Organic Functional Materials for Clean Energy

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Edited by

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CHAPTER 1

ORGANIC ELECTRODE MATERIALS

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1 Introduction

In recent years, the rapid development of consumer electronics, electric vehicles, and energy storage stations has driven a substantial increase in the demand for batteries. This trend suggests a significant rise in battery production in the foreseeable future. Currently, commercial lithium-ion batteries (LIBs) heavily rely on transition-metal oxide or phosphate materials (such as $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$) as cathodes.[1, 2] However, these materials are primarily derived from limited ores rather than renewable resources. The extensive use of LIBs is anticipated to result in the substantial consumption of these transition metals, potentially leading to supply chain issues. Additionally, the synthesis of transition-metal-based materials is associated with significant carbon emissions, which are detrimental to the environment.[3] Therefore, it is imperative to explore sustainable electrode materials for the next generation of LIBs. Organic electrode materials have emerged as promising candidates for sustainable energy storage due to their composition of earth-abundant and sustainable nonmetallic elements (such as C, H, O, S, and N). These materials also offer multiple tunable redox potentials that are compatible with current LIB charge/ discharge processes.[4]

The investigation of organic electrode materials dates back to the 1960s when carbonyl compound, such as dichloroisocyanuric acid (DCCA), were first employed as cathode in primary lithium batteries[5]. Unfortunately, the high solubility of carbonyl compounds in electrolyte has hindered their further development. From the early 1980s to the late 1990s, various conductive polymers (e.g., polypyrrole, polyaniline and polythiophene) were explored as active electrode materials for rechargeable batteries.[6-8] Coin-type batteries with polyaniline cathodes were developed in the late 1980s[9], although their performance remained insufficient for practical applications. Conductive polymers store charge through oxidation or reduction doping reactions. But the doping level of conductive polymers is usually less than 50% with less than half of the redox active groups involved in the reaction. Consequently, the actual capacity of conducting polymer as electrode usually does not exceed 150 mAh g^{-1}.[7, 8] To identify new high-capacity organic electrode materials, researchers turned their attention to organosulfur compounds[10]. The discharge and charge process of organosulfur compounds electrode is accompanied by the cleavage and formation of S–S bonds, which often shows high discharge capacity. But the kinetics of this process are generally sluggish. In addition, similar to carbonyl compounds, organosulfur compounds are also dissolved in the electrolyte, leading to side reactions and poor cycling stability[11]. Meanwhile, nitriles, electron-poor molecules with highly reversible redox chemistry and organic radicals have also been investigated as organic electrode materials.[12, 13] Unlike organosulfur compounds, organic radicals tend to undergo rapid redox reactions (orders of magnitude faster than organosulfur compounds) because almost no rearrangement of bonds occurs during discharge and charging.[14, 15] Despite these advancements, the successful commercialization of LIBs based on inorganic electrode materials led to a decline in interest in organic electrode materials during the 1990s and early 2000s.[16] However, with growing concerns about resource availability and environmental impact, interest in organic electrode materials resurged around 2008, marked by the publication of several key papers on the topic.[17-20] Over the past decade, research on organic electrode materials has focused on the development of novel electrode materials with popular functional groups and other redox-active centers, and expanding the application of organic electrode materials beyond LIBs to include sodium-ion batteries, potassium-ion batteries, zinc-ion batteries, magnesium-ion batteries and aluminium-ion batteries.[16]

In this chapter, we initially present the advantages of organic electrode materials and discuss key organic-based materials that have been investigated as electrodes, including organic carbonyl compounds, conductive polymers, organosulfur compounds, organic free radical compounds, nitrogen-containing compounds, and overlithiated compounds. We then provide a concise overview of the energy storage mechanisms associated with various types of electrode materials. Despite the significant benefits offered by organic electrode materials, their commercialization as electrodes for various metal-ion batteries remains challenged by issues such as low mass density, high solubility, and low electronic conductivity. These challenges will be thoroughly discussed in this section. Finally, we address strategies aimed at enhancing their electrochemical properties, including output voltage, specific capacity, rate performance, and cycling stability.

2 Advantage of organic electrode materials

In recent years, many organic photoelectric materials have been successfully applied in photoelectric devices[21, 22], such as organic light-emitting diodes (OLEDs), photovoltaic (PV) devices and field-effect transistors (FETs). The performance of organic materials is comparable to, and in some cases surpasses, that of conventional inorganic materials. Compared to transition-metal-based inorganic materials, organic materials offer several unparalleled advantages, as outlined below.

(1) Sustainability: The large-scale use of transition metal-based electrode materials is unsustainable due to limited resources and environmental pollution.[23] In contrast, many organic electrode materials are abundant in nature and can be sourced directly from natural biomass resources (such as plants, microorganisms, and animal products) or synthesized through mild processes, resulting in low environmental impact.[24] For example, as shown in Fig. 1-1, the electrochemically active $Li_xC_6O_6$ organic molecules can be prepared from natural sugars myo-inositol common in living systems, which can be extracted from corn.[18] Similarly, malic acid from apples can undergo polycondensation to a polyquinone that is electrochemically active to lithium.[17]

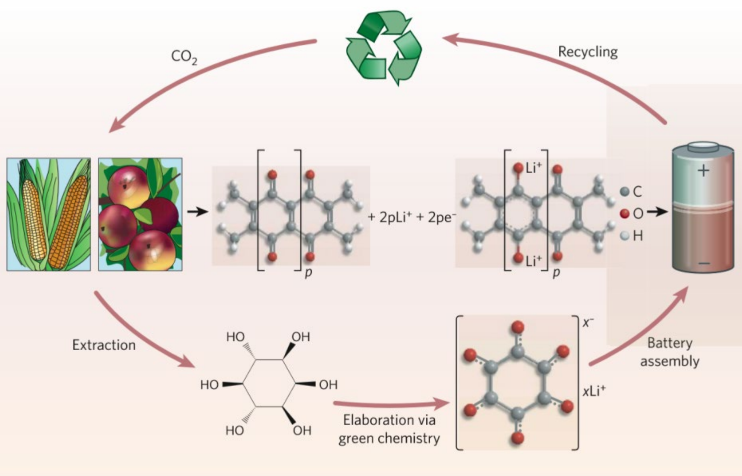


Fig. 1-1 Proposed sustainable organic-based batteries based on electrode

materials made from biomass. Source:[17]. Reproduced with permission of Springer Nature.

(2) Enhanced structural diversity: Despite significant efforts, the discovery of novel inorganic cathode materials and breakthroughs in battery performance is becoming increasingly challenging. In contrast, organic electrode materials possess an inherent advantage due to their flexible design capabilities for molecular and crystal structures, such as functional groups. This flexibility allows for the convenient customization of their redox potential and electrochemical properties, including output voltage, capacity, specific theoretical energy density, and power capability.[25] For example, Qiu et.al designed and synthesized a new p-type organic material, 4,4′-(10H-phenothiazine-3,7-diyl) bis (N, N-diphenylaniline) (PTZAN), by coupling the triphenylamine molecule with the phenothiazine molecule.[26] As shown in the Fig. 1-2a and 2b, the charge storage mechanism of PTZAN is based on the oxidation/reduction of the phenothiazine heterocycle and the triphenylamine unit, showing four-electron transfer reactions. As a result, the PTZAN||Zn battery reach excellent stability (2000 cycles), high operating voltage (about 1.3V vs. Zn/Zn^{2+}) and high capacity (145 mAh g^{-1} at 0.1 A g^{-1}).

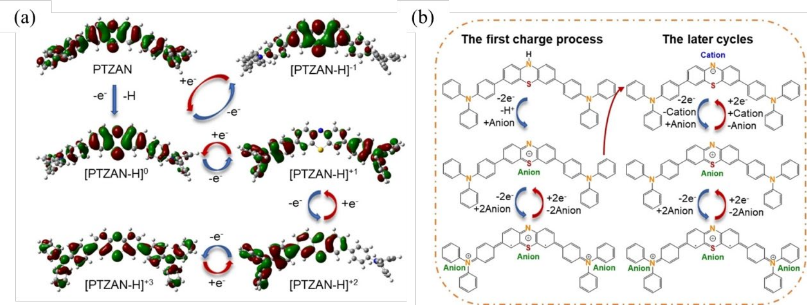


Fig. 1-2 (a) The potential oxidation sites of the PTZAN electrode is most possibly taking place. (b) Proposed charge storage mechanism of PTZAN electrode. Source:[26] . Reproduced with permission of © Wiley-VCH.

(3) Flexibility: The charge storage mechanism of inorganic electrode materials relies on a reversible metal ion intercalation-based redox reaction, making them highly sensitive to the cation radius (Fig. 1-3a). The rapid insertion and de-insertion of metal ions can result in structural transformation and degradation of the electrode material lattice[27], thus affecting the rate performance and cycle life of the battery. Unlike inorganic electrode materials, the charge storage of organic electrode materials is achieved through the alteration of the charge state of redox-active organic species (Fig. 1-3b). Organic electrode materials with flexible framework structures and general

redox mechanisms are typically not constrained by counterion selection, enabling them to prevent structural collapse and accommodate a wide range of metal ions, such as Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Al^{3+} and Ca^{2+}.[28, 29] In addition, organic electrodes materials typically have a soft molecular skeleton, which is advantageous for the production of flexible or wearable electrodes and devices. For example, a belt-shaped aqueous zinc battery using an organic cathode have been fabricated, which demonstrated superior electrochemical and flexible performances.[30]

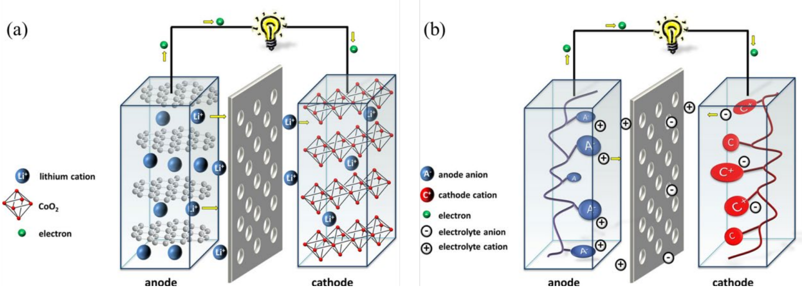


Fig. 1-3 Schematic representation of (a) inorganic and (b) organic electrodes-based lithium-ion cells. Source: [31]. Reproduced with permission of © American Chemical Society.

(4) High energy density: Due to their light constituent elements and multi-electron transfer ability, some organic electrode materials can provide higher specific capacities than transition metal-based electrode materials (e.g. $LiCoO_2$[32, 33], $LiFePO_4$[34] and nickel cobalt manganese oxide (NCM)[35, 36]). In addition, it is found that organic electrode materials such as rhodizonate[37] or cyclohexanehexone[38] derivatives can obtain four or six electron transfers per molecule, respectively, delivering capacities of about 484 mAh g^{-1} or 902 mAh g^{-1} and energy densities of 726 Wh kg^{-1} or 1533 Wh kg^{-1}. In comparison, transition metal-based electrode material, due to their high metal content, offer a limited theoretical capacity of about 270 mAh g^{-1}.[39] Although the high specific capacities of organic electrodes generally come at the cost of a low redox potential, achieving high energy density remains possible. For instance, 1,4-benzoquinone (BQ) exhibits a high energy density of exceeding 1000 Wh kg^{-1}, with an average discharge potential of ~2.5 V (vs. Li^+/Li) and a specific capacity of 501 mAh g^{-1}.[40] This performance is significantly higher than that of commercial $LiCoO_2$ (~550 Wh kg^{-1}) and the potential $xLi_2MnO_3{\cdot}(1-x)LiMO_2$ (~1000 Wh kg^{-1}).[41]

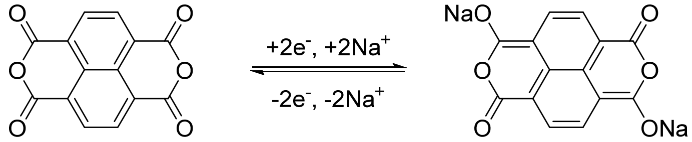
3 Classification of organic electrode materials

3.1 Organic carbonyl compounds

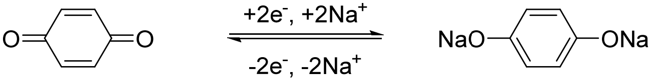
3.1.1 Organic small molecules

Small organic carbonyl compounds have gained widespread consideration owing to their unique advantages such as high specific capacity and multi-electron reactions. Currently, the well-known electroactive small carbonyl compounds could be generally classified into three types, that is anhydrides, quinones, and carboxylates (Fig. 1-4). First, the anhydrides are normally connected to aromatic conjugated rings, which could disperse the negative charge by electron delocalization effect. Second, the quinones are formed by binding carbonyl groups to conjugated rings, which can fuse an additional aromatic structure through different reduction. Third, the carboxylate derivatives are linked with aromatic rings, which can form a conjugated structure containing alkali metal ions (AMIs). The above three types carbonyl derivatives show specific characteristics. For example, anhydrides exhibit high specific capacities, while quinones show high redox potentials. In contrast, carboxylates demonstrate low alkali metal insertion voltages. Therefore, this type carbonyl small compounds could be only used as anode materials. All of the above organic carbonyl small molecules can be directly prepared from renewable resources. The following section will discuss this topic in detail.

(a) Anhydrides



(b) Quinones



(c) Carboxylates

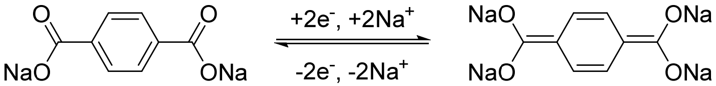


Fig. 1-4 Diagram of the redox mechanisms of three representative organic carbonyl compounds for sodium ion batteries.

(1) Anhydrides

The organic electrode materials made by anhydride derivatives with an aromatic core and several anhydride units such as pyromellitic dianhydride (PMDA), perylene tetracarboxylic dianhydride (PTCDA), and naphthalenetetracarboxylic dianhydride (NTCDA), which have been well studied for alkali metal batteries (AMB) because of their advantages such as high specific capacity and multi-electron reactions. Specifically, PTCDA has attracted great attention and shown more application potentials. For example, Luo et al. have reported that commercial PTCDA could be used as a promising cathode for sodium ion batteries (SIBs).[42] Wang et al. have reported that the anhydride groups play a key role for cathode by comparing with other kinds of aromatic compounds without these groups.[43] In this report, the aromatic core and carbonyl units can form a conjugated structure, which could facilitate to promote the redox evolution reactions. In addition, the carbonyl units connected with the aromatic rings can capture sodium ions to form sodium enolate, which could also further promote sodium ions reactions in condensed aromatic architectures. In fact, this small aromatic anhydride with two anhydride units could been reduced by four electrons and display their capacity up to 240 mAh g^{-1}.[44] In contrast, in the potential range 1–3 V, the reversible capacity could be achieved to be 150 mAh g^{-1}. When the potential decreased to be less than 0.6 V, an additional capacity could be realized (Fig. 1-4a).[42] After a deep-discharge to be 0.01 V, the capacity could be reached to be as high as 1017 mAh g^{-1} in the first cycle. This might be attributed to a solid electrolyte interphase formation and sodium ion insertion into the conjugated aromatic structures.[43] Unfortunately, the crystal structure of PTCDA would be destroyed after the deep-discharge process and thus the capacity display a dramatic drop to as low as 300 mAh g^{-1} after only five cycles.[42] In addition, the PTCDA working voltage for SIBs should also be taken consideration because of the inherent 0.3 V more reduction potential of sodium than lithium (Fig. 1-5).

The highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energy levels of the small organic molecules can be adjusted to gain different redox potentials. The molecular orbital theory has demonstrated that the molecules with a lower LUMO energy presents larger electron affinity, better oxidizability, and thus higher reduction potential.[44-46] Two strategies have been developed to decrease the LUMO energy. The first one is to enhance the aromatic conjugation system.[44, 47] This strategy can not only increase the small carbonyl molecules practical capacity and ion intake, but also reduce their HOMO–LUMO gap and decrease polarization degree. For example, the LUMO energy was decreased after changing the aromatic structure from PMDA to NTCDA and then to PTCDA, thus corresponding average discharge voltage was decreased as well. The second strategy is to attach electron-withdrawing moieties to the molecular structure to decrease the LUMO energy.[48-51] For example, Banda et al. reported a perylene diimides derivative that showed its discharge potential increased from 2.1 to 2.6 V versus Na^+/Na after substitution by several electron withdrawing groups (Br and CN).[52] Detailed analysis results demonstrated that the calculated LUMO energy values and the differential capacity plots showed a linear relationship. The electron-withdrawing substituents insertion would lead to the higher reduction potentials.

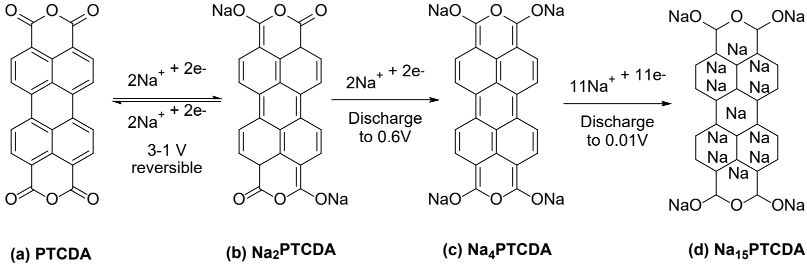


Fig. 1-5 Diagrams of the proposed electrochemical reactions for sodiation/ desodiation of PTCDA.[42]

(2) Quinone

The small organic electrode materials made by quinones derivatives such as simple quinones, fused heteroaromatic quinones, oxocarbon salts, multi-carbonyl quinones, substituted quinones, and carboxylate quinones have gained great interest in the secondary batteries because of their higher redox potentials.[53-57] Their redox potential could be finely adjust by developing the following functionalization strategy, that is, electron-withdrawing functionalities (e.g. –F, –Cl, –Br, $-SO_3Na$, –S, –N, –CN, and $-NO_2$) and (ii) electron-donating functionalities (e.g., $-NH_2$, $-CH_3$, $-OCH_3$, –OLi, and –ONa). These functional motifs can additionally have an inductive or resonance effect on charge carriers and further improve their electrochemical properties. For example, as the basic structural unit, benzoquinone and its derivatives have been used as electrode materials for SIBs.[37, 58-62] After halogenation by F, Cl, and Br, they demonstrated a pronounced tendency to gain their outermost electron. The electron-withdrawing groups introduction at the quinone structure can significantly enhance the sodium storage potential, which was further confirmed by density functional theory (DFT) calculations. It was demonstrated that the potential follows the trend of $C_6F_4O_2>C_6Cl_4O_2>C_6Br_4O_2>C_6H_4O_2$ (Fig. 1-

6a). The halogenation would decrease their LUMO level with approximately 0.2 eV negative shift (Fig. 1-6b). The quinone small molecules show lower specific capacity because of the great stabilization ability in the intermediate phase.[58] In addition, the simple quinone compounds always display high solubility in aprotic electrolyte, which lead to serious capacity fading during the charging/discharging process. Therefore, to introduce a salt structure is one effective strategy to solve this problem. The salt incorporation could increase the polarity and prohibit the organic materials dissolution in aprotic electrolyte.

Delicate tuning of the quinone based electrodes materials redox potential can be realized by changing the substitution groups. In fact, even a small structural variation induced by functional groups can have an apparent effect on the working voltage. For example, the sulfonic substitution on quinone derivatives can also increase the electrode working voltage because of its strong affinity toward electrons. Because of organic compounds chemical and molecular diversity, their LUMO energy levels and working voltages could be envisaged and predicted by density functional theory (DFT).[51] Wan et al. investigated that electrochemical performance and lithium storage voltage of the anthraquinone cathodes for lithium ion batteries (LIBs) changed dramatically after sulfonic modification.[63] They chose disulfonic acid sodium (SO_3Na^-) to modify anthraquinone (AQ) to yield anthraquinone-1-sulfonic acid sodium (AQS) and anthraquinone-1,5-disulfonic acid sodium (AQDS), respectively. The results demonstrated that the AQDS showed 2.4 V discharge voltage (vs. Li/Li^+), which was higher than that of unsubstituted anthraquinone (AQ) compound (2.1 V; Fig. 1-6c). In addition, the redox potential of AQS with a single sulfonic acid substituent is between those of AQDS and AQ, which indicate that sulfonic groups have positive effect on voltage elevation. In addition, there is a big difference in their reversible capacities because AQDS exhibits its reversible specific capacity to be 120 mAh g^{-1}, but AQ delivered only 40 mAh g^{-1} at the same condition. *In-situ* IR spectroscopy results prove that the $–SO_3Na$ groups are not active in the electrochemical reactions and only increase the AQDS working voltage. As evidenced from the peak position of S–O vibration, which gradually vanished with increasing the depth of discharge.

Meanwhile, there is an additional promotional effect of methoxy groups on the cycling stability of the battery. The resonance effect attributes to the strong π–π stacking between methoxy groups and the extended conjugate plane magnifies the intermolecular interaction. These effects are well described by Yang et al., where 2,6-dimethoxy-9,10-anthraquinone (DMAQ) displayed better stable cyclic performance than un-substituted

9,10-anthraquinone (AQ) because of the improved molecular stability of DMAQ.[64] In addition, these methoxy derivatives can provide additional ion storage sites after redox reaction. For example, Matsubara et al. prepared *2,2'*-bis-*p*-benzoquinone (BBQ) derivatives coordinated with methoxy group via a dimerization process[54] and found that the methoxy group addition resulted in a four-electron redox process. In contrast, the BBQ derivatives modified by other substituents were found to be a three-electron redox mechanism. In addition, the other electronegative elements such as S, O and N introduction could also lower the LUMO energy level (Fig. 1-6d). For example, Chen et al synthesized a series of novel quinone derivatives incorporated with heteroatomes and found it behaved as a nice organic electrode material (Fig. 1-6e).[18]

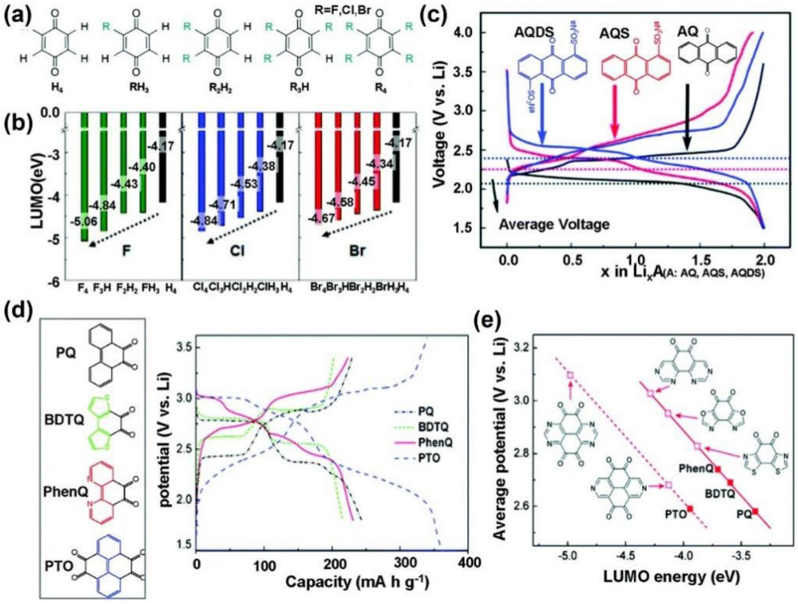


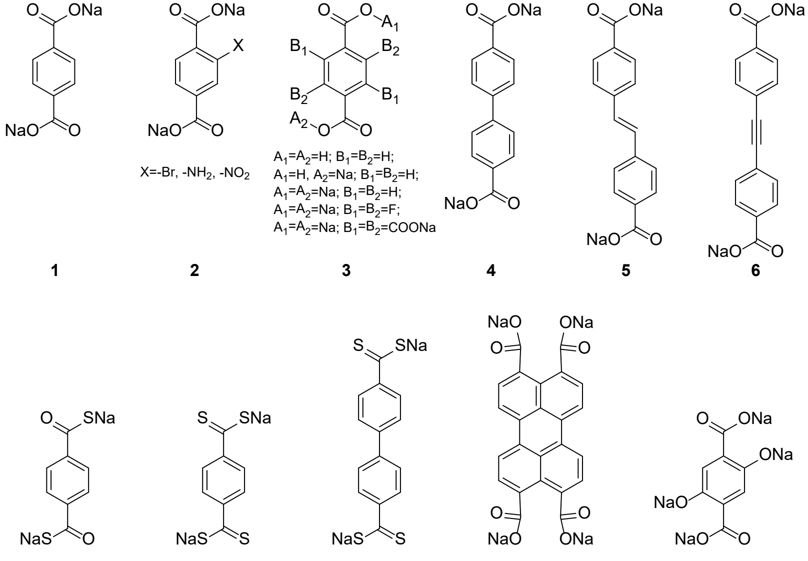
Fig. 1-6 Diagrams of carbonyl electrode materials with electron-withdrawing functional groups. (a) Molecular design of $C_6R_4O_2$ compounds where R is F, Cl, or Br. (b) Simulated theoretical LUMO energy levels of $C_6R_4O_2$[58]. Copyright 2015 American Chemical Society. (c) Charge and discharge curves of AQ, AQS and AQDS electrodes with their schematic chemical structures [63]. Copyright 2014 The Royal Society of Chemistry. (d) Galvanostatic charge/discharge profiles for four different carbonyl electrodes containing different heterocyclic structures. (e) The calculated energy levels and average potentials of PQ, BDTQ, PhenQ, and PTO.[47]. Copyright 2013 The Royal Society of Chemistry.

(3) Carboxylates

The electrode materials using carboxylate-based aromatic compounds have been widely investigated. Due to their safety and energy density advantages, this kind of organic materials display a low sodium insertion voltage. Sodium terephthalate has been found as the most widely studied carboxylate-based organic carbonyl electrode material for sodium ion batteries.[48] For example, Zhao et al. reported that sodium terephthalate **1** showed a high reversible capacity of 250 mAh g^{-1}, which is ascribed to a two-electron transfer. Specifically, this value can be further improved after coating a thin layer of Al_2O_3 on these electrode surface. Park et al. reported disodium terephthalate, which exhibited a reversible capacity of 295 mAh g^{-1} without apparent capacity fading. At the same time, the sodium terephthalate operational voltage can be well-tuned by modified with different groups **2**. In fact, the halogen substituent groups with electron-withdrawn ability always show a higher redox potential than these without substituted compounds. The amino group is special one due to competitive result of electronegative ability and dominant *p* donor effect, it displays a lower redox potential than these without substituted compounds.

The negative substitution also shows some double-edged sword effect. For example, the carbonyl compounds with *nitro* substituents exhibit higher capacity. However, their capacity fade much faster than those without substituents. For example, Abouimrane et al. assembled a sodium-ion full cell by using an organic carbonyl anode material and studied its sodium insertion in sodium terephthalate derivatives **3**. The cell delivers 238 mAh g^{-1} discharge capacity, but its capacity decay to be 7% after 50 cycles. Another example was disclosed by Wan et al. They revealed that nanosheet-like structure played a major role of effects on the electrochemical performance of sodium terephthalate. The cell with sodium terephthalate electrode exhibited higher rate capabilities, improved reversible capacity, and better cyclic performance than those with the bulk counterpart. However, these cells also demonstrated lower current density and worse performance degradation under high-rate condition.

The carbonyl compounds with extending π conjugated architecture would show high rate performance because π-conjugated system not only stabilizes the charged/discharged states and increase the charge transport rate, but also increases the intermolecular interactions and facilitates the insertion/extraction of the sodium ions. Furthermore, the sulfur atom introduction is another efficient way to get high-rate performance cell due to its high electron density and large atom radius. The S-containing carbonyl electrode materials display good electrical conductivity, thus giving rise to the function-oriented molecular design and synthesis, which are very important for these organic electrode materials. Overall, the quinone-based organic electrode materials show higher redox potentials. In contrast, the carboxylate-based organic electrode materials display lower redox potentials. Therefore, the carbonyl compounds with these two units could serve as different functional electrodes. For instance, compound **11** can be used as an active electrode material for both cathode and anode. It is the first report about all-organic sodium ion battery, which exhibit its average work voltage of 1.8 V and mass energy density of 65 Wh kg^{-1}.[65]



1 **2** **3** **4** **5** **6**

7 **8** **9** **10** **11**

Fig. 1-7 Molecular structures of reported carboxylate-based organic compounds as electrode materials for sodium ion batteries.[65]

3.1.2 Polymeric carbonyl system

Although small-molecule organic carbonyl compounds show good solubility in aprotic electrolyte, their practical application in cells was limited because of serious capacity fading. In order to solve this problem, to develop various polymers is an effective strategy. As mentioned above section, on one hand, the molecular structure with extended π-conjugation could improve the battery long-term cyclability and rate capability because the extension of the conjugated architecture can suppress carbonyl compounds solvation, increase electrical conductivity, and enhance charge transport dynamics. On the other hand, capacity degradation might be alleviated because the molecular instability of organic materials toward liquid electrolyte is enhanced. Furthermore, the highly conjugated organic polymers show low electrical conductivity, leading to a poor rate capability and limited charge kinetics. Therefore, the conjugated polymers with carbonyl modulation have been a promising solution to solve the above problems. In fact, there are two crucial strategies to get the conjugation architecture. The first one is modulation of aromaticity and linearity. The second strategy is to elongate conjugation length *via* polymerization.

(1) Polyquinones

Polyquinones (PQs) used for lithium-ion batteries (LIBs) have made great progress in recent years. Several excellent review papers about PQs have been reported by Kim,[66] Oubaha,[67] Haupler,[68] Wu,[69] Han,[70] Wang,[71] et al. There are four advantages about PQs as energy storage materials are described below. (1) Two carbonyl active sites provide high specific capacity;[72] (2) the carbonyls and enols could undergo tautomerism, which facilitate fast kinetics in LIBs;[73] (3) PQs always demonstrate stable amorphous structure and insolubility;[74] (4) Various PQs could be designed and synthesized.[71] Based on molecular skeleton, the diverse and tunable PQs can be classified into four types as follow: (1) simple PQs such as (poly(1,4-anthraquinone) (P14AQ) and poly(1,5-anthraquinone) (P15AQ)[75]); (2) *S*-coupled PQs such as (lithiated poly (dihydroxyanthraquinonyl sulfide) (LiDHAQS),[76] poly(benzoquinonyl sulfide) (PBQS),[72] PDB,[73] poly(benzo[1,2-b:4,5-b′]dithiophene-4,8-dione-2,6-diyl sulfide) (PBDTDS),[74] poly(anthraquinonyl sulfide) (PAQS),[77, 78] and poly(2,5-dihydroxy-p-benzoquinonyl sulfide) (PDHBQS)[79]); (3) *N*-coupled PQs such as (poly(5-amino-1,4-dyhydroxy anthraquinone) (PADAQ),[80] and poly(1,5-diaminoanthraquinone) (PDAQ)[81]); (4) side substituted PQs such as (poly(naphthotriazolequinonesty rene) (PNTQS),[82] poly(2-vinyl-4,8-dihydrobenzo(1,2-b:4,5-b′)-dithiophene-4,8-dione) (PVBDT),[83] poly(N-(anthraquinone-2-yl)-N,N-diphenylamine) (PDPA-AQ),[84] poly(3-vinyl catechol)(RPN3a), and poly(4-vinyl catechol) (RPN4a)[85]). The four types PQs molecular structures are presented in Fig. 1-8.

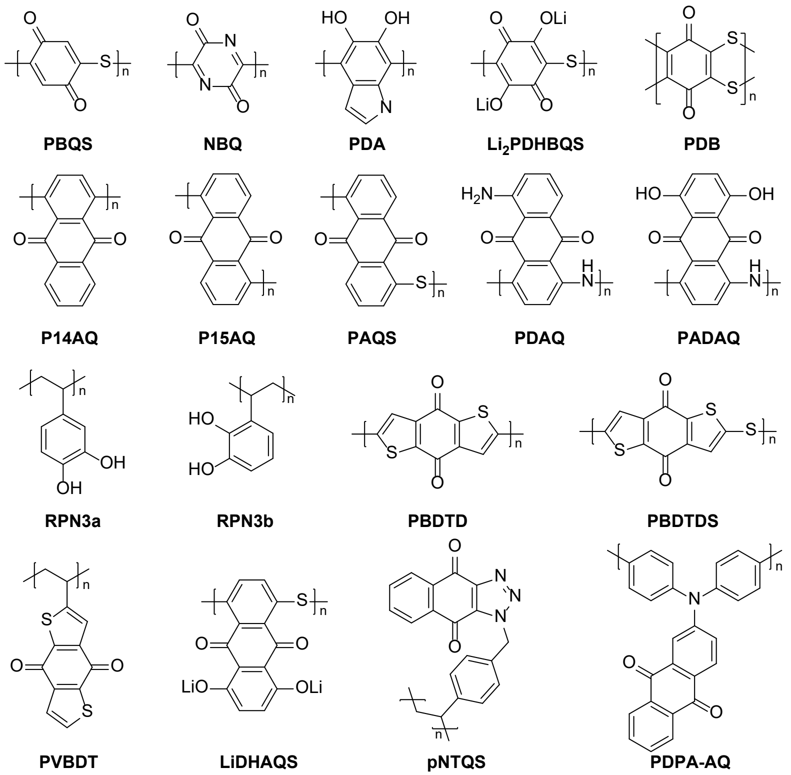


Fig. 1-8 Molecular structures of four types typical PQs.

S-coupled PQs showed much higher redox potential than that of simple PQs.[72, 73] The LUMO level of PQs were demonstrated in Fig. 1-9, which shows that the PAQS was lower than P14AQ and P15AQ. Therefore, PAQS exhibits a higher voltage plateau due to the lower bandgap (Fig. 1-9b).[75] However, Jing et al. found that the thioether bonds in the PQs would alter the molecular conformation and thus disturb the conjugation architecture (Fig. 1-9c).[74] In fact, the thioether bond would break PBDTD planar molecular conformation and transfer it to helical conformation, which lead to inefficient π–π stacking and bad electron hopping. Therefore, the PBDTDS based electrode presented poorer specific capacity and lower rate capability than PBDTD (Fig. 1-9d).

In contrast, *N*-coupled PQs could undergo special redox reaction due to the PANI backbone.[80, 81] For example, the PADAQ based electrode exhibited three redox peaks and its specific capacity as high as 322 mAh g^{-1}

(Fig. 1-9e).The redox peak at 3.34/3.16 V is ascribed to the doping/de-doping reaction of PANI backbone.[80] However, the cyclic performance of the PADAQ based electrode was poor due to the side reaction at hydroxide group position. On the contrary, the side substituted PQs behaved better cyclic life than *N*-coupled PQs. But they showed decreased capacity and low rate capability due to their inactive polymer backbone.[84, 85] For example, the PNTQs based electrode presented its cyclic lifetime as long as 1000 cycles with a capacity of 135 mAh g^{-1} at 1 C (Fig. 1-9f).[82]

In addition, the PQs can be classified into polynaphthoquinones (PNQs),[86] polybenzoquinones (PBQs), polyanthraquinones (PAQs)[77, 78], and fused heterocycle PQs according to the position of the conjugated aromatic nuclei.[82, 83] The types of conjugated aromatic nuclei of PQs would affect the theoretical capacity and their redox potential. The conjugated aromatic nucleus extension of PQs would lead to their theoretical capacity decreases due to the high molecular weight. In fact, different conjugation extent and electronic structures of PQs would great affect their redox potentials.

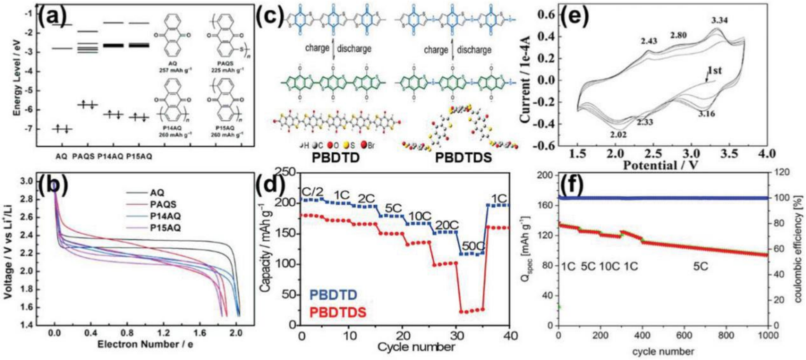


Fig. 1-9 (a) Electron configurations and (b) CV curves at 0.05 mV s^{-1} of AQ, PAQS, P14AQ, and P15AQ. [75] Copyright 2015, WILEY-VCH. (c) Conjugation evolution process, molecular conformations, and (d) rate performance of PBDTD and PBDTDS (blue: cross-conjugation; green: through-conjugation). Adapted with permission.[74] Copyright 2017, Elsevier. (e) CV curves of PADAQ electrode at 0.5 mV s^{-1}. Adapted with permission.[80] Copyright 2013, Elsevier. (f) Specific capacity and Coulombic efficiency of pNTQs electrode. Adapted with permission.[82] Copyright 2018, American Chemical Society.

(2) Polyimides

Polyimides (PIs) have been well-investigated in LIBs because of their electrochemical reversibility, excellent redox activity, good crystallinity and thermal stability.[87] Yang et al.[88] first found that the PIs possessed high electrochemical reversibility by the XRD measurement. The as-prepared perylene-PI (PDI) peak at [021] disappeared after discharging at 1.5 V and restored after charging at 3.5 V (Fig. 1-10a). The PIs can be divided into pyromellitic-PI (PMDI), PDI, and naphthalene-PI (NDI) depending on the aromatic nuclei attaching position. When the aromatic nuclei volume increases, the redox potential would increase due to the decrease of bandgap (Fig. 1-10b). However, the theoretical capacity would decrease because of the high molecular weight (Fig. 1-10c). [89] In fact, PIs as electrode always face the tradeoff between capacity and voltage. Xu et al.[90] successfully developed a PI based electrode up to 2.5 V by attaching electron-withdrawing sulfonyl group, which had little effect on the cell capacity. In addition, Casado et al.[91] Mumyatov et al.,[92] Sharma et al.,[93] Wu et al.,[94] and Ba et al.,[95] successively modified redox-active units into PIs to increase their capacity. These units include quinones, carbonyl, and phenothiazine, etc. The PI with carbonyl units and NDI with BQ moiety shows their capacities of 130 and 165 mAh g^{-1}, respectively which are much higher than that with ethyl group with only 80 mAh g^{-1}. [92, 93]

The molecular structures of PIs play a key role for their cycling stability. For example, Shestakov et al.[96] reported that the capacity loss are highly related to the cleavage of N–N bonds under reduction. Because the N-N cleavage interrupted the conjugated system and generated low molecular dissolved species, thus leading to loss of active materials and capacity. Ba et al.[95] and Zhao et al.[97] demonstrated that the structural change would be reduced in porous structure during the charge and discharge cycles. It is reported that the aggregation can be impaired for the PIs with long spacers due to more possibility for porous structure.[89, 97, 98] The PIs based electrode with an active linker demonstrated a porous structure and a cyclic life as long as 1000 cycles at 0.5 C (Fig. 1-10d,e). The capacity could maintain retention rate of 80.3% because the conductive additives help to reduce capacity loss in compact structure PIs. [95]

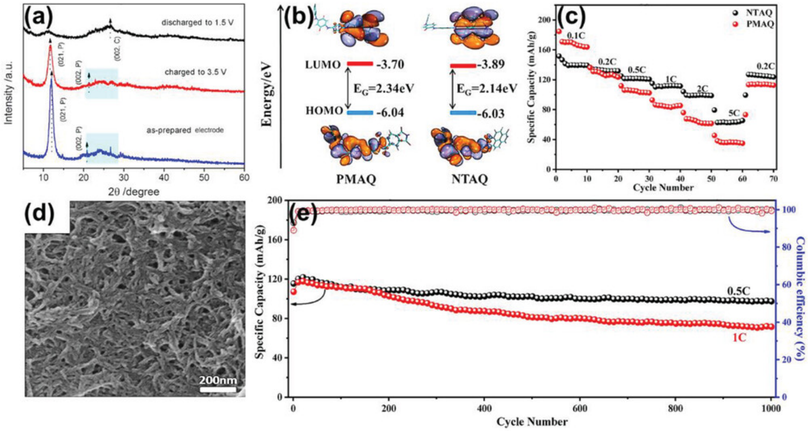


Fig. 1-10 (a) XRD patterns of PDI cathode at 1.5 and 3.5 V. [88] Copyright 2020, Elsevier. (b) HOMO/LUMO energy and (c) rate performance of PIs with pyromellitic nucleus (PMAQ) and naphthalene nucleus (NTAQ). (d) SEM image and (e) cycling performance of polyimide electrode with porous structure.[95] Copyright 2020, American Chemical Society.

PIs are a good choice for both anode and cathode materials. Polyimide anodes performed high discharge capacity and long cyclic life. Wang et al.[99] reported a tetracarboxylimide derivative anode, which displayed its initial discharge capacity as high as 1757 mAh g^{-1} at 42 mA g^{-1} and retained 420 mAh g^{-1} after 1000 cycles. He et al. reported a poly(pyromellitic diimde-alt-terephthalamide) anode that showed initial discharge capacity about 2350 mAh g^{-1} at 50 mA g^{-1}.[100] Moreover, these polymer based anode displayed good thermal stability up to 60 °C, which made it be applied in high temperature fields. However, the above two PIs based anodes showed poor initial Coulomb efficiency (lower than 60%), which may be not benefit for the future application of PI anodes.

3.2 Conductive polymers

Conductive polymers (CPs) with π conjugated skeleton have been widely used as electrode materials.[101] The conductive mechanism is based on orbitals of adjacent carbon atoms that overlap to form conjugated π bonds in the molecular skeleton.[102] Although the π-electrons along the conjugated skeleton are delocalized, they are hard to escape the polymer chain, i.e., the CPs are insulative. After doping ions were inserted to the CPs, the π-bonds are broken and the electron migration was promoted between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), which lead to conductive CPs.[103] Therefore, the conductivity of CPs is highly dependent on the doping level,[104] which determine the number of transferred electrons (or the redox level) and the CPs theoretical capacity.[105]

The CPs such as polyaniline,[106-108] polypyrrole,[109, 110] and polythiophene[109, 111, 112] are widely studied as well because of their redox potentials and high theoretical capacities. In addition, some other similar electronic architecture CPs could be used as the electrode materials of LIBs. Although great progress has been made, the practical application of these CPs based electrodes has been impaired by their inherent solubility and uncontrollable conductivity.[113] Much more work should be done to optimize molecular structures of CPs with different doping strategies to enhance their electrochemical properties.[114, 115]

3.2.1 Polyaniline (PANI)

PANI as CPs was first proposed by Macdiarmid in 1987,[116] who described a proton acid doping mechanism with detailed molecular structure model. As shown in Fig. 1-11a, two forms of PANI structural units and three redox eigenstates containing emeraldine base, leucoemeraldine base, and pernigraniline base were demonstrated.[103] The above three redox states are insulative and can transform to conductive states by proton acid doping.[117] The underlying doping mechanism is based on the intramolecular redox reaction, which lead to the charge redistribution between conjugated structural units. The proton is inserted to the conjugated polymer chain and lead to uneven charge distribution, which thus enhances the possibility of molecular charge migration. This charge constant migration eventually makes PANI to be conductive.[103]

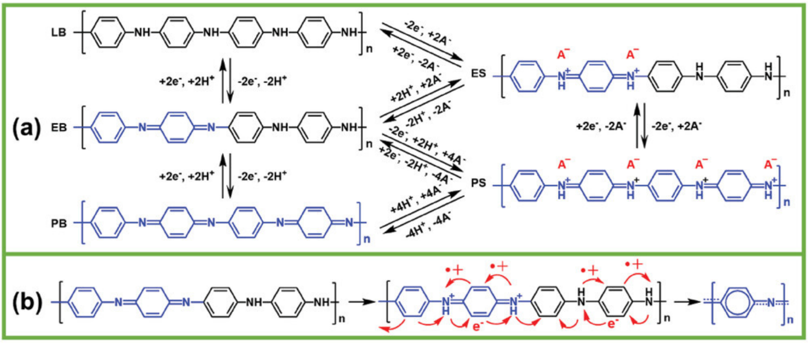


Fig. 1-11 Diagrams for (a) transformation between three redox eigenstates and two salt states of PANI (black part is phenylene-type unit and blue part is quinone-type unit), (b) proton acid doping mechanism of PANI.

Commercial PANI batteries have been developed by Bridgestone Seiko since the 1980s.[9] Unfortunately, this kind battery was soon kickout because of its low actual capacity and unstable problem.[9] Nowadays, PANI is still attractive electrode material for its high theoretical capacity (294 mAh g^{-1}), high conductivity (up to 1×10^{3} S cm^{-1}), and voltage plateau (≈3.1 V).[108, 118, 119] Unfortunately, the doped PAIN electrode only display an actual specific capacity half of its theoretical value because of the technically low doping level. Its specific capacity can be effectively improved if people can increase the doping ions. For example, Yang et al.[106] prepared a highly phosphomolybdic polyanion doped PANI and found that their discharge capacity of electrode was significantly enhanced to 183.7 mAh g^{-1} because of the multi-electron redox reaction (Fig. 1-12). However, the cyclic life was less than 50 times because of the PANI chains degradation and peroxidation reaction at high voltage. The active substances were lost during the charge/discharge process. Furthermore, the PANI based hybrid electrode using sulfonic acid derivative as dopant materials shows better stability, enhanced discharge capacity and excellent capacity retention rate because of electrostatic interaction and hydrogen bond interaction between the PANI and doping materials.[120] To increase the redox potential might be another strategy to improve the stability of PANI. By modifying electron-withdrawing groups and salinization are proved to be useful in this way.[107, 121] After CN-functionalization, the oxidation potential of PANI was higher than that of original PANI (Fig. 1-12f). This effect can be ascribed to the electron-withdrawing effect, which could stabilize the PANI structure and reduce HOMO level. [107] In addition, a lithiated PANI electrode showed its redox peak at 4.0 V, which was higher than bulk PANI.[121] Moreover, a stable PANI electrode was developed with discharge capacity of 180 mAh g^{-1} over 400 cycles. This is another good example about salinization can improve the PANI stability.

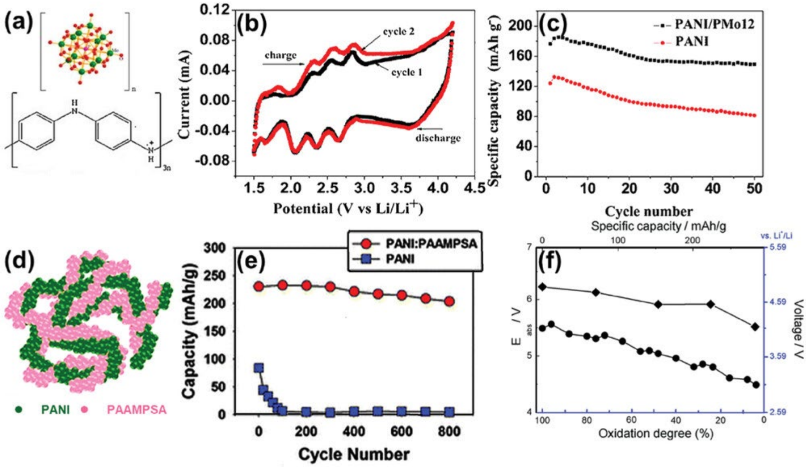


Fig. 1-12 Diagrams of (a) molecular structure and (b) cyclic voltammogram (CV) curves at 0.2 mV/s of PANI/PMo12 electrode. (c) Cyclic performance of PANI/PMo12 and bulk PANI electrodes at 0.1 C.[106] Copyright 2013, American Chemical Society. (d) Structural schematic of PANI:PAAMPSA hybrid electrode. (e) Cycle performance of PANI:PAAMPSA and bulk PANI electrodes at 50 C.[120] Copyright 2013, Royal Society of Chemistry. (f) Absolute oxidation potential (left axis) and estimated voltage (right axis) for bulk PANI (filled circles) and CN-functionalized PANI (filled rhombuses) at different degrees of oxidation.[107] Copyright 2017, Royal Society of Chemistry.

3.2.2 Polypyrrole (PPy)

PPy behaved as an electrode material for LIBs has been widely investigated Since its electrical conductivity of PPy was found in 1963.[122] PPy is a good candidate polymer for either cathode or anode because of its wide redox potential.[109, 123] Yuan et al.[109] prepared a peroxidized PPy anode by gas phase polymerization method (Fig. 1-13a). This PPy electrode showed good lithium ion storage performance with two reduction bands centered at 0.5 and 1.42 V, respectively. The fast Li^+ insertion/extraction property is attributed to its polymer chains with ordered layered structure, which lead to its excellent rate performance about 10 C and long cycling life up to 1000 cycles (Fig. 1-13b). Unfortunately, this anode specific capacity was measured to be only 215 $mAh\,g^{-1}$, which is much lower than that of commercial graphite one. Numazawa et al. reported a PPy derivative based anode showing its specific capacity as high as 730 $mAh\,g^{-1}$.[110] This high capacity was ascribed to unsaturated carbon atoms in pyrrole units, which could be used for the Li^+ storage. Actually, the underlying mechanism for lithium storage is super-lithiation.

On the other hand, the PPy performance is dependent on the out stress and substitution. Nucleophilic of lithiated pyrrole would break the polymer backbone and consume the electrolyte, which would lead to poor cycling property.[124, 125] Therefore, the PPy based anodes with high performance might be realized if reasonable strategies could be developed to stabilize the super-lithiated PPys. In contrast, PPy based cathodes are found to demonstrate a good theoretical capacity and cyclic stability. Yang et al.[123] synthesized sulfonic acid doping PPy electrodes by electrochemical way and found that the polymer chain was enhanced and deposited potential was decreased because of the intrinsic conductivity. Thus, this PPy based electrode showed much stabler architecture than that without modified electrode (Fig. 1-13c, and d). The capacity retention rate could be reached to be 88.5% after 800 cycles (Fig. 1-13e). The battery capacity of this cathode was measured to be 120 mAh g^{-1}, which was higher than the theoretical value because several components underwent redox reactions to improve the electrodes specific capacity.[123, 126, 127] The PPy Femi level (EF) was close to $Fe(CN)_6$ and ferrocene. Therefore, PPy electrodes modified by $Fe(CN)_6$ or ferrocene have widely investigated. In fact, these electrodes demonstrated higher capacities than the original PPy. And the $Fe(CN)_6$/PPy electrochemical property is even better than that of the ferrocene/PPy because of former large molecular weight and steric hindrance.[127]

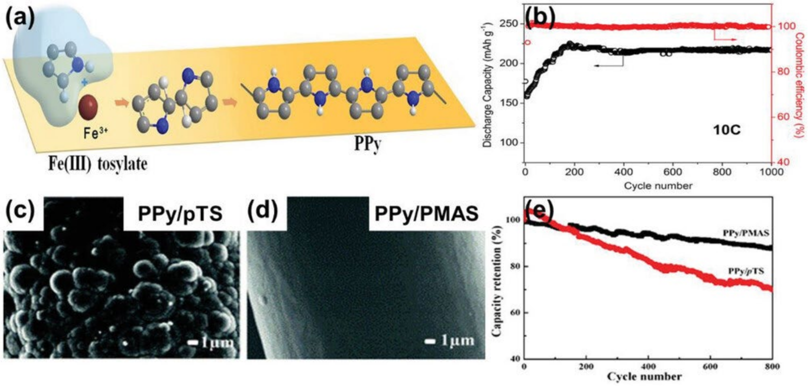


Fig. 1-13 Diagrams for (a) the preparation of PPy film, (b) cyclic performance of PPy anode.[109] Copyright 2016, American Chemical Society. SEM images of (c) PPy/pTS and (d) PPy/PMAS electrodes. (e) Capacity retention versus cycle number at 1 A/g for PPy/pTS and PPy/PMAS electrodes.[123] Copyright 2013, Royal Society of Chemistry.

3.2.3. Polythiophene (PTh)

PTh derivates (PThs) are a kind of active polymers under both high and low potential condition, so they could be used as LIBs cathode or anode. The PTh-based cathodes show high redox reversibility and low specific capacity, but the PTh-based anodes exhibit poor reversibility and high specific capacity.[128, 129] Liu et al. prepared a porous PTh based cathode showing its discharge plateau up to 3.7 V and a high capacity around 50 mAh g^{-1} after 500 cycles.[130] In contrast, the PTh based anode demonstrates a reversible capacity about 300 mAh g^{-1} and a short cyclic life. Therefore, how to further increase cyclic life and the specific capacity of PTh-based electrode becomes very necessary. For example, Sivakkumara et al.[54] studied that the low capacity of PTh could be ascribed to the disordered crosslinked molecular structure, which was caused by the indiscriminate polymerization of monomers at different position. These polymers structures can be tuned by using different monomers and polymerization temperature.[54] Their specific capacities can be enhanced by attaching redox moieties, such as disufide, oxygen radical and so on.[114, 131, 132] On the other hand, PTh-based anodes showed increased cyclic life by changing molecular structures.[133, 134] Xu et al. made PThs analogues named pBAT and pBABT and found both of them with hollow tube architectures (Fig. 1-14a, and b).[111] However, the pBABT based electrode showed better electrochemical data both in specific capacity and cyclic life (Fig. 1-14c). In addition, the conjugated microporous polymer (P33DT) based electrode behaved excellent electrochemical property with a specific capacity up to 663 mAh g^{-1}.[135] It can retain its capacity about 500 mA g^{-1} after 1000 cycles, which are resulted from the conjugated and crosslinked architecture (Fig. 1-14e).