect of structural modification and the increase of conductive

Table 1. Electrochemical parameters of small molecules as anodes for LIBs and SIBs

Molecule	CC/wt.%	1st Capacity/Rate	1st CE/%	Cycles/Capacity/Rate	Capacity/High rate	Battery	Reference
NTCDA	AB/35	724/100 mA g⁻¹	57	30/899/100 mA g⁻¹		Li	[29]
PTCDA	AB/30	436/25 mA g⁻¹	60.9	300/117/200 mA g⁻¹	68/2 A g⁻¹	Na	[31]
DDQ	SP/60	~755/50 mA g⁻¹	39	50/579/50 mA g⁻¹	181/5 A g⁻¹	Li	[32]
DHCQ	SP/60	921/50 mA g⁻¹	41	50/1009/50 mA g⁻¹	207/5 A g⁻¹	Li	[32]
MA	AB/40	1234/46.2 mA g⁻¹	45.9	500/852/2.31 A g⁻¹	571/46.2 A g⁻¹	Li	[38]
cHBC	SP/10	~230/400 mA g⁻¹	~85	150/~260/400 mA g⁻¹	88/2 A g⁻¹	Li	[33]
F-cHBC	SP/10	160/100 mA g⁻¹ 125/100 mA g⁻¹		400/200/1 A g⁻¹ 110/~100/400 mA g⁻¹	100/7 A g⁻¹ 65/4 A g⁻¹	Li Na	[34]
H₂TP	SP/30	~320/50 mA g⁻¹	~40	500/194/500 mA g⁻¹	240/1 A g⁻¹	Li	[35]
IA	SP/40	1270/30 mA g⁻¹	66.2	200/1074/300 mA g⁻¹	531/30 A g⁻¹	Li	[39]
PMDA	AB/40	1472/30 mA g⁻¹	68.4	500/878/600 mA g⁻¹	563/30 A g⁻¹	Li	[40]
PTCDA	SP/15	~118/100 mA g⁻¹	89.3	500/~0/2.5 A g⁻¹	70/10 A g⁻¹	Na	[36]
DMQA	SP/45	498/100 mA g⁻¹	43.7	600/200/2 A g⁻¹	385/5 A g⁻¹	Li	[30]
2,3-Pzdc 2,5-Pzdc 2,6-Pzdc	AB/40	1276/32 mA g⁻¹ 606/32 mA g⁻¹ 701/32 mA g⁻¹	56.9 56.4 54.9	400/1255/640 mA g⁻¹	489/32 A g⁻¹	Li	[37]
CHDA	SP/40	1195/100 mA g⁻¹		100/249/0.1 A g⁻¹	125/2 A g⁻¹	Na	[44]

CC: conductive carbon; CE: Coulombic efficiency; AB: acetylene black; SP: Super-P.
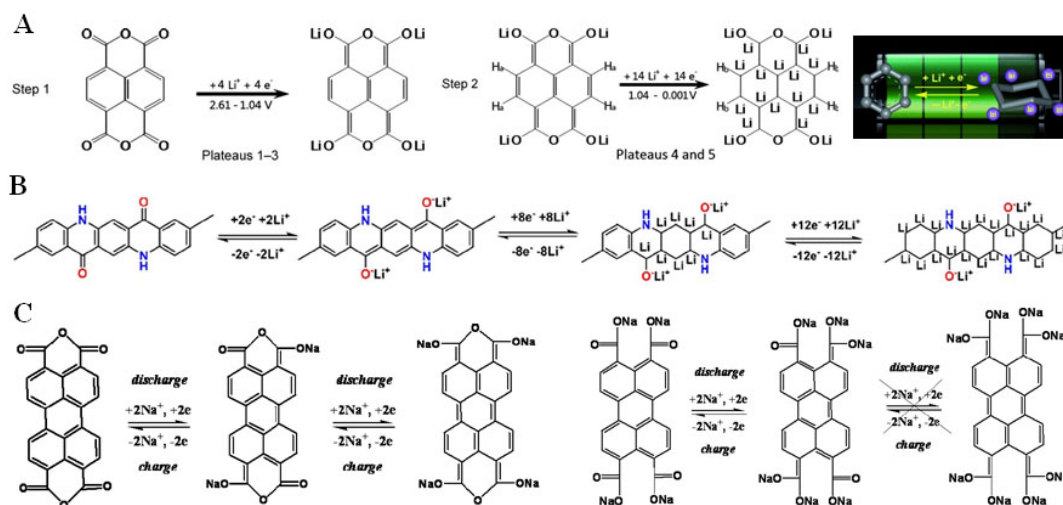
Figure 3. Schematic of proposed reversible electrochemical redox mechanism of (A) NTCDA[29],Reproduced from Ref.[29]with permission from John Wiley and Sons. (B) 2,9- DMQA[30],Reproduced from Ref.[30] with permission from Elsevier. (C) PTCDA and NaPTCDA[31]. Reproduced from Ref.[31] with permission from Royal Society of Chemistry.

carbon. They synthesized 2,3-dichloro-5-hydroxy-6-cyano-1,4-benzoquinone (DHCQ) by simple chemical hydrolysis of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [Figure 4A]. The optimized anode delivered a reversible capacity of 921 mA h g⁻¹ at 50 mA g⁻¹, with retention higher than 78% obtained after 400 cycles at 500 mA g⁻¹. This proved that the electrochemical performance could be improved by the combined effect of molecular modification and the increase in conductive additive in the composites. In addition, Park *et al.*[33] developed a new contorted hexabenzocoronene (cHBC) anode and introduced fluorine atoms into it (F-cHBC) to achieve superior cycle capabilities [Figure 4B][34]. The synthesized F-cHBC anode could work for more than 400 cycles without capacity decay. This enhanced performance
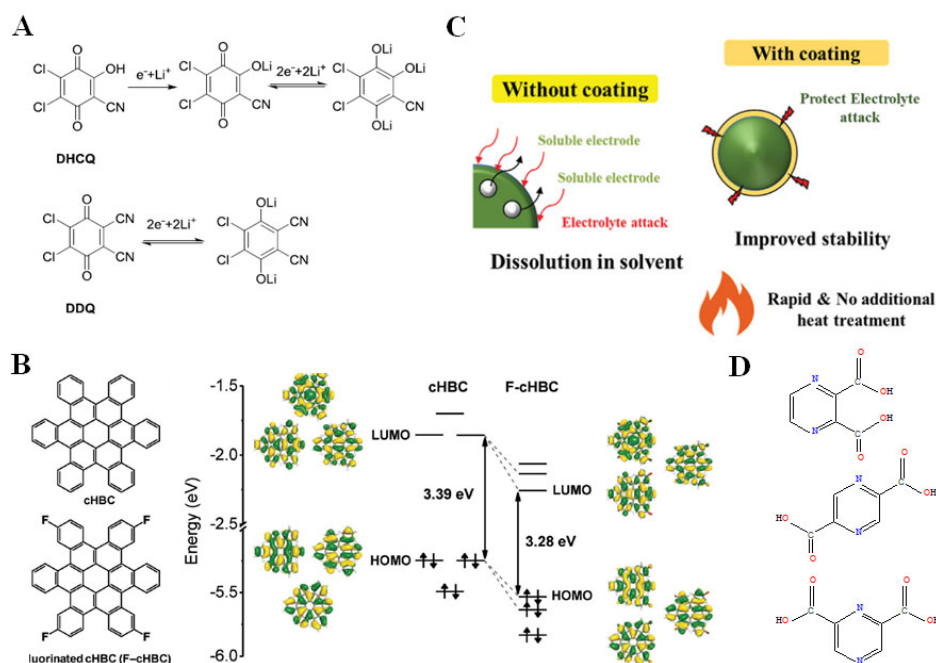
Figure 4. Examples for improving electrochemical properties of small molecules: (A) OH-substituted DDQ[32];reproduced from Ref.[32] with permission from Elsevier. (B) Fluorinated-contorted HBC[33,34];reproduced from Ref.[33] with permission from Royal Society of Chemistry. Reproduced from Ref.[34] with permission from John Wiley and Sons. (C) Metal oxide-coated PTCD[36];reproduced from Ref.[36] with permission from John Wiley and Sons. (D) Heterogeneous Pzdc[37]. Reproduced from Ref.[37] with permission from Elsevier.

mainly resulted from the electronegative fluorine atoms promoting Li-ion diffusion and accelerating fast Li-ion uptake and release. It is noteworthy that the F-cHBC anode could also be used in SIBs. Of course, this is not the only small molecule with universality, since terephthalic acid (H_2TP) was unveiled to be the first example of an organic anode exhibiting universal Li-, Na- and K-ion storage capabilities[35].

In addition to the above-mentioned optimization methods, the stability of organic electrodes can also be solved by the atomic-level manipulation of organic molecules. Thangavel *et al.*[36] studied a series of ultrathin metal oxide coatings (Al_2O_3, ZnO and TiO_2) to modify perylene-3,4,9,10-tetracarboxylicacid dianhydride (PTCD) [Figure 4C]. The interphase stability and the Na-ion kinetics could be considerably enhanced by utilizing an ultrathin metal oxide coating and the obtained stability (89% for 500 cycles) was better than that of the traditional organic electrode (70% for 200 times). In addition, our group[37] found that the carboxyl position of pyrazinedicarboxylic acid (Pzdc) has a significant effect on its electrochemical behavior [Figure 4D]. At 32 mA g^{-1}, 2,3-Pzdc has the highest lithium storage capacity with a discharge specific capacity of 1200 mA h g^{-1}, which is nearly twice that of the 2,5-Pzdc (530 mA h g^{-1}) and 2,6-Pzdc (550 mA h g^{-1}) anodes. The highest lithium storage capacity of 2,3-Pzdc is related to its highest lithium conductivity and lowest resistance. Based on these works, it can be seen that the cycling performance of small molecules can be improved by introducing functional groups, adjusting the group positions and using ultrathin coatings. We believe that the combination of these methods will further enhance the electrochemical performance of small molecules.

Interestingly, not all unmodified small molecules have poor cycling performance. Our group[38] adopted maleic acid (MA) as the anode for LIBs without any modification [Figure 5A]. This anode exhibited an ultrahigh reversible capacity of ~1500 mA h g^{-1} at 46.2 mA g^{-1} and retained 570.8 mA h g^{-1} even at 46.2 A g^{-1}. Notably, the capacity retention was as high as 98.1% after 500 cycles at 2.31 A g^{-1}. Furthermore, an itaconic
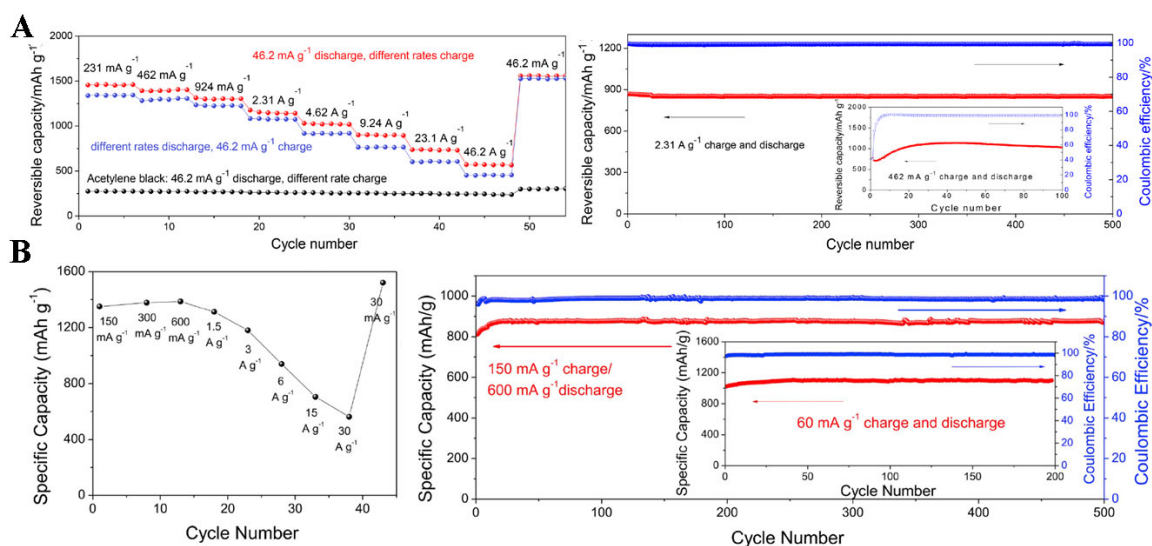
Figure 5. Examples of unmodified small molecule anodes with stable cycling: (A) MA[38]; reproduced from Ref.[38] with permission from American Chemical Society. (B) PMDA[40]. Reproduced from Ref.[40] with permission from Elsevier.

acid (IA) anode[39] showed a specific capacity of 1270 mA h g^{-1} in the first cycle and retained a reversible capacity of 1074 mA h g^{-1} after 200 cycles at 300 mA g^{-1}. Pyromellitic anhydride (PMDA)[40] reversibly provides 1472.2 mA h g^{-1} at 30 mA g^{-1} and retains 878.2 mA h g^{-1} after 500 electrochemical cycles at a 150 mA g^{-1} charge/600 mA g^{-1} discharge [Figure 5B]. All these unmodified small molecules have high specific capacities and stable cycling performance. However, large quantities of conductive carbon additives (40 wt.%) were added to these electrodes, resulting in a reduction in energy density. Therefore, it is necessary and important to improve the electronic conductivity of organic electrodes whilst controlling the content of conductive carbon additives at a low level. In addition, although it is noteworthy that these organics are based on the conjugated carbonyl structure to realize lithium storage, the first Coulombic efficiency of the IA (66.2%) and PMDA (68.4%) anodes is obviously higher than that of the MA (45.9%) anode. It is well known that binders also play a critical role in electrode performance[41-43]. Thus, water-soluble binders may be more suitable for organic materials than oil-soluble binders, although the underlying mechanism needs to be further studied.

Of course, there are also small molecules containing non-conjugated structures used as anodes. Ma *et al.*[44] reported 1,4-cyclohexanedicarboxylic acid ($C_8H_{12}O_4$, CHDA) containing one non-conjugated ring and two carboxylic acid groups as an anode for SIBs. In contrast to the classical double bond breaking/reforming mechanism employed in conjugated systems, CHDA stores sodium ions by a hydrogen-transfer-mediated mechanism, i.e., the transition of -COOH to -C(OH)$_2$ between two adjacent carboxylic acid groups achieves electron stabilization from π* to σ. Furthermore, non-conjugated compounds generally have greater steric hindrance than planar conjugated compounds to avoid free radical coupling effects. The proposal of this strategy is beneficial to expanding the application of organic materials from conjugated compounds to non-conjugated compounds and provides concepts for the design of more non-conjugated compounds.

Organic salts

Organic salts are derived from small molecules and have been widely studied as anodes for LIBs and SIBs. Table 2 shows the electrochemical parameters of typical organic salts used as LIB and SIB anodes. Many novel organic salts have been reported as potential anode materials for energy storage. For example, 4,4'-tolane-dicarboxylate (Li$_2$TDC)[45] can react reversibly with nearly two Li$^+$ ions at a potential of 0.65 V,

Table 2. Electrochemical parameters of organic salts as anodes for LIBs and SIBs

Molecule	CC/wt.%	1st Capacity/Rate	1st CE/%	Cycles/Capacity/Rate	Capacity/High rate	Battery	Reference
Li_2TDC	SP/50			50/~180/1Li^+ 20h^{-1}	~133/5Li^+ h^{-1}	Li	[45]
Na_2BDC	SP/35	264/20 mA g^{-1}	46.0	50/203/10 mA g^{-1}		Na	[60]
Na_2BDC	SP/35	173/20 mA g^{-1}	52.4	100/200/20 mA g^{-1}		Li	[60]
NaHBDC	SP/30	273/10 mA g^{-1}	40	50/244/20 mA g^{-1}		Na	[60]
H_2BDC		204/10 mA g^{-1}	25.5			Na	[60]
$(COONa)_2Na_2BDC$		152/20 mA g^{-1}	49.8			Na	[60]
F_4Na_2BDC		179/20 mA g^{-1}	25.1			Na	[60]
Na_4TDC		171/20 mA g^{-1}	65			Na	[60]
Li_4DHTPA	Carbon/20	254/0.1 C	71	50/232/0.1 C	175/5 C	Li	[55]
Li_4PTCA	AB/10$^+$SP/10	200/25 mA g^{-1}	45	100/103/25 mA g^{-1}	110/400 mA g^{-1}	Li	[65]
Na_4PTCA	AB/10$^+$SP/10	100/25 mA g^{-1}	~43	100/100/25 mA g^{-1}		Na	[65]
NaHBPDC	SP/28.6	200/0.1 C	47	150/170/0.1 C	0/20 C	Na	[58]
Na_2BPDC	SP/28.6	225/0.1 C	81	150/180/0.1 C	100/20 C	Na	[58]
Na_4DHTPA	SP/20	207/0.1 C	65	100/184/0.1 C	117/5 C	Na	[69]
Na_2BDA	CB/33	162/0.025 C	91	100/50/0.025 C		Na	[67]
Li_4PTCA	SP/40	105/2 Li^+ h^{-1}	~48	50/90/5 Li^+ h^{-1}	82/10 Li^+ h^{-1}	Li	[63]
Na_2BDC	SP/40	225/1 A g^{-1}	49	400/62/1 A g^{-1}	22/10 A g^{-1}	Na	[59]
Na_2SDC	SP/40	260/50 mA g^{-1} 247/1 A g^{-1}	69 80	50/204/50 mA g^{-1} 400/112/1 A g^{-1}	72/10 A g^{-1}	Na	[59]
Li_4PTCA	AB/35	153/24 mA g^{-1}	78.5	50/120/240 mA g^{-1}		Li	[66]
Na_4PTCA	AB/35	119/24 mA g^{-1}	44.6	300/94/20 mA g^{-1}		Na	[66]
Na_2TPA	AB/40	248/25 mA g^{-1}	~35.4	100/105/250 mA g^{-1}	59/1250 mA g^{-1}	Na	[56]
Lithium humate	CB/	480/50 mA g^{-1}	43.2	100/492/100 mA g^{-1}	193/750 mA g^{-1}	Li	[70]
Li_2BDP	SP/50	1733/1 Li^+ 50h^{-1}	93	100/200/1 Li^+ 5h^{-1}	100/500 mA g^{-1}	Li	[48]
SR	CB/20	190/0.1 C		100/171/0.1 C	95/10 C	Na	[57]
Li_2BPDC	SP/40	221/0.2 e^- h^{-1}	~63.7	25/200/0.2 e^- h^{-1}		Li	[47]
Li_2ATPA	Super C65/50	200/1Li^+ 10h^{-1}	44	50/160/1Li^+ 10h^{-1}	~50/500 mA g^{-1}	Li	[46]
Li_4-BPTC	AB/40	150/40 mA g^{-1} 124/40 mA g^{-1}	36.6 31.9	100/92/160 mA g^{-1} 200/107/160 mA g^{-1}		Li Na	[68]
CoTPA	CB/30	1004/60 mA g^{-1}	51.8	107/692/60 mA g^{-1}	175/400 mA g^{-1}	Li	[53]
Na_2TPA	CB/30	294/50 mA g^{-1}	18	100/132/500 mA g^{-1}	~188/1 A g^{-1}	Na	[61]
Na_2S_2TPA	CB/30	466/50 mA g^{-1}	34	100/224/500 mA g^{-1}	~310/1 A g^{-1}	Na	[61]
Na_2S_4TPA	CB/30	567/50 mA g^{-1}	34	100/369/500 mA g^{-1}	~380/1 A g^{-1}	Na	[61]
Na_2S_4BPTPA	CB/30	436/50 mA g^{-1}	17	100/218/500 mA g^{-1}	~290/1 A g^{-1}	Na	[61]
ZnTPA	CB/30	237/0.5 C	38	100/180/0.5 C		Na	[54]
SO	SP/30 SP/40	188/50 mA g^{-1} 316/50 mA g^{-1}	 83.1	200/354/50 mA g^{-1} 200/620/50 mA g^{-1}	90/2 A g^{-1} 157/2 A g^{-1}	Li	[49]
SC	SP/30 SP/40	166/50 mA g^{-1} 260/50 mA g^{-1}	 58.2	200/189/50 mA g^{-1} 200/392/50 mA g^{-1}	 131/2 A g^{-1}	Li	[49]
ST	SP/30 SP/40	176/50 mA g^{-1} 230/50 mA g^{-1}	 56.3	200/295/50 mA g^{-1} 200/404/50 mA g^{-1}	 145/2 A g^{-1}	Li	[49]
SP	SP/30 SP/40	185/50 mA g^{-1} 236/50 mA g^{-1}	 81.5	200/246/50 mA g^{-1} 200/278/50 mA g^{-1}	 140/2 A g^{-1}	Li	[49]
SND	CB/30	~174/200 mA g^{-1}	26	100/~110/200 mA g^{-1}	108/2 A g^{-1}	Li	[62]
SNB	CB/30	~240/200 mA g^{-1}	27	100/~160/200 mA g^{-1}	137/2 A g^{-1}	Li	[62]
Li_2TPA	SP/40	433/0.1 C	80	1000/130/1 C	120/10 C	Li	[64]
Na_2NDC	SP/10+KB/15			200/135/2 C	133/5 C	Na	[50]
Na-1,2,4-BTC	KB/30	258/25 mA g^{-1}	~28	500/85/1 A g^{-1}	62/2 A g^{-1}	Na	[51]
SC	SP/40	234/2 A g^{-1}	~60	1770/777/2 A g^{-1}		Li	[52]
Na_2HA	SP/30	333/100 mA g^{-1}		100/118/100 mA g^{-1}	113/1 A g^{-1}	Na	[71]

$Li_4C_8H_2O_6$	SP/20	215.7/50 mA g^{-1}	73	150/200/0.1 A g^{-1}	102.8/2 A g^{-1}	Li	[72]
$Li_4C_4H_2O_6$	SP/20	215.6/50 mA g^{-1}	54.5	150/95/0.1 A g^{-1}	70/2 A g^{-1}	Li	[72]

CB: carbon black; KB: Ketjen black. CC: conductive carbon; CE: Coulombic efficiency; AB: acetylene black; SP: Super-P.

lithium 2-aminoterephthalate (Li$_2$ATPA)[46] has a stable lithium storage capacity of ~180 mA h g^{-1}, dilithium 4,4'-biphenyldicarboxylate (Li$_2$-bpdc)[47] maintains up to 180 mA h g^{-1} in 25 cycles at a 2 e$^-$/h rate and dilithium benzenedipropiolate (Li$_2$BDP)[48] can reduce and reversibly oxidize its unsaturated carbon bond, resulting in a lithium/carbon ratio of 1:1.

In addition to lithium salts, organic sodium salts have also been widely investigated. Xu *et al.*[49] studied four kinds of sustainable sodium carboxylate-derived materials, including sodium oxalate (SO), sodium citrate (SC), sodium tartrate (ST) and pyrolytic sodium (SP). Due to differences in the molecular structures and intermolecular interactions, they show different initial capacities of 619.6, 392.3, 403.7 and 278.1 mA h g^{-1}, respectively. Dicarboxylate sodium naphthalene-2,6-dicarboxylate (Na$_2$NDC)[50] shows a reversible two sodium insertion of ~0.4 V (with Na$^+$/Na) and a capacity ~200 mA h g^{-1} at 0.5 C. Sodium benzene-1,2,4-tricarboxylate (Na-1,2,4-BTC)[51] delivers a high initial desodiation capacity of 258 mA h g^{-1} and remarkable cyclability of > 500 cycles. SC[52] delivers a high lithium storage capacity of 776.8 mA h g^{-1} at 2 A g^{-1}.

Beyond lithium- and sodium-substituted organic salts, there are also some other metal-substituted organic salts. Wang *et al.*[53] used cobalt terephthalate (CoTPA) and zinc terephthalate (ZnTPA)[54] as anodes for LIBs, and it was found that the discharge capacity of ZnTPA (180 mA h g^{-1}) is lower than that of CoTPA (700 mA h g^{-1}). Although the preparation of organic salts is considered to be one of the most effective methods to improve the cyclic stability of small molecules, their capacity will be reduced to a certain extent. It can therefore be concluded that the type of substituted metal ion also affects the final electrochemical performance of organic salts.

Similar to small molecules, there are many factors that can affect the electrochemical performance of organic salts. Morphology is one of the most important factors and many organic salts with different morphologies have been compared. For example, 2,5-dihydroxyterephthalic acid (Li$_4$DHTPA) with a nanosheet morphology has better electrochemical performance than that with bulk and nanoparticle morphologies[55]. Compared with bulk disodium terephthalate (B-Na$_2$TP), Na$_2$TP nanosheets have better electrochemical performance[56]. Nanorod-structured sodium rhodizonate has better performance than that of microbulk and microrod structures[57]. The main reason is that nanostructures are more conducive to the migration of ions and electrons due to their shorter transmission distance and the better conductive network than bulk particles. Thus, the utilization of active materials can be enhanced and the kinetics of the electrochemical reactions are improved.

In addition to morphology, other factors also affect the electrochemical performance of organic salts. Choi *et al.*[58] reported that the degree of deprotonation in a sodium salt of bpdc affects both the electrochemical performance and reaction mechanisms [Figure 6A]. The Coulombic efficiency and rate performance of the partially deprotonated bpdc-monosodium salt (NaHbpdc) were lower than that of the fully deprotonated bpdc-disodium salt (Na$_2$bpdc). During sodiation and desodiation, Na$_2$bpdc showed a reversible phase transition, while NaHbpdc exhibited an irreversible phase transition. Wang *et al.*[59] proved that the expansion of a π-conjugated system is an effective method to improve the cyclic stability of organic salts [Figure 6B]. The capacity of sodium phenyldicarboxylate (SBDC) degraded to 62 mA h g^{-1} after 400 cycles, while the expanded π-conjugated system of sodium 4,4'-stilbene-dicarboxylate (SSDC) retained 112 mA h g^{-1} at the same conditions.
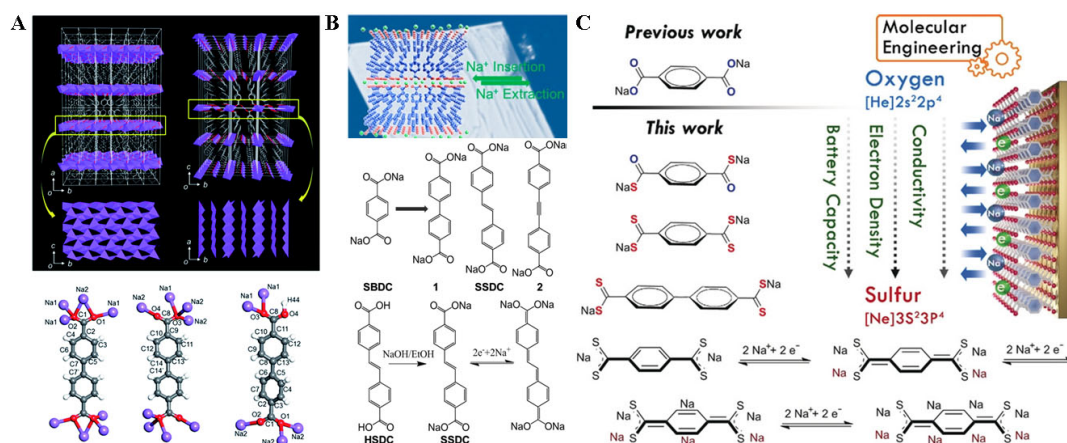
Figure 6. Examples of factors affecting the electrochemical performance of organic salts: (A) bpdc with different deprotonation[58]. Reproduced from Ref.[58] with permission from Royal Society of Chemistry. (B) Extended π-conjugated system of SBDC[59]. Reproduced from Ref.[59] with permission from American Chemical Society. (C) Sulfur-substituted PTA-Na[61]. Reproduced from Ref.[61] with permission from John Wiley and Sons.

Abouimrane *et al.*[60] found that the electrochemical performance of terephthalate (BDC) can be regulated by replacing a substituent. They successfully inserted sodium into a series of carboxylate-based anode materials, including disodium terephthalate (Na_2BDC), monosodium terephthalate (NaHBDC), terephthlaic acid (H_2BDC), disodium tetrafluoratherphthalate (F_4Na_2BDC), 1,2,4,5-tetrasodium terephthalate [(COONa)$_2Na_2BDC$], 1,4,5,8-naphthalenetetracarboxylic dianhydride and tetrasodium 1,4,5,8-naphthalenetetracarboxylate (Na_4TDC), and various lithium storage capabilities were obtained. Zhao *et al.*[61] developed a family of sulfur-substituted sodium salts of terephthalate (PTA-Na) [Figure 6C]. By introducing two sulfur atoms into PTA-Na, the reversible capacity reached 466 mA h g^{-1} at 50 mA g^{-1}, and the capacity increased to 567 mA h g^{-1} when four sulfur atoms were introduced. The reason for this can be ascribed to the improvement of electron delocalization, conductivity and sodium absorption capacity by gradually replacing the oxygen atoms in PTA-Na with sulfur atoms. The advantage of replacing oxygen with sulfur has also been confirmed by Wang *et al.*[62]. They systematically studied applications of sodium naphthalene-2,6-dicarboxylate (SND) and sodium naphthalene-2,6-bis(carbothioate) (SNB) in LIBs. By introducing fewer electronegative sulfur atoms into the carboxyl group at the molecular level, SNB showed better rate performance and cycle stability than SND.

Fédèle *et al.*[63] explored the lithium storage capability of tetra-lithium perylen-3,4,9,10-tetracarboxylate (Li$_4$-PTC) and found that the lowering of the cutoff potential enabled an increase in the first reversible capacity. The capacity retention and Coulombic efficiency were also affected by the cutoff potential. Furthermore, the electrochemical properties of organic electrodes can be improved by optimizing the binders. Zhang *et al.*[64] used sodium alginate as an aqueous binder for dilithium terephthalate (Li$_2$TP). It showed a significant improvement in electrochemical performance compared with a poly(vinylidene fluoride) binder because Li$_2$TP has high water solubility and could be evenly distributed in the sodium alginate-based electrode. Based on these studies, it can be concluded that the electrochemical performance of organic salts can be improved by adjusting their morphologies, introducing functional groups, extending conjugate length and optimizing binders.

In addition to the reports related to organic salts used in LIBs or SIBs, some organic salts and their homologs can store both Li and Na ions. Zhao *et al.*[65] synthesized a lithium and sodium salt of 3,4,9,10-perylenetetracarboxylic acid (Li_4PTCA and Na_4PTCA) for the reversible bonding of Li and Na ions, respectively [Figure 7A]. The capacity attenuation of both anodes is almost imperceptible in 100 cycles, demonstrating the possibility of using these organic anodes for LIBs and SIBs. This was also verified by Veerababu *et al.*[66], who improved the rate capability and capacity of a Li_4PTCA electrode by the in-situ coating of Li_4PTCA with conducting acetylene black carbon, which is also applicable to Na_4PTCA [Figure 7B]. Furthermore, Mihali *et al.*[67] compared the sodium storage behavior of disodium benzenediacrylate (Na_2BDA) with the lithium storage behavior of its lithium-ion homolog, Li_2BDA [Figure 7C], and highlighted that transferring from LIBs to SIBs is less straightforward and involves an associated chemical complexity. In addition to the molecules mentioned above, Medabalmi *et al.*[68] found that a [1,1'-biphenyl]-3,3',4,4'-tetracarboxylate tetralithium salt (Li_4-BPTC) can be used as a negative electrode material for both LIBs and SIBs. As shown in Figure 7D, at a current of 160 mA g^{-1}, the anode provides a stable capacity of 92 mA h g^{-1} after 100 cycles for lithium storage and shows a reversible capacity of 107 mA h g^{-1} after 200 cycles for sodium storage.

In addition to anode half cells, it is noteworthy that some organic salts can be used as both positive and negative electrodes. For example, Li_4DHTPA has been used to produce all-organic LIBs with an average operating voltage of 1.8 V and an energy density of 130 W h kg^{-1} [Figure 8A]. Wang *et al.*[69] provided the first example of an all-organic SIB using 2,5-dihydroxyterephthalic acid (Na_4DHTPA), which exhibited an average working voltage of 1.8 V and an energy density of 65 W h kg^{-1} [Figure 8B]. In addition, there are also reports on all-organic batteries using different anode and cathode materials. Hu *et al.*[70] first fabricated all-renewable-biomolecule-based full LIBs with emodin-based cathodes and humic acid-based anodes [Figure 8C]. The reversible discharge capacity could be stably retained at 60 mA h g^{-1} at a current of 100 mA g^{-1} after 100 cycles. These works indicate that although it is possible to develop all-organic batteries, there are still challenges to overcome regarding their electrochemical performance.

In addition to the above-mentioned conjugated organic salts, non-conjugated organic salts have also been reported as anode materials. Wu *et al.*[71] reported that sodium humate (Na_2HA) containing non-conjugated carboxylate groups can serve as a highly reversible anode material for SIBs. Functionalized by reduced graphene oxide (rGO), it achieved a high capacity retention of 91.6% over 2000 cycles at a current density of 500 mA g^{-1}. Zhang *et al.*[72] compared the performance of conjugated carboxylate ($Li_4C_8H_2O_6$) and non-conjugated carboxylate ($Li_4C_4H_2O_6$) as anode materials for LIBs. They found that the former stored lithium ions through a traditional double bond breaking/reforming mechanism, while the latter stored lithium ions based on the binding of lithium ions to carbonyl sites to generate free radicals. Although the capacity and cycling stability of non-conjugated carboxylates are lower than those of conjugated carboxylates, they still have the potential as electrode materials for high-performance energy storage devices.

Polymers

To solve the problem of dissolution, the construction of skeleton stable organic polymers is considered to be one of the most effective strategies. The electrochemical parameters of polymer anodes for LIBs and SIBs are listed in Table 3. It is regarded that conjugated ladder polymers are promising candidates for organic anode materials. Wu *et al.*[73] reported that poly (benzobisimidazobenzophenanthroline) (BBL) and its derivative (SBBL) have excellent cycle and rate capabilities in LIBs, especially at high temperatures [Figure 9A]. During 1000 cycles at 50 °C under 3 C, BBL showed no obvious capacity fading and retained 496 mA h g^{-1} at the 1000th cycle. They believed that the large π-conjugated structure, rich nitrogen and oxygen heteroatoms and multiring aromatics were the important reasons for the excellent electrochemical performance. The advantages of conjugated ladder polymer-containing nitrogen heteroatoms as anodes for

Table 3. Electrochemical parameters of polymers as anodes for LIBs and SIBs

Polymer	CC/wt.%	1st Capacity/Rate	1st CE/%	Cycles/Capacity /Rate	Capacity/High rate	Battery	Reference
PAQS	KB/50	220/180 mA g^{-1}		200/185/1.6A g^{-1}	175/3.2 A g^{-1}	Na	[90]
Schiff base-1	KB/50	360/26 mA g^{-1}	~24	30/320/26 mA g^{-1}	200/260 mA g^{-1}	Na	[84]
PDCzBT	SP/30	1000/20 mA g^{-1}	~45	400/312/200 mA g^{-1}	117/2 A g^{-1}	Li	[89]
PDCzBT	SP/30	150/20 mA g^{-1}	~29	200/99/100 mA g^{-1}		Na	[89]
BBL	CNT/20	1641/0.05 C (50℃)	57.3 (50℃)	1000/496/3 C (50℃)	461/3 C (50℃)	Li	[73]
SBBL	CNT/20	1508/0.05 C	57.1	1000/320/3 C (50℃)	308/3 C (50℃)	Li	[73]
Schiff base-2	Super C-65/15 +KB/5	268/0.1 C	40.6	150/~185/1 C	~25/5 C	Na	[85]
Schiff base-3	Super C-65/15 +KB/5	260/0.1 C	36.1	150/~125/1 C	~50/5 C	Na	[85]
PQL	CNT/20	995/100 mA g^{-1} 1140/100 mA g^{-1} (50℃)	49.9 47.4 (50℃)	100/1550/100 mA g^{-1} 1000/500/4555mA g^{-1} (50℃)	203/9110 mA g^{-1} 303/9110 mA g^{-1} (50℃)	Li	[74]
Schiff base-4	AB/40			400/130/1 C	60/16 C	Li	[86]
PDB	CNT/10	1050/100 mA g^{-1}	65.1	100/681/100 mA g^{-1}	107/4.2 A g^{-1}	Li	[77]
Na$_2$PDS	SP/30	185/100 mA g^{-1}	~60	500/138/500 mA g^{-1}	131/1 A g^{-1}	Na	[78]
PPCQ	CNT/20	1678/100 mA g^{-1}	41	1000/489/2.5 A g^{-1}	329/5 A g^{-1}	Li	[75]
PSB	SP/10	97/10 mA g^{-1}	30.8	100/160/10 mA g^{-1}	40.3/80 mA g^{-1}	Li	[87]
BTO	CNT/30+AB/30	1098/42 mA g^{-1}	62	1000/559/420 mA g^{-1}	58/2.1 A g^{-1}	Li	[81]
P-1Na	AB/37.5	222/10 mA g^{-1}	~47	130/128/30 mA g^{-1}		Na	[80]
PT	AB/40	745/45 mA g^{-1}	~37	1000/90/500 mA g^{-1}	141/3 A g^{-1}	Li	[83]
P33DT	AB/40	1403/45 mA g^{-1}	~56	1000/663/500 mA g^{-1}	387/5 A g^{-1}	Li	[83]
P(Te-BnV)	CB/30			45/502/100 mA g^{-1}	252/2 A g^{-1}	Li	[91]
PTAT	SP/40	~300/100 mA g^{-1}	~36	500/179/0.5 C	~80/4 C	Li	[76]
PTAT@LiCl	SP/40	895/100 mA g^{-1}	66.8	500/528/2 C	200/4 C	Li	[76]
PMTA	AB/30	955/100 mA g^{-1} 1016/1000 mAg^{-1} (60℃)	58.3 59.2 (60℃)	500/497/1 A g^{-1} 500/990/1 A g^{-1} (60℃)	240/5 A g^{-1} 470/5 A g^{-1} (60℃)	Li	[82]
PPTS	AB/60	1737.6/0.1 A g^{-1}	40.12	100/406.8/0.1 A g^{-1}	335.4/1 A g^{-1}	Li	[79]
PPTS	AB/60	588.8/50 mAg^{-1}		100/137/50 mAg^{-1}	75.7/1 A g^{-1}	Na	[79]

CB: carbon black; KB: Ketjen black. CC: conductive carbon; CE: Coulombic efficiency; AB: acetylene black; SP: Super-P.

LIBs were also proved by other polymers. A poly(1,6-dihydropyrazino[2,3g]quinoxaline-2,3,8-triyl-7-(2H)-ylidene-7,8dimethylidene) (PQL) anode delivered a high reversible capacity of 1770 mA h g^{-1} at 0.05 C under 50 °C and maintained 500 mA h g^{-1} after 1000 cycles at 2.5 C [Figure 9B][74]. Poly(1,4-dihydro-11H-pyrazino[2′,3′:3,4]cyclopenta[1,2-b]quinoxalin-11-one) (PPCQ) exhibited a high capacity of 1678 mA h g^{-1} in the first cycle and maintained a stable capacity of ~500 mA h g^{-1} over 1000 cycles at a high rate of 2.5 A g^{-1} [Figure 9C][75].

Although large π-conjugated aromatic systems have been proved to be beneficial in improving the electrochemical properties of organics, lithium ions are difficult to insert into the active sites of the inner layer because of their closely packed structures with strong π-π interactions. To address this problem, Yang *et al.*[76] prepared lithium-doped poly(triazatruxene) (PTAT@LiCl) to optimize the lithium storage of PTAT [Figure 9D]. By inserting lithium ions into the polymer network using the noncovalent cation-π interaction, a wider range of intermolecular channels was obtained, which makes the reaction between lithium ions and
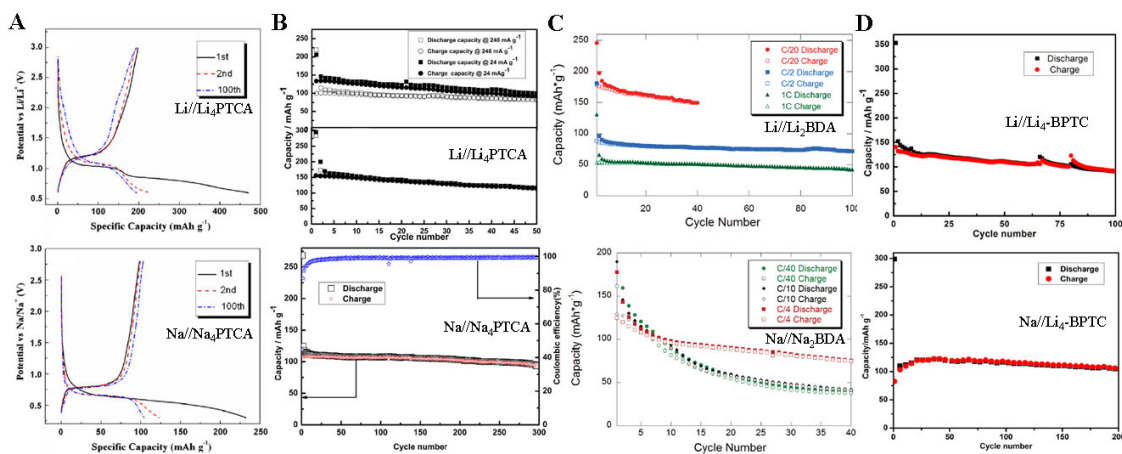
Figure 7. Electrochemical behavior of organic salts used in both LIBs and SIBs: (A) Na//Na$_4$PTCA and Li//Li$_4$PTCA[65]. Reproduced from Ref.[65] with permission from Elsevier. (B) Na//Na$_4$PTCA and Li//Li$_4$PTCA with in-situ carbon coating method[66]. Reproduced from Ref.[66] with permission from Elsevier. (C) Na//Na$_2$BDA and Li//Li$_2$BDA[67]. Reproduced from Ref.[67] with permission from Royal Society of Chemistry. (D) Na//Li$_4$-BPTC and Li//Li$_4$-BPTC[68]. Reproduced from Ref.[68] with permission from Elsevier.
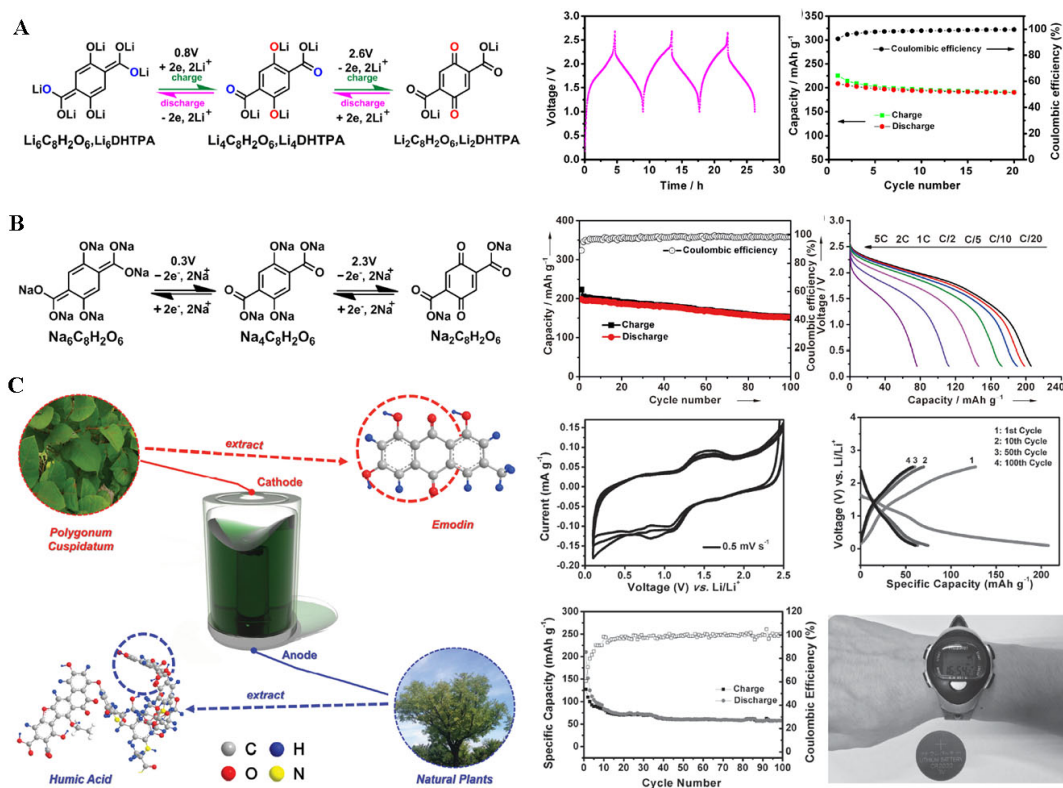
Figure 8. Redox reaction mechanism and electrochemical performance of full cells assembled with (A) Li$_4$DHTPA and (B) Na$_4$DHTPA[69]. Reproduced from Ref.[69] with permission from John Wiley and Sons. (C) Configuration of renewable-biomolecule-based full LIBs and their electrochemical performance[70]. Reproduced from Ref.[70] with permission from John Wiley and Sons.

active groups faster and more sufficient. The average capacity of PTAT@LiCl at 100 mA g^{-1} was 892 mA h g^{-1}, significantly higher than 371 mA h g^{-1} for the pristine PTAT anode. This work indicates that the performance of organics can be enhanced through the noncovalent cation-π interaction between lithium ions and large π-conjugated aromatic rings.
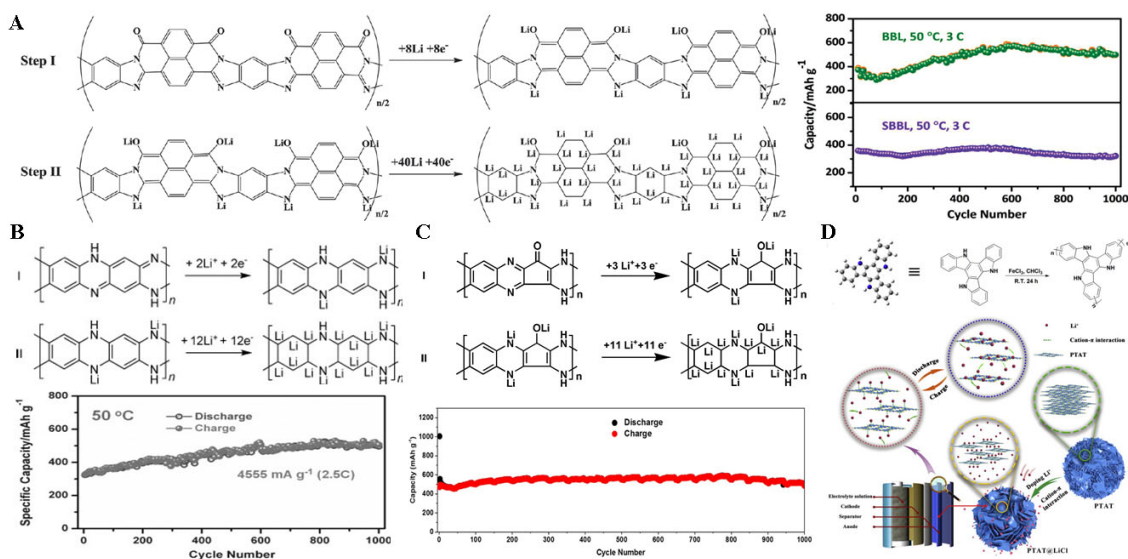
Figure 9. Redox reaction mechanism and electrochemical performance of conjugated ladder polymers: (A) BBL[73]. Reproduced from Ref.[73] with permission from John Wiley and Sons. (B) PQL[74]. Reproduced from Ref.[74] with permission from John Wiley and Sons. (C) PPCQ[75]. Reproduced from Ref.[75] with permission from American Chemical Society. (D) PTAT@LiCl[76]. Reproduced from Ref.[76] with permission from Elsevier.

As well as the above-mentioned conjugated ladder polymers, ladder-structured polymers containing thioether bonds can also be used as anodes for LIBs and SIBs, such as poly(2,3-dithiino-1,4-benzoquinone) (PDB), which delivered a reversible lithium storage capacity of 1050 mA h g^{-1} at 100 mA g^{-1} and retained 681 mA h g^{-1} after 100 cycles[77]. Poly(2,5-dihydroxyp-benzoquinonyl sulfide) (Na$_2$PDS) had a first sodium storage capacity of 309 mA h g^{-1} at 100 mA g^{-1} and the capacity retention ratio after 500 cycles was 44.7%[78]. In addition to conjugated ladder polymers, linear polymers containing a large number of carbonyl groups are believed to play a significant role in solving the solubility problem. Li *et al.*[79] synthesized a linear polymer poly(pyrenetetralone sulfide) (PPTS) linked by thioether bonds, which contained a large number of carbonyl groups as active sites. It is noteworthy that the introduction of a large number of S atoms can effectively improve the conductivity of the material, which effectively improves the performance. When used as an anode, it provided an initial reversible lithium storage capacity of 697.1 mA h g^{-1} and an initial reversible sodium storage capacity of 205.2 mA h g^{-1}, and the cycling stability was significantly better than the monomer precursor.

Conjugated carbonyl compounds have attracted significant attention as anode materials because of their excellent structural stability and high capacity. Some research has shown that the combination of carbonyl groups with polymers enables stable cycling. Yamamoto *et al.*[80] decorated sodium terephthalate (Na$_2$TP) with a polymer and used it as an anode for SIBs. Compared to the capacity retention of Na$_2$TP after 130 cycles at 30 mA g^{-1} (61%), the polymer-linked Na$_2$TP showed higher capacity retention of 77%. Wang *et al.*[81] introduced carbonyl functional groups into the conjugated structure to obtain a novel benzophenolne-3,3',4,4'-tetracarboxylimide oligomer (BTO) anode material for LIBs. It could maintain 88% of its initial capacity after 1000 cycles at 420 mA g^{-1}. He *et al.*[82] synthesized a multi carbonyl polyimide material (PMTA) by the polymerization of 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) and terephthalamide (TA). It maintained 97% of its first charge capacity after 500 cycles at 1 A g^{-1}. In addition, poly(thiophene) (PT), as a kind of n-doped conjugated polymer, can be employed as an anode material for energy storage. Zhang *et al.*[83] investigated a series of thiophene-containing conjugated microporous polymers, including PT and poly(3,3'-bithiophene) (P33DT) with different thiophene contents and surface

areas. They found that the thiophene content, crosslinked porous structure and surface area have an important impact on the electrochemical performance. The optimized P33DT delivered an ultrahigh capacity of 830 mA h g^{-1} at 500 mA g^{-1} and could retain 663 mA h g^{-1} after 1000 cycles.

In recent years, polymeric Schiff bases have opened up a new broad field in the area of low-voltage organic electrodes for LIBs and SIBs. Figure 10 shows some structures of polymeric Schiff bases. Castillo-Martínez *et al.*[84] reported that crystalline polymeric Schiff bases can reversibly store more than one sodium atom per azomethine group and the redox potential can be tuned by changing the polymeric chains and substituents. Furthermore, they found that the electrochemical performance of Schiff bases can be optimized by maximizing the number of active units[85]. The hyperbranched conjugated Schiff base polymer synthesized by Sun *et al.*[86] exhibited outstanding cyclic stability with only a slight capacity decline over 400 cycles at 1 C. Ye *et al.*[87] synthesized a highly conjugated polymeric Schiff base via a facile solid-phase condensation reaction between 1,4-diaminoanthraquinone and p-phthalaldehyde. It delivered a first charge capacity of 97 mA h g^{-1}, and the capacity retention after 100 cycles was 50.8%.

Similar to organic salts, there are also some polymers that can be used in both LIBs and SIBs. The optimized polydopamine (PDA) derivative has ultrahigh capacities of 1818 mA h g^{-1} for LIBs and 500 mA h g^{-1} for SIBs, with remarkable cycle performances of 93% capacity retention after 580 cycles for LIBs and no obvious capacity decrease during 1024 cycles for SIBs [Figures 11A and B][88]. Zhang *et al.*[89] explored polymer 4,7-dicarbazyl-[2,1,3]-benzothiadiazole (PDCzBT) as a high-performance anode material for LIBs and SIBs [Figures 11C and D]. In LIBs, it showed a high reversible capacity of up to 1042 mA h g^{-1} at 20 mA g^{-1} and delivered 312 mA h g^{-1} after 400 cycles at 200 mA g^{-1}. In SIBs, a reversible capacity of 145 mA h g^{-1} was achieved after 100 cycles at 20 mA g^{-1}. The lower capacity for sodium storage than lithium storage is attributed to the larger ionic radius and more sluggish kinetics of Na^+ than Li^+. In addition to half cells, a novel all-organic SIB based on a polymeric cathode and anode was reported by Deng *et al.*[90] The full cell assembled with a polytriphenylamine (PTPAn) cathode and a poly(anthraquinonyl sulfide) (PAQS) anode could achieve considerable specific energy of 92 W h kg^{-1}. Finally, polymer-based electrodes are also expected to be used in flexible electronics[91].

COFs

Compared with the organics mentioned above, COFs have ordered two- or three-dimensional structures, and this special molecular design provides more active sites for the storage of Li or Na ions. The electrochemical parameters of COFs as anodes for LIBs and SIBs are shown in Table 4. The redox mechanism of COFs has been studied by many groups. Kang *et al.*[92] believed that the polyanthraquinone-triazine (PAT) electrode undergoes a 17-electron redox reaction and interfacial storage in the PAT pores during the lithium storage process, thus delivering a high reversible capacity of 1770 mA h g^{-1} at 200 mA g^{-1}. Lei *et al.*[93] found that each C = N group in COFs can reversibly bind with one lithium ion, and the benzene ring in few-layer COFs can store lithium ions, but this phenomenon is not obvious in bulk COFs. As shown in Figure 12A, in the few-layer COF, lithium ions are first combined with C = N and then with the benzene ring to finally achieve a 14-electron redox mechanism after five stages. Thus, these COF@CNTs can provide an ultrahigh capacity of 1536 mA h g^{-1} without obvious decay after 500 cycles. They also studied covalent imine networks-1 (CIN-1) and Schiff base networks-1 (SNW-1) composites with CNTs as anodes for LIBs[94]. It was confirmed that when the COF material has a few-layer structure, the triazine and benzene rings can be reversibly combined with lithium ions [Figure 12B] and both of them can contribute a high capacity of ~1000 mA h g^{-1} at a current density of 100 mA g^{-1}.

Table 4. Electrochemical parameters of COFs as anodes for LIBs and SIBs

| COF	CC/wt.%	1st Capacity/Rates	1st CE/%	Cycles/Capacity/Rates	Capacity/High rate	Battery	Reference
TThPP		$401/1\ A\ g^{-1}$	64.3	$200/381/1\ A\ g^{-1}$	$195/4\ A\ g^{-1}$	Li	[99]
NG-HCP	CNT/20	$1319/20\ mA\ g^{-1}$	52.8	$600/423/1.2\ A\ g^{-1}$	$257/2.3\ A\ g^{-1}$	Li	[98]
2D-CAP	SP/10	$250/0.1\ A\ g^{-1}$	51	$7700/114/5\ A\ g^{-1}$	$118/5\ A\ g^{-1}$	Na	[97]
IISERP-CON1	SP/25	$720/100\ mA\ g^{-1}$		$100/720/100\ mA\ g^{-1}$	$460/2\ A\ g^{-1}$	Li	[96]
PAT	SP/25	$1305/200\ mA\ g^{-1}$	51	$400/1770/200\ mA\ g^{-1}$	$540/2\ A\ g^{-1}$	Li	[92]
COF@CNTs	AB/10	$383/100\ mA\ g^{-1}$	41.3	$500/1032/100\ mA\ g^{-1}$		Li	[93]
TFPB-TAPT		$245/30\ mA\ g^{-1}$	44	$500/125/30\ mA\ g^{-1}$	$145/200\ mA\ g^{-1}$	Na	[100]
PTTE	AB/40	$934/500\ mA\ g^{-1}$	46	$100/585/500\ mA\ g^{-1}$	$279/3\ A\ g^{-1}$	Li	[101]
PTTE	AB/40	$300/200\ mA\ g^{-1}$	~32	$100/230/200\ mA\ g^{-1}$	$134/1\ A\ g^{-1}$	Na	[101]
E-TFPB-COF	SP/10	$1274/0.1\ A\ g^{-1}$		$300/968/0.1\ A\ g^{-1}$		Li	[95]
E-TFPB-COF/MnO$_2$	SP/10	$1211/0.1\ A\ g^{-1}$		$300/1359/0.1\ A\ g^{-1}$		Li	[95]
E-CIN-1/CNT	SP/	$1269/520\ mA\ g^{-1}$	41	$250/744/0.1\ A\ g^{-1}$	$97/5\ A\ g^{-1}$	Li	[94]
E-SNW-1/CNT	SP/10	$1470/761\ mA\ g^{-1}$	51.8	$250/687/0.1\ A\ g^{-1}$	$212/5\ A\ g^{-1}$	Li	[94]
SND	CB/30	$198/50\ mA\ g^{-1}$	26	$100/85/50\ mA\ g^{-1}$	$108/2000\ mA\ g^{-1}$	Li	[62]
SNB	CB/30	$280/50\ mA\ g^{-1}$	27	$100/123/50\ mA\ g^{-1}$	$137/2000\ mA\ g^{-1}$	Li	[62]

CB: carbon black; CC: conductive carbon; CE: Coulombic efficiency; AB: acetylene black; SP: Super-P; Gra: graphite; G: graphene; COF: covalent organic frameworks; LIBs: lithium-ion batteries; SIBs: sodium-ion batteries.
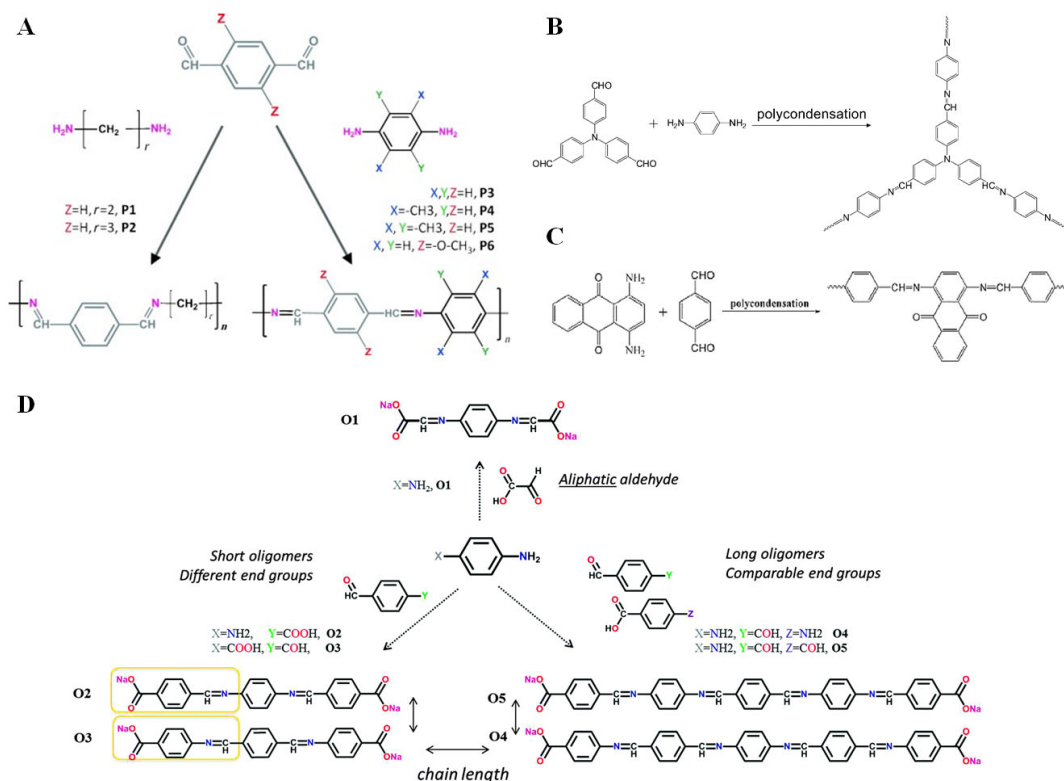
Figure 10. Structures of polymeric Schiff bases[84-87]. Reproduced from Ref.[84] with permission from John Wiley and Sons. Reproduced from Ref.[85,86] with permission from Royal Society of Chemistry. Reproduced from Ref.[87] with permission from Elsevier.
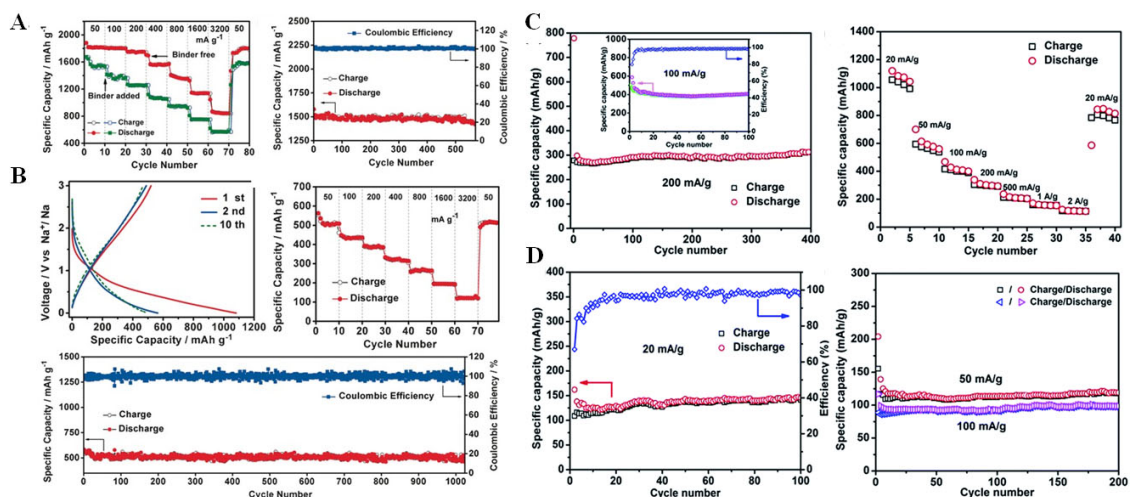
Figure 11. Electrochemical behavior of polymers used in both LIBs and SIBs. Optimized PDA-2 anode for (A) LIBs and (B) SIBs[88]. Reproduced from Ref.[88] with permission from John Wiley and Sons. PDCzBT anode for (A) LIBs and (B) SIBs[89]. Reproduced from Ref.[89] with permission from Royal Society of Chemistry. LIBs: lithium-ion batteries; SIBs: sodium-ion batteries.
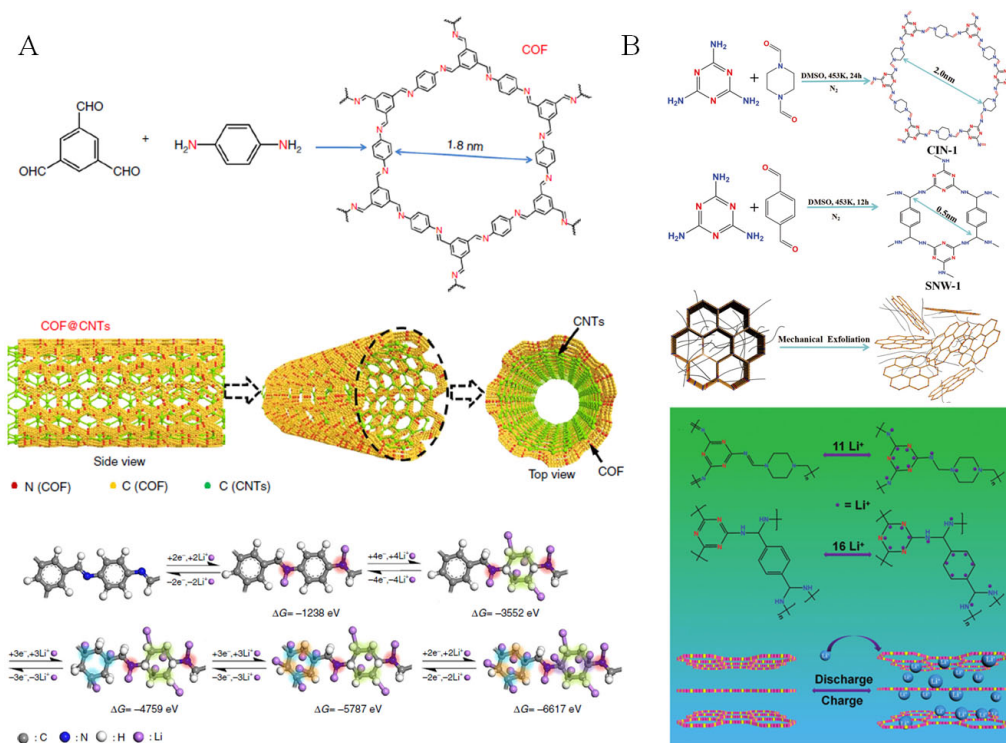
Figure 12. Schematic diagram of lithium storage in (A) COF@CNTs[93] and (B) CIN-1 and SNW-1[94]. Ref.[93] with permission from Springer Nature. Reproduced from Ref.[94] with permission from John Wiley and Sons. COF: covalent organic frameworks.

The lithium storage mechanism of few-layer COFs containing benzene rings was also verified by Chen *et al.*[95]. Compared to bulk TFPB-COF, the exfoliated E-TFPB-COF has larger interlayer spacing and new active Li storage sites on the C_6 ring. In addition, the advantages of the exfoliated COF structures were also reported by other groups[96-98] and all of these structures show stable cycling. Most COF materials are two-dimensional structures[99], but some COFs with spherical structures have also been prepared. Patra *et al.*[100]

used 1,3,5-tris(4-formyl phenyl) benzene and 1,3,5-tris(4-amino phenyl)-triazine with a C3-C3 symmetrical topology (TFPB-TAPT) as the anode material for SIBs, which showed an initial capacity of 246 mA h g^{-1}. Wang *et al.*[101] used polytetra(2-thienyl)ethylene (PTTE) with a solid sphere morphology as the anode for LIBs and SIBs, which provided a reversible lithium storage capacity of 973 mA h g^{-1} at 100 mA g^{-1} and a reversible sodium storage capacity of 370 mA h g^{-1} at 50 mA g^{-1}.

Others

Organic-inorganic composites

In order to improve the inherent solubility problems and low electronic conductivity of organic materials, organic-inorganic composite methods have been adopted by many groups. The electrochemical parameters of exampled organic-inorganic composites as anodes for LIBs and SIBs are shown in Table 5. Graphene oxide (GO) is regarded as one of the promising compositing materials because it not only improves the electronic conductivity of the electrode but can also buffer the volume change during cycling. Many organics have been composited with GO, such as croconic acid disodium salt (CADS), Na$_2$TP, Co(L)MOF and Cd(L)MOF[102-104], and all these composite anodes show improved electrochemical performance.

Furthermore, other conductive materials have been composited with organic materials[105,106]. Among these, graphite is an ideal candidate to realize the commercial application of organics, because by combining organic materials and graphite, the shortcomings of each can be compensated and complementary advantages can be achieved. On the one hand, graphite has high electrical conductivity, the addition of which can supply continuous electronic transport pathways for organics and decrease the content of conductive agents. Thus, the energy density and the first Coulombic efficiency of organic anodes can be improved. On the other hand, organics have excellent lithium storage capability, the addition of which can accelerate the transportation of lithium ions. Thus, the limited capacity and rate capability of graphite anodes based on the intercalation reaction mechanism can be significantly improved.

Our group composited maleic and itaconic acids with graphite, respectively[107-109]. Compared to the traditional graphite anode, both of the composite anodes exhibited significantly improved electrochemical performances in terms of capacity, rate and cycling. The maleic acid/graphite composite anode delivered 989.1 mA h g^{-1} after 1000 cycles at 400 mA g^{-1} and retained 889.0 mA h g^{-1} even at 8 A g^{-1}. Undoubtedly, the capacity and rate of the composite anode were significantly higher than those of the graphite anode. However, its first Coulombic efficiency was only 48.2%, although this was still higher than the pure organic anode. To solve this problem, we reduced the content of conductive carbon and the first Coulombic efficiency was enhanced to ~80%, but the specific capacity was also significantly decreased, although still higher than that of the graphite anode. Therefore, balancing the advantages of organics and graphite, and utilizing their synergistic effect to achieve high-performance anodes still requires further research. Overall, although the cyclic stability of organics can be improved by compositing with inorganics, the first Coulombic efficiencies of organic-inorganic composite anodes are generally lower than those of pure inorganic anodes. Future research on organic-inorganic composite anodes should focus on the balance between cycling stability and Coulombic efficiency.

MOFs

In recent years, MOFs have received extensive attention due to their excellent properties. The electrochemical parameters of MOFs as anodes for LIBs and SIBs are shown in Table 6. Ge *et al.*[110] prepared a Co-based MOF via the coordination assembly of Co(II) and 1,3,5-benzenetricarboxylic acid (H$_3$BTC) through a hydrothermal route (Co-BTC MOF), which provided a high initial discharge capacity of 1739 mA h g^{-1} and maintained 750 mA h g^{-1} over 200 cycles. Li *et al.*[111] *in-situ* synthesized a Cu-based MOF

Table 5. Electrochemical parameters of organic-inorganic composites as anodes for LIBs and SIBs

Composite	CC/ wt.%	1st Capacity/Rate	1st CE/%	Cycles/Capacity /Rate	Capacity/High rate	Battery	Reference
3/$Na_2C_8H_4O_4$- Ketjen black	CB/10	258/0.05 C	50.3	50/192/25 mA g^{-1}	87/2C	Na	[106]
11/CADS-GO	CB/20	332/20 mA g^{-1}	28.9	100/140/20 mA g^{-1}		Na	[102]
CaTPAG10	CB/30	233 /0.1C		50/161/2C	165/2C	Li	[105]
5%GO/Na_2TP	SP/40	354/0.1C		100/235/0.1C		Na	[103]
Co(L)MOF/RGO	AB/30	518.8 /500 mA g^{-1}	54.5	330/206/500 mA g^{-1}	646.9/1000 mA g^{-1}	Na	[104]
MA/Gra	AB/30	1067 /40 mA g^{-1}	48.2	1000/989/400 mA g^{-1}	889/8 A g^{-1}	Li	[107]
IA/Gra	AB/20	551 /25 mA g^{-1}	78.5	200/693/200 mA g^{-1}	553/10 A g^{-1}	Li	[108]
MA/G/Gra	AB/18	529 /25 mA g^{-1}	80.0	500/498/500 mA g^{-1}	498/50 A g^{-1}	Li	[109]

CB: carbon black; CC: conductive carbon; CE: Coulombic efficiency; AB: acetylene black; SP: Super-P. Gra: graphite; G: graphene.

Table 6. Electrochemical parameters of MOFs as anodes for LIBs and SIBs

MOF	CC/ wt.%	1st Capacity/Rate	1st CE /%	Cycles/Capacity /Rate	Capacity/High rate	Battery	Reference
Co-BTC MOF	AB/10	1779/100 mA g^{-1}	36	200/750/100 mA g^{-1}		Li	[110]
Co(L) MOF	AB/30			150/151.9/100 mA g^{-1}	123.4/1 A g^{-1}	Na	[104]
$Mn_2(NDC)_2(DMF)_2$	SP/35	707.2/50 mA g^{-1}	42.12	300/765.4/200 mA g^{-1}	217.7/2000 mA g^{-1}	Li	[112]
$Cd_2(NDC)_2(DMF)_2$	SP/35	514.9/50 mA g^{-1}	41.17	300/401.8/200 mA g^{-1}	188.9/2000 mA g^{-1}	Li	[112]
Mn-UMOFNs	AB/25		57	100/1187/100 mA g^{-1}	701/2000 mA g^{-1}	Li	[113]
Ni-UMOFNs	AB/25	1226/100 mA g^{-1}	67	100/546/100 mA g^{-1}	229/2000 mA g^{-1}	Li	[113]
Ni-Mn-BPTC-e-MOFs	AB/10	1320/100 mA g^{-1}	95	60/375/100 mA g^{-1}	736/6000 mA g^{-1}	Li	[114]
Ni-Mn-BPTC-g-MOFs	AB/10	510/100 mA g^{-1}	80.9	60/639/100 mA g^{-1}	185/6000 mA g^{-1}	Li	[114]
HECM	AB/15 CNTs/5	1205.9/100 mA g^{-1}		150/897/100 mA g^{-1}	388/1 A g^{-1}	Li	[111]
Cu-CA-MOF	AB/15 CNTs/5	528.8/100 mA g^{-1}		150/606.2/100 mA g^{-1}		Li	[111]
Cobtbpy	SP/30	379/0.05 A g^{-1}		50/221/0.05 A g^{-1}	114/1 A g^{-1}	Na	[115]
TTF-Co-MOF 1	SP/30	1700.3/0.2C	45.3	287/1186.6/200 mA g^{-1}	966.5/5 A g^{-1}	Li	[116]

CB: carbon black; CC: conductive carbon; CE: Coulombic efficiency; AB: acetylene black; SP: Super-P. Gra: graphite; G: graphene. MOF: metal organic frameworks. LIBs: lithium-ion batteries. SIBs: sodium-ion batteries.

via a one-step hydrothermal method, and it provided an initial capacity of 1205.9 mA h g^{-1} and maintained 897 mA h g^{-1} after 150 cycles.

In addition, it was verified that the metal type has an effect on the performance of MOFs. Gou *et al.*[112] synthesized two 1,4-naphthalene dicarboxylate-based MOFs [$Mn_2(NDC)_2(DMF)_2$ and $Cd_2(NDC)_2(DMF)_2$] by a solvothermal method. They found that the Mn-containing compound had higher specific energy than that of the Cd-based material (1679.0 mA h g^{-1} *vs.* 1241.4 mA h g^{-1} at a current of 50 mA g^{-1}). Li *et al.*[113] fabricated two Mn- and Ni-based ultrathin MOF nanosheets (Mn-UMOFNs and Ni-UMOFNs) through an ultrasonic approach. They found that Mn-UMOFNs demonstrated superior cycling stability compared to Ni-UMOFNs (818 mA h g^{-1} *vs.* 346 mA h g^{-1} at 1 A g^{-1} after 300 cycles), because Mn-UMOFNs have structural advantages, including thinner nanosheets, a smaller metal-ion radius and higher specific surface area. Yin *et al.*[114] prepared a bi-metal MOF (Ni-Mn-MOF) with a 3-dimensional spherical structure via a hydrothermal method. It provided a reversible capacity of 1380 mA h g^{-1} at 100 mA g^{-1} and retained 92% after 200 cycles. It is noteworthy that some MOFs can also achieve excellent performance in large-scale metal-ion (e.g., K- and Na-ion) batteries. Yang *et al.*[115] reported that a {$(Me_2NH_2)_2[Co_3(\mu_3\text{-}O)(btb)_2(py)$-($H_2$

O)]·$(DMF)_2(H_2O)_2\}_n$ (Cobtbpy) MOF could provide 416 mA h g^{-1} for K-ion batteries and 379 mA h g^{-1} for Na-ion batteries at a current density of 50 mA g^{-1}.

Furthermore, the addition of S atoms is considered to be one of the most effective strategies to improve the electrochemical performance of MOFs. Weng *et al.*[116] used S-rich tetrathiafulvalene (TTF) derivatives coordinated with CoII ions to prepare $[Co_2(py-TTF-py)_2(BDC)_2]$·$2DMF·H_2O$ (TTF-Co-MOF 1) and $[Co_2(py-TTF-py)_2(BPDC)_2]$·$3DMF·3H_2O$ (TTF-Co-MOF 2), and found the superiority of CoII ions, especially the synergistic effect of S-rich TTF ligands and CoII ions positively affects the performance of the electrodes. From the above studies, it can be concluded that MOFs are synthesized by a coordination reaction between metal ions and appropriate organic ligands; thus, both the types of metal ions and organic ligands affect the performance of MOFs. The development potential of MOFs in LIBs and SIBs is mainly due to the following advantages. First, the ordered porous structure of MOFs provides large ionic diffusion tunnels, enabling them to have better rate capabilities. Second, MOFs exhibit structural diversity and functional tunability at the molecular level, meaning that they can be easily adjusted to improve the electrochemical performance. However, MOFs also have some disadvantages as anodes, such as their poor electronic conductivity, which usually requires a high amount of conductive agent. In addition, the long-term electrochemical stability of MOFs needs to be further improved, because the 3D framework of MOFs can be shattered due to structural changes during the charge/discharge process. Therefore, there remain significant opportunities for improvement in the first Coulombic efficiency of MOFs.

CONCLUSION AND OUTLOOK

In this review, we systematically present the recent research progress on organic anodes in LIBs and SIBs. Redox mechanisms, structures, advantages and disadvantages and six kinds of organic anode materials, namely, small molecules, organic salts, polymers, COFs, organic-inorganic composites and MOFs, were discussed in detail. In addition to the electrochemical performance of organic anodes, we also reviewed the methods to improve their electrochemical performance, summarized the factors affecting the energy storage capabilities of organic compounds, presented typical organic materials that can store both Li and Na ions and also introduced some organic full cells. Although significant research has been carried out on the application of organic anodes in LIBs and SIBs and great success has been achieved, the practical application of organic anodes remains challenging because their electrochemical performance still requires significant improvement.

First, we must improve the utilization of the active material. Most organic materials have poor electronic conductivity, which reduces the reaction kinetics of organic materials. In order to build a whole conductive network in the anode, adding large quantities of conductive additives (20%-60%) is widely used. However, although the active material utilization can be improved, it is usually at the cost of losing the energy density of batteries. Many works have proved that the preparation of organic-carbon composite anodes is a good choice, in which carbon materials are electroactive, such as graphite, graphene and so on. Nevertheless, the related work has just begun and more research is needed to assess the advantages of energy storage with organic and inorganic materials.

Second, we need to comprehensively improve the electrochemical performance of organic anodes, including specific capacity, first Coulombic efficiency and cycling performance. Most small molecules have high specific capacity but poor cyclic stability; although the dissolution of small molecules in organic electrolytes can be suppressed by altering the molecular structure, such as synthesizing organic salts and polymers, the specific capacity is also be reduced due to the increase of molecular weight. In addition, due to the formation of the solid electrolyte interface, the addition of a large amount of conductive carbon, and the

irreversible lithium consumption of organic materials, organic anodes are characterized by low first Coulombic efficiencies (usually 20%-70%), which seriously limits the application of organic anodes in full cells. To overcome this problem, it is necessary to decrease the content of the conductive agent to reduce the contact area with electrolyte, and design the structure of organics to reduce irreversible lithium-consuming groups.

Although organic compounds have been studied for energy storage for many years, they are still in the early stage of development, and there are still many basic scientific problems to be explored, such as reasonable structure regulation, effective interface modification, targeted electrolyte optimization and optimized binder design. In addition, it is still necessary and important to find new molecules and investigate new reaction mechanisms. Obviously, organic materials as negative electrodes for LIBs and SIBs face great challenges, but their prospects cannot be ignored.

DECLARATIONS

Authors' contributions
Conceived and wrote the manuscript: Wang Y, Li X
Reviewed the manuscript, funding acquisition: Wang Y, Zheng H
Contributed to the discussion of the manuscript: Li X, Wang Y, Lv L, Zhu G, Qu Q, Zheng H

Availability of data and materials
Not applicable.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

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