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Research progress of triazine materials in energy storage batteries

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Abstract. With the increasing demand for large-scale energy storage, water-based energy storage batteries have attracted much attention due to their low cost, environmental friendliness, high ion conductivity, and safety. Compared with inorganic electrode materials, the controllable structure of organic electrode materials has been widely studied, among which triazine materials are considered as very promising organic electrode active materials due to their low cost, non-toxicity, and sustainable characteristics. This article summarizes the applications of different triazine materials, such as phenazine and its derivatives, and triazine materials with Hexaazatriphenylene (HAT) as the redox core, in various battery systems such as flow batteries, lithium-ion batteries, zinc ion aqueous batteries, etc. On this basis, the disadvantages of triazine materials and modification strategies for triazine materials were proposed, providing a broader application prospect for the use of triazine materials in energy storage batteries.

Keywords: triazine materials, energy storage batteries, aqueous batteries, organic electrodes, safe and reliable.

1. Introduction

In recent years, with the burning of fossil fuels, global warming and environmental pollution have become increasingly severe, so the demand for energy has sharply increased. Therefore, developing renewable energy technologies is crucial [1-3]. Clean energy sources such as solar, wind, hydro, and tidal energy are key to achieving sustainable development with carbon neutrality and peak carbon emissions. However, these new energy technologies are limited by environmental factors and intermittent impacts, which prevent them from being fully utilized. Therefore, it is necessary to use large-scale energy storage technologies, including batteries, to convert them into stable and available power resources for use. Among numerous rechargeable technologies, lithium-ion batteries (LIBs) have been successfully applied in portable electronic devices, electric vehicles, and energy storage stations due to their advantages in energy density and cycle life [4-5]. However, the development of commercial LIBs relies on the use of transition metal based inorganic materials such as $LiCoO_2$, $LiNi_xCo_yMnzO_2$, and $LiFePO_4$. Nowadays, lithium-ion batteries face many challenges: (1) the energy density of LIB is approaching the theoretical upper limit of inorganic transition metal materials (~400 Wh/kg), and the development space is relatively small. (2) The raw materials required for LIB, such as cobalt, nickel, manganese, lithium, etc., are expensive and are unevenly distributed, which may not be able to meet the exponentially growing demand in the energy storage market [6-7]. In this situation, scientists spare no effort in seeking advanced rechargeable battery technologies with high energy density and high resource sustainability [8].

In recent years, due to the low cost, environmental protection, high ionic conductivity, and safety of water-based electrolytes, water-based rechargeable batteries have received widespread attention and are expected to be used for large-scale energy storage. In addition to commercially available water-based batteries such as lead-acid batteries and nickel hydrogen batteries, people have also vigorously developed new types of water-based batteries [9-11]. Despite these advantages, the narrow electrochemical window (1.23 V) of aqueous electrolytes limits the material selection for aqueous batteries (such as aqueous lithium-ion batteries, aqueous zinc ion batteries, aqueous sodium ion batteries, etc.), which hinder the first step in improving energy density [12-13]. Organic electrode materials are expected to become effective electrode materials for the next generation of sustainable and multifunctional energy storage devices due to their high theoretical specific capacity, low cost, environmental friendliness, and strong designability of molecular structure. Compared with traditional inorganic electrode materials, organic electrode materials have the following advantages: (1) Organic electrode materials have a higher theoretical specific capacity; (2) Being able to flexibly adjust the voltage platform through molecular design, making it suitable for both positive and negative electrode use, is an ideal electrode material; (3) No heavy metals, no pollution to the environment; (4) Widely applicable, the charge transfer mechanism based on Li$^+$ ion organic battery systems is also applicable to other metal ions such as Na$^+$, K$^+$, Mg^{2+}, Al^{3+}, etc. And because it is mainly composed of lightweight elements such as C, H, O, N, S, etc., it is not only cheap and easy to obtain, but also has relatively soft mechanical properties, making it very advantageous for application in flexible batteries [14-15]. In addition, in energy storage devices such as flow batteries, air batteries, and supercapacitors, organic molecules can also undertake reversible electrochemical redox reactions and even have faster reaction kinetics. As early as 1969, Williams et al. attempted to apply dichloroisocyanuric acid (DCA) to the positive electrode material of lithium batteries [16]. However, there are some key issues that need to be addressed for the practical application of organic electrodes, such as poor conductivity, typically low redox potential, and dissolution in traditional organic electrolyte systems.

Among numerous organic materials, triazine based organic materials mainly include six membered single heterocycles containing two heteroatoms, such as pyridazine, pyrazine, pyrimidine, and triazine, as well as structures of five membered and six membered fused heterocycles, including phenazine and phenothiazine. Among them, phenothiazine contains one sulfur atom. Piperazine is also a type of pyrazine compound. Diazine refers to a six membered heterocyclic system containing two nitrogen atoms. Due to the different relative positions of the two nitrogen atoms in the ring, there are three isomers of triazines, named pyridazine, pyrimidine, and pyrazine. Pyridine is a compound in which two nitrogen atoms are located adjacent to each other; Pyrimidine is a position where two nitrogen atoms are in the meta position; Pyrazine is a position where two are in ortho position. Quinine based materials are considered very promising organic electrode active materials due to their low-cost, non-toxic, and sustainable properties. This article focuses on the application of triazine materials in rechargeable batteries based on their characteristics and looks forward to the future research trends of triazine materials, aiming to provide a foundation and ideas for the development of a new generation of green, environmentally friendly, high-power, high-energy density, and low-cost electrode materials.

2. Energy storage mechanism of organic materials

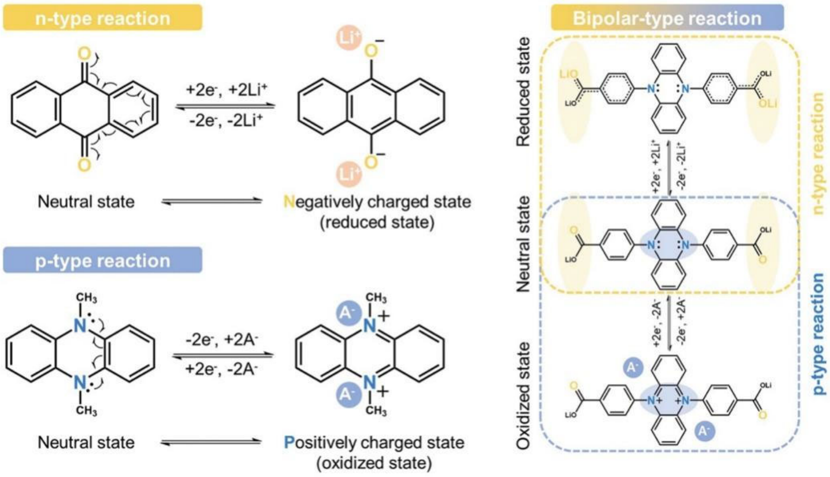

Fig.1 The operating mechanisms of the different organic materials

According to the redox activity of organic compounds during electrode reactions, they can be classified into three types: n-type, p-type, and bipolar [17]. Figure 1 illustrates the three types of redox reactions and representative molecular structures. Most known redox active organic compounds follow one or more of these redox mechanisms in rechargeable batteries. n-type organic materials (including carbonyl compounds, imine compounds, and nitroaromatic hydrocarbons) typically undergo a reduction process, where electrons are obtained and converted into negative ions. These negative ions then combine with cations (K^+, Li^+, Zn^{2+}, etc.) in the electrolyte through coordination reactions to maintain charge neutrality. p-type organic materials (including organic sulfides, conductive polymers, triphenylamine derivatives, etc.) typically undergo an oxidation process, where they lose electrons and convert to cations. These cations then combine with anions in the electrolyte (such as SO_4^{2-}, $CF_3SO_3^-$, Cl^-, etc.) to achieve energy storage. Bipolar materials typically exhibit the electrochemical properties of n-type and p-type materials. During redox reactions, their valence can vary between neutral and negatively charged states, as well as between neutral and positively charged states. For example, in the charging and discharging process of lithium-ion batteries, the n-type "cathode" is prone to accepting electrons and a corresponding amount of lithium ions during the discharge process, so a lithium containing anode is usually required. On the contrary, n-type "anodes" can be paired with traditional LIB cathodes, such as $LiMO_2$ (nickel, cobalt, manganese, aluminum, etc.), $LiFePO_4$, or $LiMn_2O_4$, which inherently contain lithium ions in their original state. During charging, p-type electrochemical reactions allow the neutral p-type cathode to release electrons and receive a corresponding number of anions from the electrolyte [19]. When a p-type cathode is paired with a lithium deficient anode (such as graphite or n-type organic anode), the battery operates using two different ion species. These batteries are commonly referred to as dual ion batteries. A few organic compounds can undergo n-type and p-type reactions simultaneously through bipolar reactions using multiple redox groups. Bipolar organic materials can serve as both positive and negative electrodes for all organic dual ion batteries [20].

3. The application of triazine materials in the field of energy storage

Quinine materials belong to imine materials and are important representative n-type materials. Compared with carbonyl-based materials, imine-based materials exhibit higher redox activity and better cycling stability in aqueous electrolytes due to their extended π conjugation effect. Phenazine (PZ), as the smallest unit of triazine materials, has a theoretical capacity of up to 298 mAh/g. Li et al. [21] prepared nano nPZ/KB composite materials using in-situ dissolution precipitation method and applied them to aqueous potassium ion batteries. Based on the uniform deposition of nano phenazine on highly conductive and porous black surfaces, metal ions K^+ and electron energy were quickly transferred to the electrochemical active sites of phenazine molecules. Therefore, nPZ/KB not only achieved an actual discharge capacity of 298 mAh/g, but also exhibited a discharge capacity of 102 mAh/g at a current density of 100 C, with a capacity retention rate of up to 76% after 100000 cycles. Therefore, given the simple synthesis of triazine materials (Schiff base reaction), more and more triazine materials are being developed and applied to different battery systems. This section will focus on the research progress of triazine materials in flow batteries and various battery systems.

3.1 Redox flow battery

Redox flow battery is a new type of rechargeable battery that achieves the mutual conversion of electrical and chemical energy through reversible redox reactions (i.e. reversible changes in valence state) of active materials in positive and negative electrolyte solutions. During charging, the positive electrode undergoes an oxidation reaction that increases the valence state of the active material, while the negative electrode undergoes a reduction reaction that decreases the valence state of the active material. The discharge process is the opposite. Unlike typical solid-state batteries, the positive and/or negative electrolyte solutions of flow batteries are stored in external storage tanks and transported to the interior of the battery through pumps and pipelines for reaction. The power density is defined by the size, design, and quantity of electrochemical cells, while the energy density depends on the application volume and composition of the electrolyte [22].

Vanadium flow batteries are widely used in markets such as wind power, photovoltaic power, grid regulation, and power supply system's due to their long lifespan, high energy efficiency, low self-discharge, and low cost. However, when the temperature of the all vanadium flow battery reaches 40 ℃, V_2O_5 as the reaction medium will precipitate during the reaction process, resulting in flow blockage during battery operation. Solar energy, a clean energy source, is the most widely used, especially in sunny areas where it can be collected. However, these areas often experience an increase in temperature conditions. Therefore, this issue greatly limits the large-scale application of vanadium flow batteries in solar rich areas with high temperature climates [23].

The limitations of current flow batteries can be addressed through aqueous organic redox flow batteries (RFBs). In recent years, many organic material families, such as those with adjustable properties such as water solubility, redox potential, and thermochemical stability, have been used as materials for organic redox flow batteries. However, a key drawback of most batteries is their high-capacity decay rate, which is mainly caused by the decomposition of organic molecules. Therefore, developing stable redox active materials has always been the current research direction. Table 1 summarizes the application of triazine materials in flow batteries.

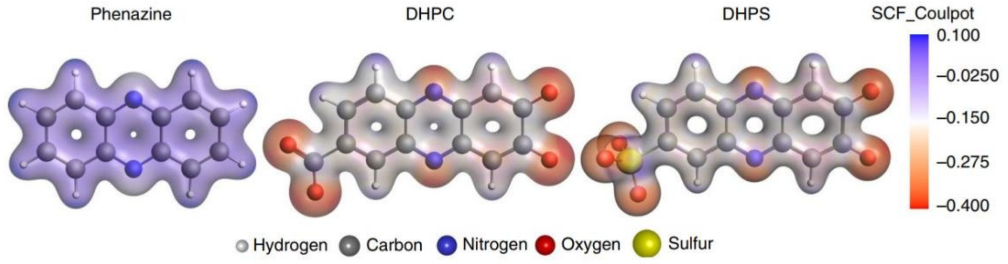

Fig.2 the Coulomb potential diagram with the highest calculated dissolution energy for triazine, where red and blue represent the electron enrichment and electron defect states of the molecule, respectively

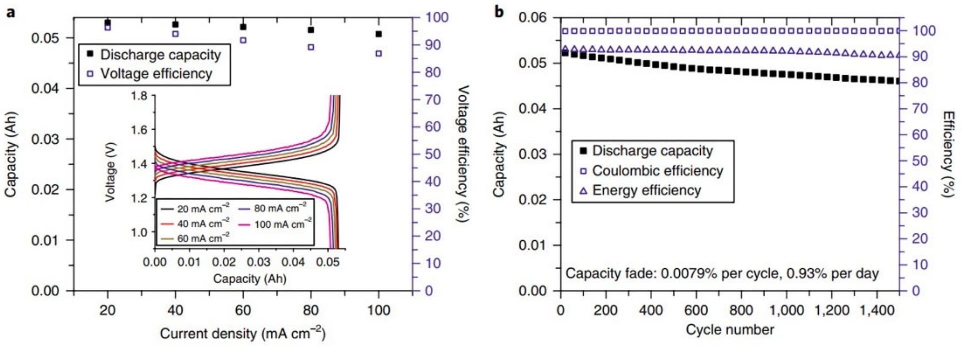

Fig.3 Performance (a) and cycling stability (b) of flow batteries at high concentrations

Wang et al. [25] also developed the phenoxide radical cationic sodium salt PSPR based on phenoxide, which has a solubility of 1.4 M in liquid phase and high stability in water. Through theoretical calculations and experimental verification, PSPR is not prone to dimerization or disproportionate reactions, and it has an appropriate electron density to avoid reactions with oxygen or water. Through UV vis spectroscopy monitoring, PSPR remained stable in water exposed to air for over 70 days without decomposition, demonstrating high stability. Using PSPR as the solute, the flow battery paired with Zn has an open circuit voltage of 1.0 V and no significant capacity degradation after 2500 cycles. At the same time, Wang et al. [26] used a strategy of connecting carboxyl groups (- COOH) to chemically inert carbon atoms instead of the triazine core to avoid nucleophilic substitution and hydrolysis reactions of organic materials in alkaline flow batteries. They studied and compared the possibility of using three types of phenanthrene substituents with different substitution positions: 1,6-PFP, 1,8-PFP, and 2,7-PFP as RFBs. The results showed that all three PFP materials exhibited high solubility, low permeability, rapid reaction kinetics, and negligible battery capacity degradation at high temperatures. Among them, 1,8-PFP showed the highest solubility, with an electron concentration of up to 2.0 M for ferrocyanide dissolved in 1.0 M KOH, an open circuit voltage of 1.15 V, and no capacity decay observed after 40 days of cycling at room temperature. Moreover, after cycling at a high temperature of 45 ℃ for 53 days, no capacity decay occurred, indicating the strong stability of 1,8-PFP in harsh environments with high temperature and strong alkalinity.

Kong et al. [27] synthesized the phenazine derivative 2,3-O-DBAP as a water-soluble and chemically stable active molecule of RFB based on phenazine. Through a combination of DFT calculations and experiments, it was found that compared to other O-DBAP isomers, 2,3-O-DBAP has superior solubility, lower redox potential (-0.699 V vs SHE), and higher chemical stability. A flow battery was formed by pairing 2,3-O-DBAP with iron/iron cyanide, with a discharge voltage of 1.12 V and a service life of 62 days (capacity decay rate less than 0.2%/day). No self-discharge phenomenon was found in the entire battery, indicating the high stability of 2,3-O-DBAP. Liu et al. [28] conducted a detailed study on the electrochemical stability of phenazine derivatives with different alkyl chains and proposed and synthesized alkyl carboxylic acid functionalized derivatives DBEP and DAEP of 2,3-dihydroxyphenazine, both of which have good reversibility and high redox kinetics. Simultaneously using DFT calculations and experimental verification, it has been shown that DAEP with low alkyl chains exhibits a more pronounced absorption effect of carboxyl molecules, tending towards alkyl chain splitting and chemical explanation. DBEP with a butyric acid chain is beneficial for the stability of the side chain and has better stability. Pairing DBEP with iron/iron cyanide to form a flow battery can achieve a high open circuit voltage of 1.17 V. RFB based on DBEP has ultra stable alkyl chains and soluble carboxyl groups with an electron concentration of 1.2 M. Its theoretical capacity utilization rate is 90%, energy efficiency is as high as 86%, and it has a high output power of up to 100 mW/cm^2. The capacity retention rate is 97.8% after 1000 cycles at a current density of 50 mA/cm^2. This study emphasizes the role of functional group modification sites.

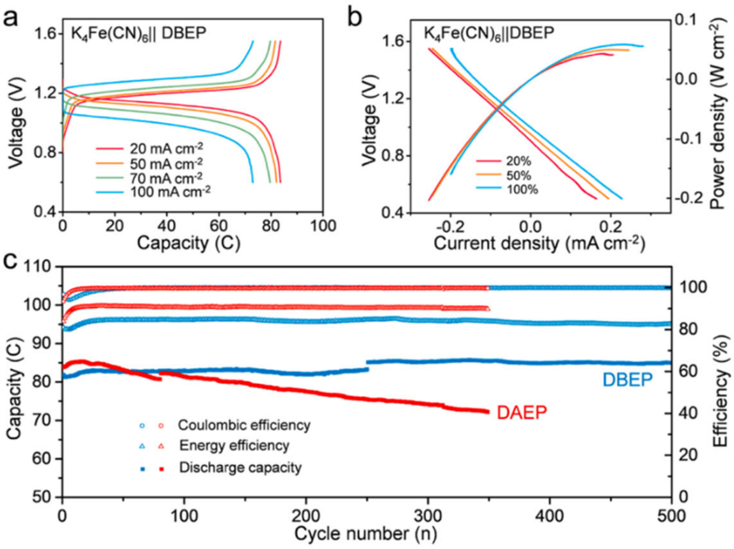

Fig.4 Electrochemical performances of the ARFBs at low concentrations. The negolyte is 5 mL of 0.1 M DBEP (or DAEP) in 1.0 M KOH solution, and the posolyte is 40 mL of 0.1 M K4Fe(CN)6 in 1.0 M KOH solution. (a) Galvanostatic charge−discharge curves of the K4Fe(CN)6||DBEP ARFB at various current densities of 20, 50, 70, and 100 mA/cm2, respectively. (b) Polarization and power density curves at 20, 50, and100% SOC, respectively. (c) Cycling performances of the K4Fe(CN)6||DAEP and K4Fe(CN)6||DBEP ARFBs at a current density of 50 mA/cm2(DAEP: red points and DBEP: blue points)

All in all, the high stability exhibited by the core of triazine reactions in high temperature and strong alkaline environments has made triazine materials stand out in the use of flow batteries and attracted great attention. At the same time, researchers used molecular engineering strategies to modify triazine materials and found that electron donating groups (such as - OH, - NH_2, etc.) caused a positive shift in the redox potential, while electron donating groups (- SO_3H, - COOH, - NO_2, etc.) caused a negative shift. The introduction of carboxyl groups increased the solubility of phenazine. And the different types and positions of functional groups on the benzene ring also play an important role in the potential and solubility of triazine materials. The use of first principles calculations, molecular dynamics simulations, and machine learning provides theoretical and experimental support for the development of next-generation flow batteries.

Table 1 Summary of Application of Different Phenazine Derivatives in Flow Batteries

Name	Solubility	energy densityWh/L	Cyclic stability %/number	reference
DHPS	1.8 M	67	99.98/500	[24]
PSPR	1.4 M	-	100/2500	[25]
1,8-PFP	2.0 M	-	100/40days	[26]
2,3-O-DBAP	0.6 M	27.6	99.21/62days	[27]
DBEP	1.2 M	-	97.8/1000	[28]

3.2 Application of Quinine Materials in Solid State Batteries

3.2.1 Lithium-ion batteries

Since Sony first achieved commercialization in 1991, lithium-ion batteries (LIBs) have been widely used as power sources in the mass market. Lithium-ion batteries have high specific capacity and high energy density, making them the most used secondary batteries nowadays. Organic lithium-ion batteries (OLIB), mainly known as LIBs with organic materials as electrodes, have been studied since the 1860s as a primary lithium battery with dichloroisocyanuric acid as the cathode and lithium as the negative electrode. To improve the cycling stability and electronic conductivity of organic electrodes, Peng et al. [29] proposed a π - conjugated material N-isoarylquinoline molecule (3Q) synthesized by condensation of cyclic carbonyl molecules with ortho phenylenediamine. 3Q contains reactive active sites with multiple pyrazine sites, promoting various redox reactions and providing a high discharge capacity of 395 mAh/g at a current density of 0.4 A/g. It has excellent cycling stability (with a capacity retention rate of 70% after 10000 cycles at 8A/g) (Figure 5). The improvement in electrochemical performance is attributed to the combination of graphene and ether-based electrolytes, as well as heteroaromatic molecules with multiple active redox sites. Unlike 3Q, N, N '- diphenyl-5,10-dihydrophenazine (p-DPPZ) follows the p-type as its redox mechanism and undergoes a double electron transfer process during the redox reaction. Manipulating conjugation can stabilize the redox active center of p-DPPZ, resulting in better stability, higher redox potential, and vibrational current energy density.

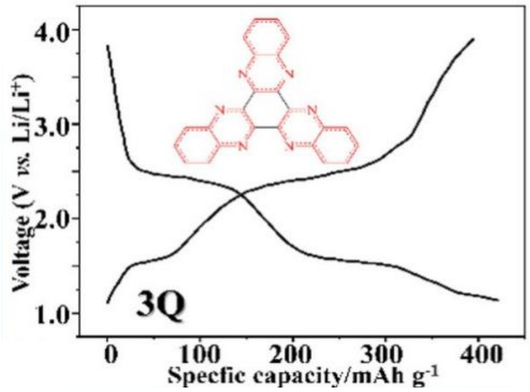

Fig.5 Charge discharge curve of 3Q

Aromatic azo compounds have extended π - conjugated structures and strong adsorption of Li by nitrogen, exhibiting superior characteristics of rapid charging ability and high-rate performance. For example, Ma et al. [30] synthesized azo fused conjugated microporous polymers by selecting different crosslinking agents for benzene (Bz), pyrene (Py), and benzothiadiazole (BT), including AzoBz, AzoPy, and AzoBT. The electronic structure of this polymer can be adjusted through different crosslinking agents. Due to the introduction of electron withdrawing BT units, AzoBT with higher electron affinity exhibits higher redox activity than AzoBz and AzoPy. Although all three polymers can be used as anodes, only AzoBT can provide more abundant active centers than AzoBz and AzoPy skeletons. The combination of redox active azo and BT units has a low LUMO energy level, making AzoBT have an ultra-high capacity of 1543 mAh/g (current density of 50 mA/g), excellent rate performance and long cycle life (1000 cycles at 2 A/g) under charge and discharge platforms of 1.2-2.5 V. Introducing heteroatoms containing lone pair electrons (O, N, etc.) into large π - conjugated organic systems can reduce the free energy of lithium ion intercalation and facilitate redox reactions. Each poly (1,6-dihydropyrazino-quinoxaline-2,3,8-triayl-7- (2H) - ylidene-7,8-dimethylene) (PQL) monomer containing nitrogen heteroatoms can insert 14 lithium cations, making it a highly reversible electrode with high capacity. Especially, nanostructured PQL exhibits good thermal stability at 40 ℃ and better electrochemical performance at high temperatures than at room temperature. As shown in Figure 6, a high reversible capacity of 1550 mAh/g (100 mA/g) can be achieved at room temperature, and a high reversible capacity of 1770 mAh/g can be achieved at 50 ℃. This is attributed to its high electronic conductivity (2.1 × 10^{-3} S/cm), fast charging mobility, and good structural stability.

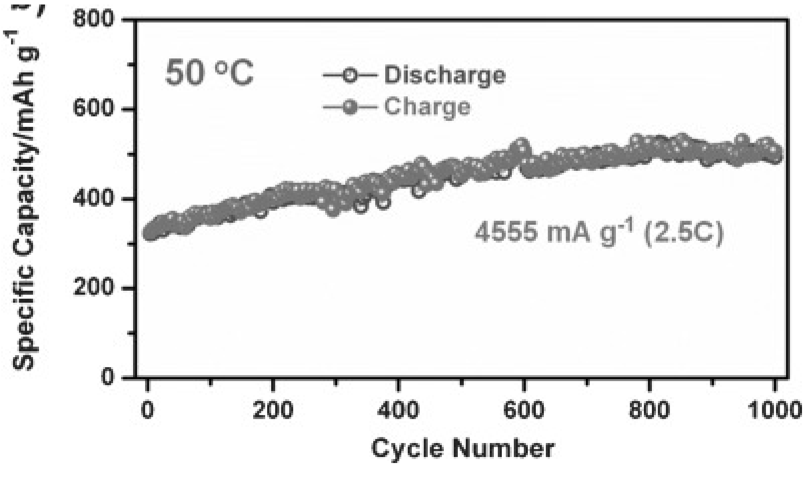

Fig.6 Cycle curve of PDL at 50 ℃

3.2.2 Water based zinc ion battery

Water based zinc electrodes have many obvious advantages, including high theoretical specific capacity (820 mAh/g), suitable redox potential (-0.76 V vs. SHE), inherent safety and low cost of aqueous electrolyte, making water-based zinc batteries a research hotspot [31].

Li et al. synthesized π - conjugated heteroaromatic hexaazatriphenyltriazine (HATN-PNZ) molecules for the first time through the condensation reaction of hexaketocyclohexane (C_6O_6) and 2,3-diaminophenazine (DAP). Due to the conjugated elongation of the triazine and aromatic ring, HATN-PNZ with a larger charge area can effectively transfer electrons within the molecule and lead to rapid kinetic reactions [32]. Firstly, three electrode tests were conducted on HATN-PNZ, and the electrochemical reversibility and cycling stability of HATN-PNZ were measured through cyclic voltammetry and electrostatic charge discharge. As shown in Figure 7, the CV curve has three reduction peaks at -0.26, -0.33, and -0.44V, and three oxidation peaks at -0.28 V and -0.14 V, which are attributed to the three redox states of HATN-PNZ during the ion coordination process. In addition, the oxidation-reduction peak current and potential did not change during multiple cycles, indicating the stability of the chemical properties of HATN-PNZ. Meanwhile, after 10000 cycles, there were no significant changes observed at a current density of 50 A/g, demonstrating the high stability and reversibility of HATN-PNZ. As shown in Figures 7c and d, under the same current density, the capacity of HATN-PNZ positive electrode is significantly higher than that of PNZ positive electrode. This indicates that the capacity and rate performance are effectively improved due to the increase in the conjugated length and number of delocalized electrons of phenazine. PNZ has discharge capacities of 167, 159, 153, 149, 145, 141, 135, 128, 119, 110, and 97 mAh/g at current densities of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 A/g. The capacity of HATN-PNZ was significantly enhanced, with discharge capacities of 257, 241, 187, 187, 177, 162, 156, 150, and 144 mAh/g at current densities of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 A/g, respectively. When the current density decreased from 100 A/g to 20 A/g, the capacity returned to its original equivalent level. At the same time, a full battery was assembled with Zn as the negative electrode, 2.0 mol/L $ZnSO_4$ as the electrolyte, and HATN-PNZ as the positive electrode. The discharge capacity of the battery was 226 mAh/g at a current density of 5 A/g and 131 mAh/g at a current density of 60 A/g. And the capacity of the battery reached 159 mAh/g after 30000 cycles at a current density of 30 A/g, with a capacity retention rate of 92.7%. Wang et al. used small molecule phenazine (PNZ) as the positive electrode material for aqueous zinc ion batteries. At a current density of 20 mA/g, its discharge capacity reaches 232 mAh/g. Even at a current density of 1 A/g, the discharge capacity of the PNZ electrode is still 85 mAh/g, and the capacity retention rate remains at 79% after 1000 cycles.

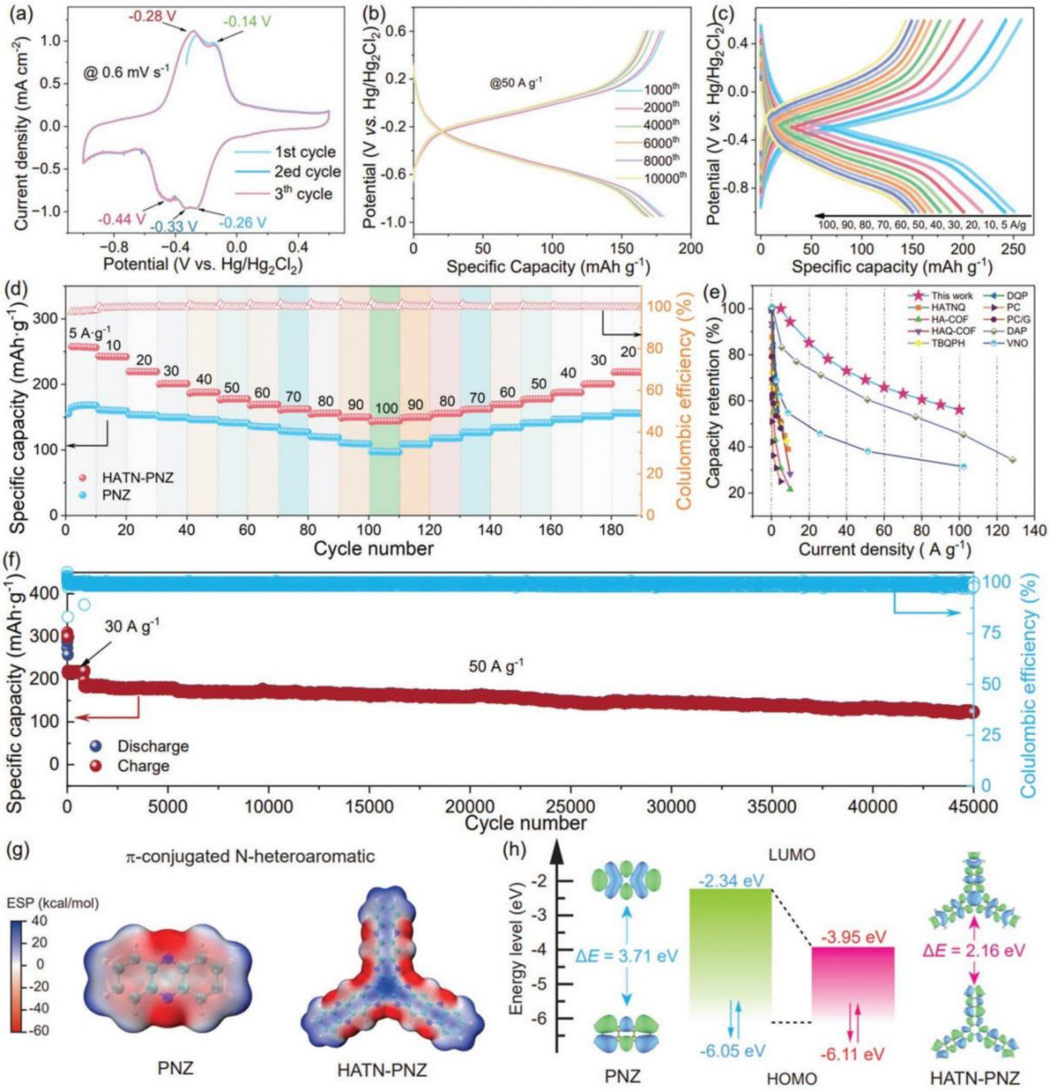

Fig.7 Electrochemical performance of the HATN-PNZ cathode. (a) CV curves of HATN-PNZ cathode in 2.0 M $ZnSO_4$ aqueous solution at a scan rate of 2.0 mV/s. (b) Galvanostatic discharge/charge curves of HATN-PNZ at 50 A/g. (c) Rate (dis-)charge curves of HATN-PNZ at different current densities. (d) Rate specific capacity of HATN-PNZ and PNZ at different current densities and the corresponding Coulombic efficiency of HATN-PNZ. (e) Capacity retention comparison with reported typical cathode materials in aqueous ZIBs. (f) Cycling stability and Coulombic efficiency of HATN-PNZ at 50 A/g. (g) Calculated ESP distribution of the HATN-PNZ and PNZ molecules. (h) Calculation of the relative HOMO/LUMO energies and optimized structures of the molecules used in the DFT method calculation

3.2.3 Sodium ion battery

Sodium ion batteries (SIBs) also operate through a "rocking chair" mechanism, in other words, sodium ions continuously insert/remove from the electrodes and move between the positive and negative electrodes during the charging and discharging process [33]. Water based sodium ion batteries have excellent cycling performance, high energy and power density, safety, cost-effectiveness, and environmental friendliness. At present, due to the difficulty of organic synthesis, there are few reports on aromatic nitrogen-containing organic cathodes in SIBs. Pyrazine contains C=N and theoretically can undergo a 2-electron redox reaction in SIBs to form two N anions (Figure 8a). In 2014, natural pyridine derivatives with pyrazine nuclei as organic cathodes for SIBs were first developed by Hong and colleagues (Figure 8b) [34]. These pyridine derivatives are all diazonium structures and serve as redox centers [35]. Among them, studies and comparisons were conducted on chromium pigments with simple structures (7,8-dimethylpyroazine, LC), pyroazine (ALX), and 4-dioxa-tetrahydropiperidine

(LMZ). Their discharge capacities are 221, 250, and 327 mAh/g, respectively. In a half cell using a mixed solution of 1 M $NaPF_6$ and diethylene glycol dimethyl ether (DEGDME), LC, ALX, and LMZ have similar reduction potentials at around 2 V, with discharge capacities of 138, 168, and 70 mAh/g, respectively (current density of 10 mA/g). After adding CNTs during the electrode preparation process, the discharge capacities of LC, ALX, and LMZ (current density of 50 mA/g) were increased to 222, 255, and 220 mAh/g, respectively. However, poor cycling stability was observed due to the dissolution issues caused by their neutral and small molecule organic structures (all compounds maintained a capacity retention rate of over 50% after 20 cycles). In 2019, Kapaev and his colleagues applied pyrazine related polymers (referred to as P1) using quinoxaline units to sodium ion batteries. Triquinoxaline units have three π - conjugated pyrazine units, allowing for a 6-electron redox reaction. The condensation reaction between dimethyl benzidine tetrahydrochloride and cyclohexanone can construct a star shaped polymer structure of P1, with a CT value of up to 418 mAh/g (Figure 8c) [36]. However, P1 only exhibited a peak discharge capacity of around 200 mAh/g, which may indicate that not every pyrazine unit is involved in the redox reaction of sodium ion batteries. Based on the insolubility and large π conjugation of polymers, P1 exhibits a stable specific capacity of 117 mAh/g after 1950 cycles at a current density of 10 A/g in half cells (0.7~3.2 V).

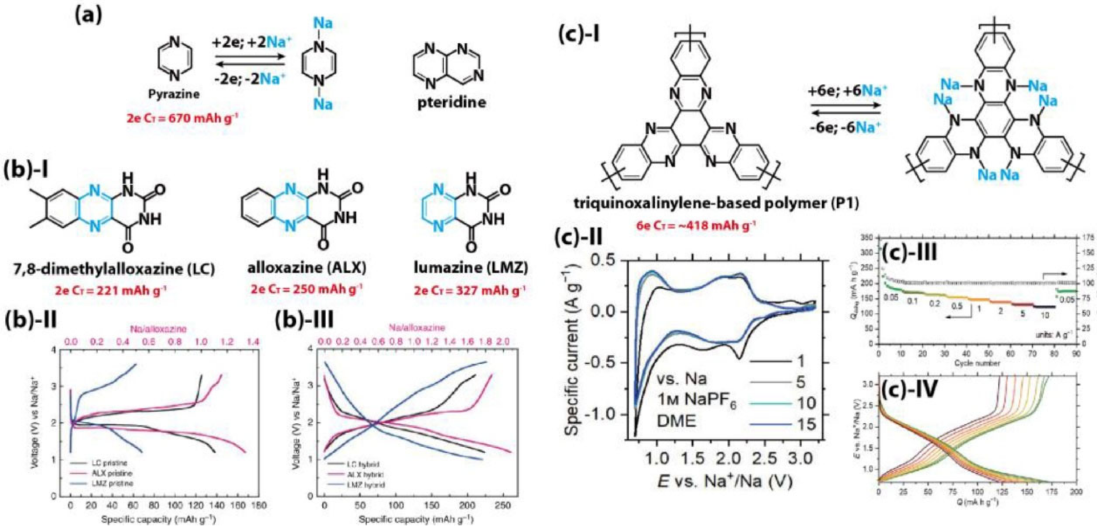

Fig.8 (a) Reaction process of pyrazine; (b) The structural formulas and charge discharge curves of LC, ALX, and LMZ; (c) The reaction process and charge discharge curve of P1 in sodium ion batteries

3.2.4 Water based potassium ion battery

As mentioned in sodium ion batteries, the structural advantage of polymer electrodes over small molecule electrodes is their insolubility in liquid electrolytes. However, the degree of polymerization and purity of insoluble polymers in PIBs deserve attention. In 2016, JI et al. reported that the organic polymer positive electrode applied to PIBs [37] was poly (anthraquinone sulfide) with redox active AQ units (PAQS, 1C=223 mAh/g). In a K-ion half-cell using 0.5 mol/L KTFSI/DME+DOL, PAQS exhibited satisfactory discharge capacity (200 mAh/g) with two typical discharge potentials at an average of 2.1 and 1.6 V, but its cycling stability was poor. In 2020, Lu et al. improved the cycling stability of PAQS using a high concentration electrolyte of 5 mol/L KTFSI/DME+DOL [38], and PAQS was able to maintain a capacity of 77 mAh/g after 1200 cycles (1 A/g). In 2019, Kapaev et al. applied a large π - conjugated hexaazaphenanthrene based polymer cathode (P1) to PIBs (Figure 9a) [39]. In a K^+ half-cell using 1 mol/L KPF_6/DME, P1 exhibits a high specific capacity of 169 mAh/g and a peak discharge capacity of 245 mAh/g after 4600 cycles at a high current density of 10 A/g. Subsequently, Kapaev compared two NTCDI based polymers (mPI and pPI) with benzene as the π - bond for PIBs (Figure 9b, c) [40]. The oxidation-reduction potential of both polymer cathodes is 1.5~3 V, and the discharge capacity is 100~125 mAh/g. Like SIBs, mPI exhibits better cycling stability and rate performance than pPI.

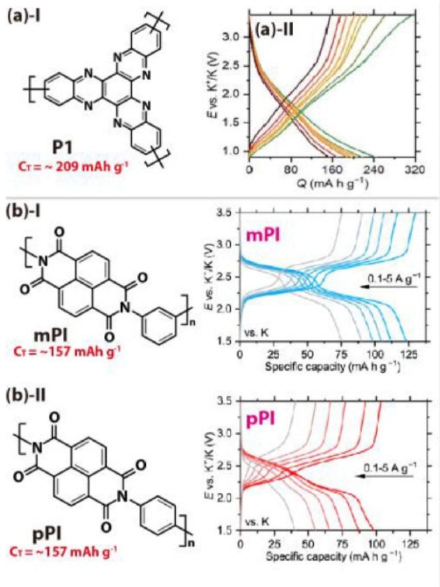

Fig.9 Structural formulas and charge discharge curves of P1, mPI, and pPI

3.2.5 proton batteries

For water-based metal batteries, significant solvation size and strong electrostatic interactions with filler anions can lead to a decrease in capacity stability. Since protons exhibit the smallest and lowest molar mass compared to other charge carriers, aqueous proton batteries (APBs) are popular as alternatives to metal batteries. More importantly, thanks to the Gretha’s mechanism like Newton's cradle, protons as charge carriers can achieve ultrafast ion conduction in aqueous solutions. Therefore, the development of electrode materials capable of inserting protons is of great significance for the development of high-performance APB devices [41-42]. Low cost and resource rich organic compounds are ideal energy storage materials. Shi et al. designed and synthesized a rod-shaped diquinoxaline-phenazine (DPZ) organic compound through a simple dehydration method, as shown in Figure 10. The proton redox process of DPZ organic electrode was investigated for the first time through in-situ Raman spectroscopy and theoretical calculations. Research has shown that the three C-double bond N electroactive regions in each DPZ molecular unit can simultaneously coordinate with two protons, and the redox reaction between the C-double bond N and the C-single bond N is highly reversible during proton insertion/extraction. As expected, the DPZ organic electrode has a proton storage capacity of up to 218 mAh/g and long-term cycling performance and has no significant solubility in acidic aqueous electrolytes. Subsequently, the team prepared a highly redox active polydiquinolone triazine (PDQPZ) polymer with extensive electron delocalization, optimized molecular orbitals, and extraordinary proton storage capabilities [43]. This PDQPZ polymer exhibits high kinetic redox activity between imine conjugated polymer frameworks, achieving highly reversible, rapid, and excellent proton storage in aqueous solutions. The obtained PDQPZ polymer provides excellent reversible capacity as an electrode material (specific capacity of 205.2 mAh/g at a current density of 1A/g), with a significant rate capacity of 137.1 mAh/g even at a high current density of 22A/g, and excellent cycling stability over 10000 cycles, with a capacity retention rate of up to 91.1%.

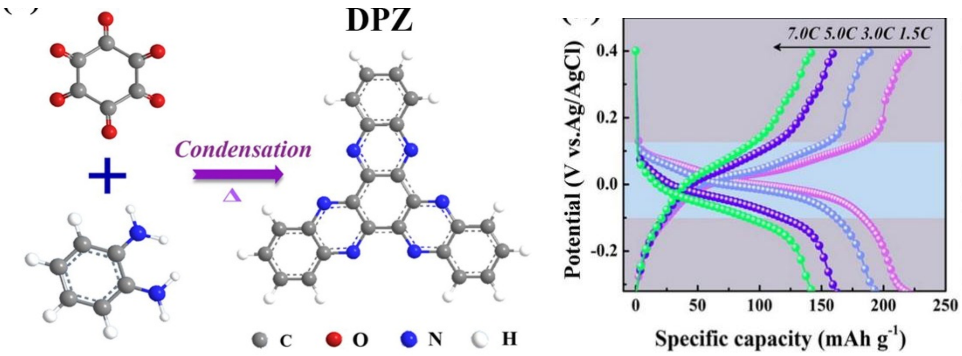

Fig.10 DPZ preparation process and its GCD curve

4. Summary and Prospect

Although triazine materials themselves have many advantages, they still face the drawbacks of most organic materials that need to be overcome.

(1) Low conductivity and water solubility. Design flexible triazine materials by utilizing the characteristics of organic electrode materials. The design of polymer electrodes with high activity and insolubility in electrolytes remains one of the main choices for aqueous batteries. In addition, the use of composite electrodes is also a major issue in suppressing leaching and improving the conductivity of electrode materials.

(2) The availability of organic triazine materials for energy storage is relatively limited, and materials can be designed to have high activity for easy use in battery systems. The development of more triazine materials is a key focus of future research on water-based batteries.

(3) The charge storage mechanism of organic electrodes has not been clearly elucidated in water-based rechargeable batteries. The insight into the charge storage mechanism of organic electrode materials during electrochemical cycling largely depends on the development of advanced characterization and combination techniques, especially in-situ characterization techniques.

(4) The narrow electrochemical window of aqueous solutions limits the selection of organic electrode materials and restricts the energy density of water-based rechargeable batteries. Using high concentration electrolyte or hydrogel is an effective strategy to broaden the electrochemical window. These strategies provide the possibility of applying various electrode materials to aqueous batteries and can also inhibit their dissolution.

(5) Compared with inorganic electrode materials, organic electrode materials have better flexibility and elasticity, making them suitable for developing water-based flexible batteries. The development of flexible water-based organic electrode systems is promising due to their high-water solution safety.

(6) The loading number of active substances. Due to the low conductivity of triazine materials, a large amount of conductive carbon black needs to be loaded, which limits the loading number of active substances. In addition, due to the lower compaction density and volumetric energy density of the reported organic electrode materials compared to inorganic materials. Therefore, increasing the electronic conductivity of organic materials under actual mass load is necessary for the practical application of electrode materials in batteries.

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