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Modification and Electrochemical Performance of Phenazine based Electrode Materials

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Abstract. Organic electrode materials hold great promise for advancing the development of aqueous batteries due to their structural diversity and sustainability. However, they still encounter challenges such as low electroactive mass contribution and undesirable cycling performance resulting from intrinsic poor electronic conductivity. Herein 1, 2-dihydroxyphenazine (DHP) was designed based on phenazine. Compared with the negative electrode of phenazine, the introduction of hydroxyl groups can reduce the redox potential by 0.2 V. The fast transport channel formed by intramolecular hydrogen bonding can significantly improve the redox kinetics. The optimized DHP‖$Ni(OH)_2$ battery has a discharge capacity of 240 mAh/g and a high energy density over 50 Wh/kg.

Keywords: aqueous batteries, organic negative electrode, high energy density, electron donating group, phenazine derivatives.

1. Introduction

In response to the depletion of fossil fuels and environmental degradation, the rational allocation of new energy sources such as wind energy and tidal energy is uneven in time and space distribution [1]. Safe and efficient energy storage technology has attracted greater interest [2]. Among them, lead-acid batteries are widely used due to their low price and safety [3], but their disadvantages are short life, low energy density, and high operation and maintenance costs. Although lithium-ion batteries (LIBs) have high energy density [4,5], they are potentially flammable and explosive. To meet the increasing demand for energy storage, aqueous organic batteries (ARBs) are the most promising battery technology [6]. ARBs use organic materials as the positive or negative electrode of the battery. Due to the diversity of their structure, adjustability, and the fact that organic electrode materials are not restricted by geographical resources, more and more organic materials (such as carbonyl compounds, imine compounds, conductive polymers, COFs materials, MOFs materials, etc.) [7-14] have been developed and applied to ARBs.

Among them, azine materials (such as phenazine) have the characteristics of high specific capacity and high stability and are promising electrode materials for use in aqueous battery systems. Chen et al. [15] applied phenazine (PZ) to alkaline aqueous batteries, showing high specific capacity (176.7 mAh/g at 4 C current density) and ultra-long cycle life (13,000 cycles with a capacity retention rate of 80%). Li et al. [16] used an in-situ dissolution-precipitation method to prepare nanoscale nPZ/KB composite materials, which not only achieved the theoretical capacity of PZ 298 mAh/g, but also achieved a capacity retention rate of 76% after 100,000 cycles. Although PZ has excellent electrochemical properties, phenazine is not conductive. Therefore, when preparing electrode sheets, it is necessary to add more conductive agents (ketjen black, carbon nanotubes, etc.) [17], so that the proportion of active materials is generally less than 60%, and the mass loading is mostly 1-3 mg/cm^2, which makes the overall density of the battery low. An effective means to enhance the electrochemical performance of organic materials is to improve the conductivity of electrode materials by adjusting the molecular functional groups [18-21]. Hydroxyl (-OH) as an electron-donating group can effectively adjust the electronic properties of organic molecules. At the same time, the intermolecular interaction

of hydroxyl groups provides a fast charge transfer channel, reduces the charge transfer impedance, and provides excellent rate performance.

In this study, we proposed and synthesized a phenazine derivative, dihydroxyphenazine (DHP). Cyclic voltammetry tests showed that the introduction of hydroxyl groups could reduce the redox potential of DHP by 0.2 V compared to that of PZ. At the same time, the discharge platform of DHP reached 1.2 V, which increased its energy density by 20%. DHP exhibited a discharge capacity of 240 mAh/g at a current density of 0.5 C, reaching 94% of the theoretical capacity.

2. Experimental Method

2.1 Synthesis of DHP

DHP can be produced by heating 2,5-dihydroxybenzoquinone and o-phenylenediamine at 80°C under neutral conditions [22]. Dissolve 0.71 g of 2,5-dihydroxybenzoquinone in 130 mL of deionized water and heat to 80°C under a N_2 atmosphere to obtain solution A. Slowly add 0.5 g of o-phenylenediamine to solution A and heat to 80°C for about 7 h. Cool naturally to room temperature, wash the obtained product with a large amount of deionized water until it is colorless, and then filter and dry in vacuo to obtain the product.

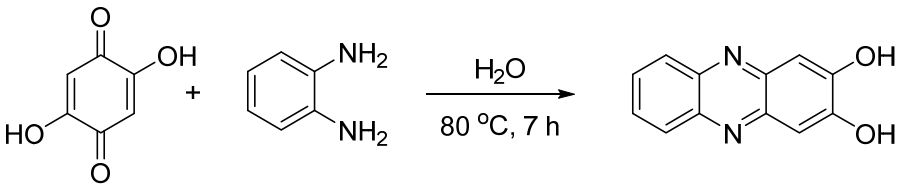
2.2 Preparation of Electrode Materials

Phenazine and DHP have poor conductivity and need to be mixed with a conductive agent to form an electrode material and add a binder. Ketjen black (KB) is selected as a conductive agent and polytetrafluoroethylene (PTFE) emulsion is selected as a binder. The amount of binder added is 10% of the total mass. Taking the ratio of DHP to KB as 5:5 as an example, 0.2 g DHP and 0.2 g KB are added to an agate mortar, a small amount of anhydrous ethanol is added, and 0.074 g of 60% PTFE emulsion is added after grinding for about 10 min. Grind for about 20 min and vacuum dry at 45℃ to obtain the electrode material. Adjust the ratio of active material and KB as needed to obtain different materials.

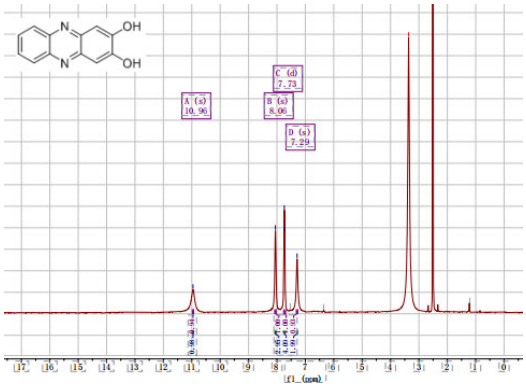
3. Experimental results and discussion

3.1 Structural and morphological analysis of the DHP organic compounds

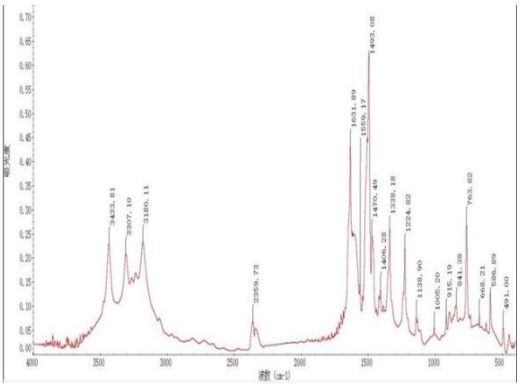
DHP organic compound is obtained by heating 2,5-dihydroxybenzoquinone and o-phenylenediamine at 80℃ under neutral conditions (Figure 1a). The structural composition of DHP is measured by nuclear magnetic resonance (NMR) spectroscopy. The 1H NMR spectrum in Figure 1(b) shows that the peak at 3.36 ppm is generated by hydrogen in water molecules. According to literature, hydrogen in hydroxyl groups is active hydrogen and appears in an unfixed position or with a relatively blunt peak or even no peak in the NMR spectrum [23]. The peaks at 7.29 ppm, 7.73 ppm and 8.06 ppm are the three types of hydrogen atoms on the benzene ring in the DHP molecule. At the same time, the Fourier transform spectrum (Figure 1c) shows that the peaks at 3433.81 cm-1, 3307.10 cm^{-1} and 3180.11 cm^{-1} are caused by the stretching vibration of N-H, the absorption peak at 1631 cm^{-1} is generated by the stretching vibration of C=N, and the absorption peak at 1470 cm^{-1} is generated by C-N=. The absorption peak at 1338 cm^{-1} is generated by the C-N= structure. The chemical bond information obtained from the infrared spectrum is consistent with the molecular structure of DHP. Combined with the nuclear magnetic resonance hydrogen spectrum, it can be proved that the synthetic product is DHP.



(a)The synthetic process of DHP



(b)1H NMR spectrum



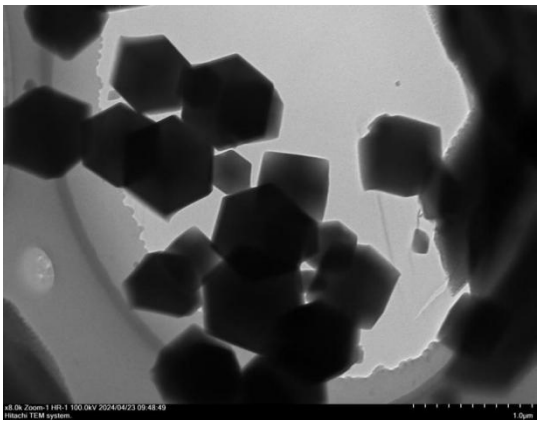
FTIR spectrum

Fig.1 The synthetic process and physical characterization of DHP

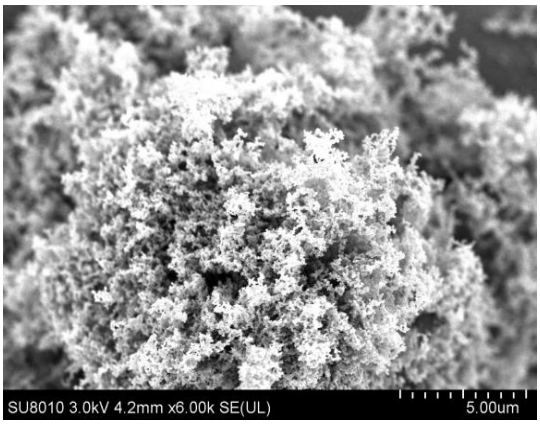
Figure 2a shows the morphological characteristics of DHP organic compound. The results show that DHP is granular, small and tightly stacked. Figure 2b shows the morphological characteristics of DHP and KB after compounding. The results show that the composite material presents a porous and loose structure. Figure 2c is an enlarged morphology diagram, which shows that the composite material presents a uniform spherical structure. This structure is conducive to the transfer of electrons and ions inside the electrode material, thereby improving the actual discharge capacity of DHP.

3.2 Characterization of DHP

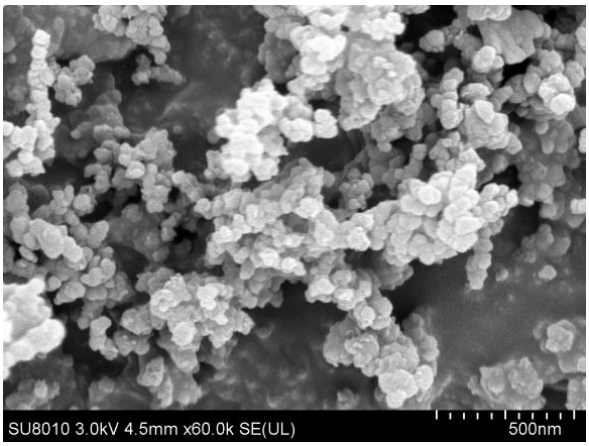
Figure 3 shows the cyclic voltammetric (CV) curve of phenazines and dihydroxyphenazines in 6 M KOH electrolyte, where the PZ shows an oxidation peak at-0.60 V (vs. Hg / HgO) and a corresponding reduction peak of-0.80 V (vs. Hg / HgO) with an accompanying acromion at-0.64 V (vs. Hg / HgO). DHP appeared at two oxidation peaks at-0.95 V and-0.88 V (vs. Hg / HgO), respectively, with the corresponding reduction peaks of-1.0 V and-0.95 V (vs. Hg / HgO). It is therefore known that the redox potential of DHP shifts by 200 mV to the left relative to the PZ



(a)The TEM picture



(b)The SEM picture ofDHP/KB



(c)The SEM picture of DHP/KB at 60000 times

Fig.2 The microcosmic structure of DHP and DHP/KB

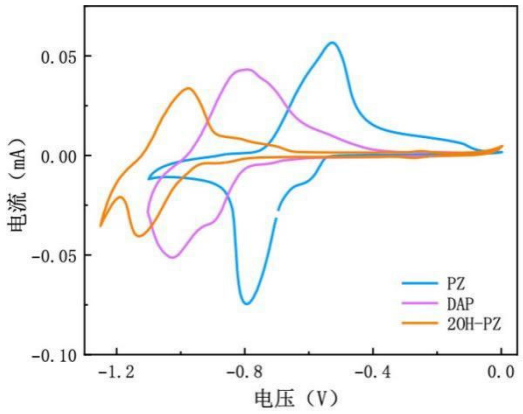


Fig.3 The CV of PZ and DHP at 5 mV/s

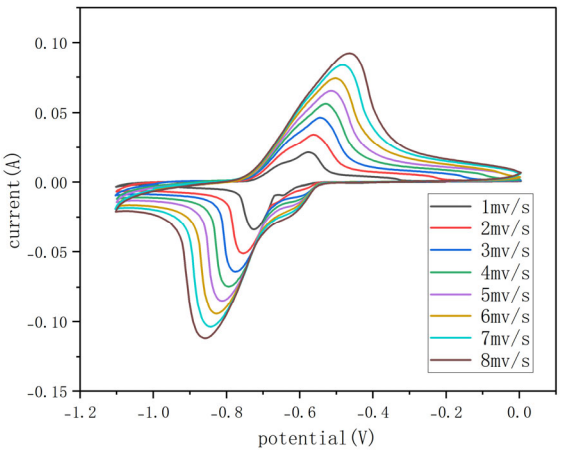
To further characterize the effect of the introduction of the electron donor group (-OH) on the electrochemical properties of PZ, the PZ and DHP electrodes were tested at different sweeps (1 mV/s to 8 mV/s), and their peak current density was linearly fitted in Equation 1.

Taking the inverse of both sides of equation 1, we get equation 2, where b can be obtained by and fitting straight line. When the b value is close to 0.5, the ion storage behavior belongs to the diffusion control process, when the b value is close to 1, the ion storage behavior belongs to the capacitance control process, and when 0.5＜b＜1, the ion storage behavior belongs to the pseudo capacitance control process.

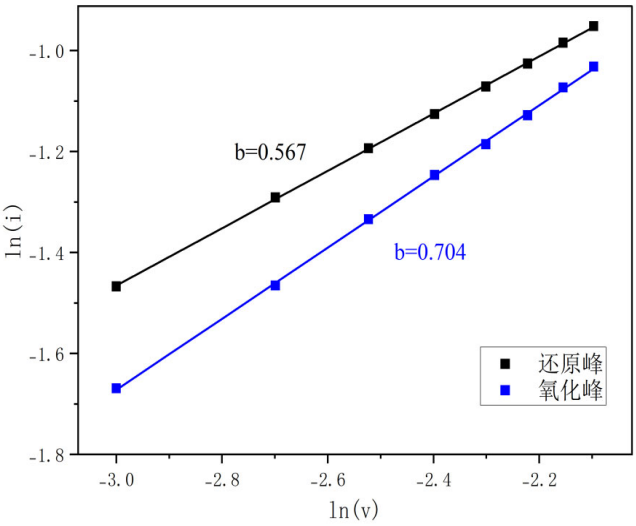
$$i = a * v^b \tag{1}$$

$$logi = loga + blogv \tag{2}$$

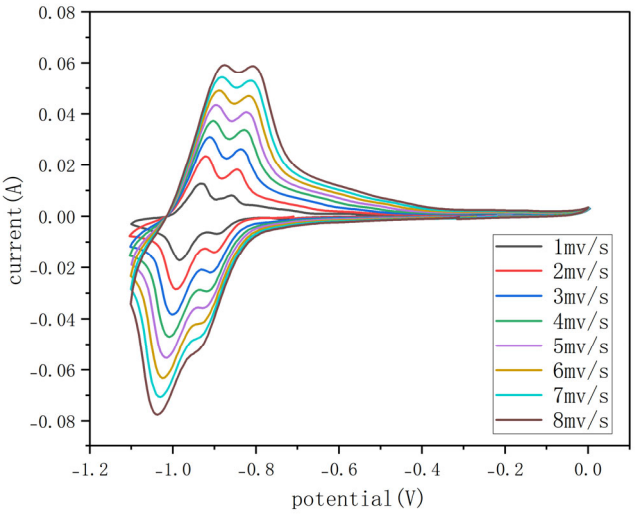
Figure 4a is the cyclic voltammogram of PZ at different scan rates, and Figure 4b is the corresponding linear fit of the peak current density. It can be seen from the figure that the b values of the redox peaks of phenazine are 0.704 and 0.567, respectively, indicating that the battery ion storage process is a pseudocapacitive control process. Figure 4c is the cyclic voltammogram of DHP at different scan rates, and Figure 4d is the corresponding linear fit of the peak current density. It can be seen from the figure that the b values of the redox peaks of DHP are 0.772 and 0.724, respectively, and the b value of DHP is greater than that of PZ. This is because the introduction of electron-donating groups changes the electronic structure of the oxazine molecules, thereby enhancing their pseudocapacitive control process.



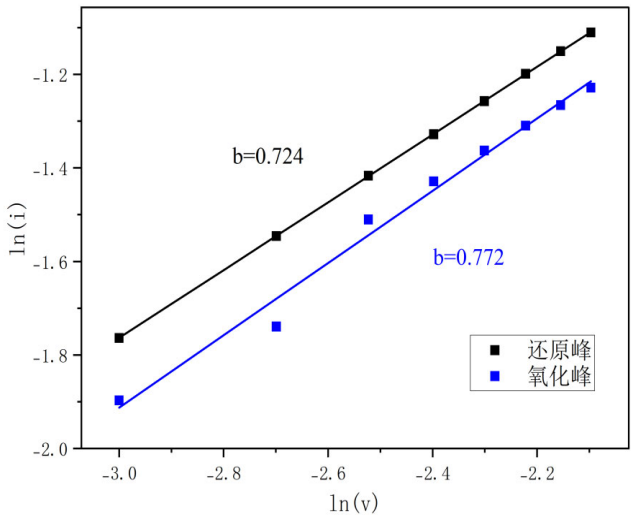
(a)The CV curves of PZ at different scan rate



(b)The linear fitting of peak current density of PZ



(c)The CV curves of DHP at different scan rate



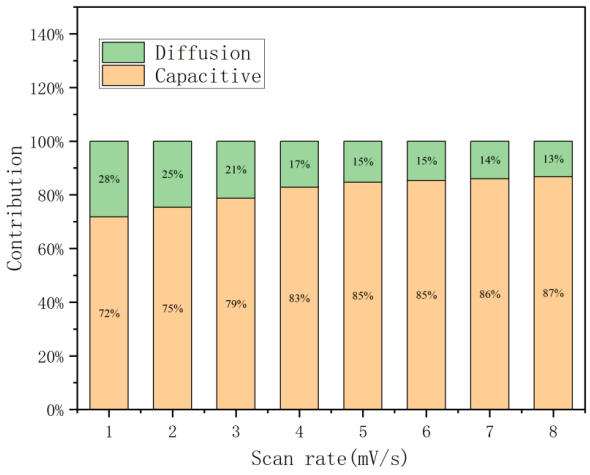
(d)The linear fitting of peak current density of DHP

Fig.4 The CV curves of DHP and PZ at different scan rate and linear fitting of peak current density

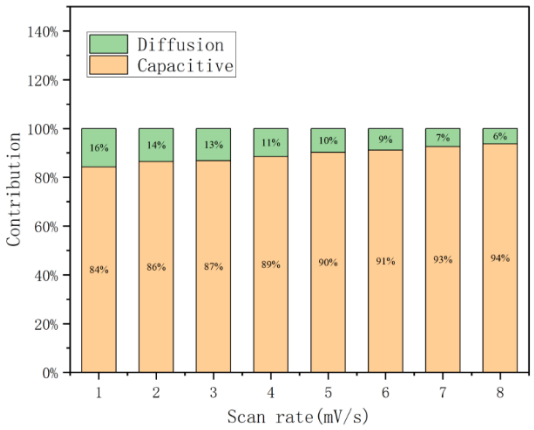
To quantitatively determine the role of capacitance control and diffusion control in the electrochemical process, the total current can be calculated by the formula (3) to calculate the capacity contributed by the capacitance control process and the diffusion control process. Where and represent the capacity of capacitance control and diffusion control, respectively. The higher the contribution of the former, the faster the diffusion rate.

$$i(V) = k_1 v + k_2 v^{1/2} \quad (3)$$

Figure 5a is a graph of the capacity contributed by capacitance control and diffusion control of PZ at different scan rates. It can be seen from the figure that when the scan rate is 1 mV/s, the capacity contributed by capacitance control accounts for 72%; as the scan rate increases, the capacitance contribution capacity increases. When the scan rate is 8 mV/s, the capacitance contribution capacity reaches 87%. Figure 5b is a graph of the capacity contributed by capacitance control and diffusion control of DHP at different scan rates. It can be seen from the figure that the capacity contributed by DHP capacity control at different scan rates is higher than that of PZ, and when the scan rate is 8mV/s, the capacity contributed by capacitance control is as high as 94%, which is consistent with the linear fitting result of the peak current density. This shows that the introduction of electron-donating groups can improve the reaction kinetics of the battery and enable the battery to have better electrochemical performance.



(a)The capacitive contributions of PZ at different scan rates

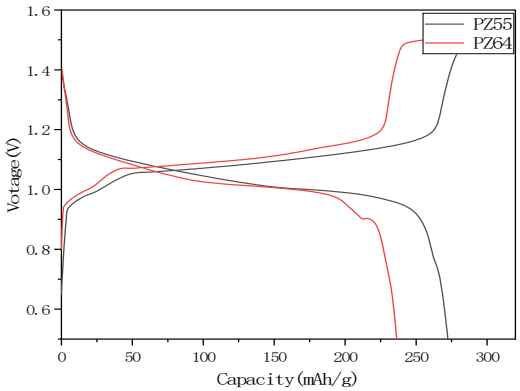


(b)The capacitive contributions of DHP at different scan rates

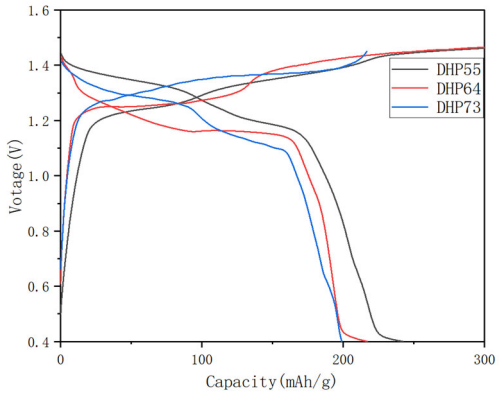
Fig.5 The capacitive contributions of PZ and DHP at different scan rates

From the cyclic voltammetry test and the linear fitting of the peak current density, the introduction of the electron-donating group hydroxyl (-OH) increases the electronegativity and reaction kinetics of DHP. In order to further explore the effect of the introduction of hydroxyl on the electrochemical

properties of azine materials, PZ and KB were prepared into negative electrodes PZ55, PZ64, and PZ73 at a ratio of 5:5, 6:4, and 7:3, respectively, and formed a full battery with $Ni(OH)_2$. Figure 6a is the charge and discharge curve of PZ at different ratios. It can be seen from the figure that at a current density of 0.5 C, the discharge capacity of PZ55 reaches 272.4 mAh/g, reaching 91.4% of the theoretical capacity (1 C=298 mAh/g), the discharge capacity of PZ64 is 236.4 mAh/g, and the capacity of PZ73 is more difficult to test. This is because PZ as an organic material itself is not conductive, so a large amount of conductive carbon needs to be added when it is made into an electrode. When the content of conductive carbon is low, it is difficult for PZ to be effectively charged and discharged, which also leads to a low energy density of organic materials. In the same way, DHP and KB were compounded to prepare DHP55, DHP64, and DHP73, and then combined with $Ni(OH)_2$ to form a full battery. Figure 6b is the charge and discharge curve of DHP at a current density of 0.5 C. It can be seen from the figure that the discharge capacity of DHP55 is 242.21 mAh/g, reaching 94.98% of the theoretical capacity (1 C = 255 mAh/g), and the discharge capacity of DHP64 is 217.08 mAh/g. When DHP: KB=7:3, the discharge capacity of DHP73 can still reach 199.02 mAh/g. The introduction of hydroxyl groups changes the non-conductive properties of PZ itself, which is consistent with the above test results.



(a)The cycle performance of PZ55 and PZ64 at 0.5 C



(b)The cycle performance of DHP55、DHP64 and DHP73 at 0.5 C

Fig.6 The cycle performance of PZ and DHP at 0.5 C

Although the electronegativity of DHP obtained by introducing hydroxyl groups based on phenazine is enhanced, hydroxyl groups are hydrophilic groups, and DHP is more easily dissolved in the electrolyte than PZ. To test the cycle stability of DHP, Figure 7 shows the cycle test of DHP under three electrodes. It can be seen from the figure that at a current density of 1 C, the first discharge capacity is 222.2 mAh/g, and the capacity decays to 186.6 mAh/g during the first few cycles, and then the capacity gradually increases to 212.4 mAh/g. After 110 cycles, the discharge capacity is 203.3 mAh/g. This shows that the electrode is an electrode activation process in the early stage of charge and discharge. This is due to the dissolution and precipitation of the active material during the

charge and discharge process, which leads to a more uniform and sufficient compounding of the active material and the conductive carbon [24].

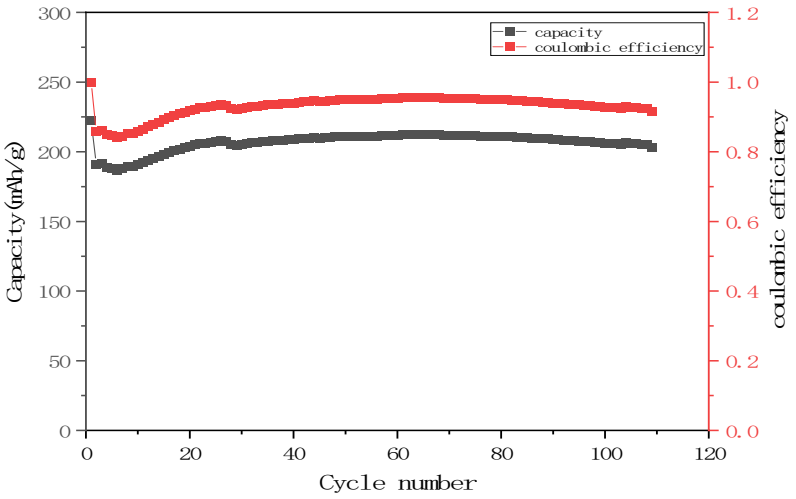
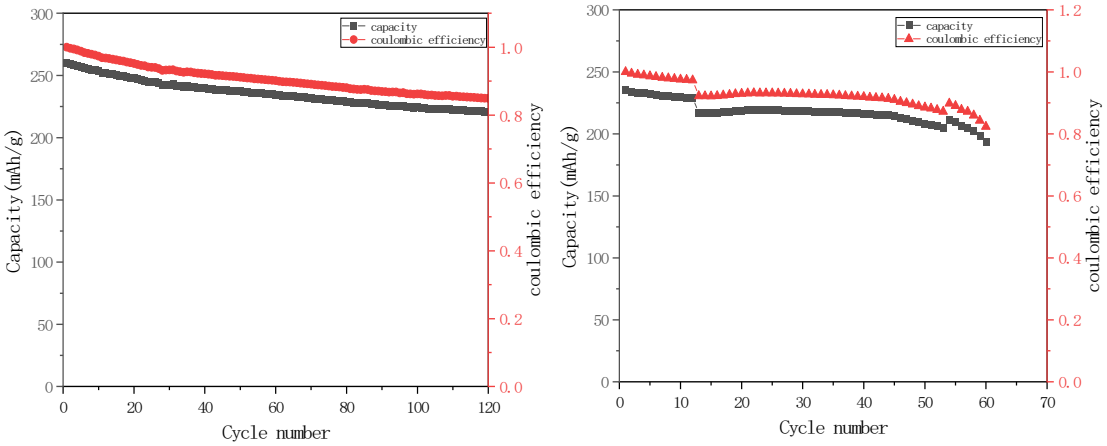


Fig.7 The cycle life of DHP at a current density of 1 C

Based on the DHP three-electrode capacity test, PZ55 and DHP55 were selected as negative electrode materials, $Ni(OH)_2$ was used as the positive electrode to prepare full batteries, and constant current charge and discharge tests were performed. Figure 8a is the cycle stability test of PZ55 at a current density of 0.5 C. It can be seen from the figure that the first discharge capacity of PZ55 is 260.25 mAh/g, and the discharge capacity of PZ is 221 mAh/g after 120 cycles, with a capacity retention rate of 84.92%. Figure 8b is the cycle stability test of DHP55 at a current density of 0.5 C. It can be seen from the figure that the first discharge capacity of DHP is 235 mAh/g, and the capacity decays to 217 mAh/g in the first 10 times, and then the capacity gradually increases to 219 mAh/g, which corresponds to the activation process of DHP in constant current charge and discharge, which is consistent with the three-electrode test. After 60 cycles, the discharge capacity of DHP is 193.8 mAh/g, and the capacity retention rate is 82.47%. Therefore, the introduction of hydrophilic groups (hydroxyl groups) enhances the solubility of DHP, making its cyclic stability slightly worse than that of PZ.



(a)The cycle life of PZ55 at 0.5 C (b)The cycle life of DHP55 at 0.5 C

Fig.8 The cycle life of PZ55 and DHP55 at 0.5 C

In order to further determine the feasibility of DHP organic electrode materials in practical applications, DHP64 was used as the negative electrode and Ni(OH)2 was used as the positive electrode to assemble a soft-pack battery, in which the positive and negative electrodes were separated by a PP/PE separator, 6 mol/L KOH was used as the electrolyte, and it was encapsulated in a

laminated aluminum-plastic film. According to the surface density of the positive electrode and the negative electrode capacity/positive electrode capacity (p/n) of 1.2, the surface density of the DHP negative electrode was designed to be about 20 mAh/cm_2. Figure 9 is the constant current charge and discharge curve of DHP. When the current density is 0.5 C, the discharge capacity of DHP reaches 229.85 mAh/g, and the overall battery energy density reaches 53.42 Wh/kg, which is significantly better than PZ (26.64 Wh/kg) and better than the currently commercially used lead-acid batteries and nickel-hydrogen batteries. This is due to the introduction of hydroxyl groups. The discharge platform of DHP is 1.2 V, which is 20% higher than that of PZ. The introduction of hydroxyl groups changes the electronegativity and reaction kinetics of DHP, doubling the energy density of DHP relative to PZ.

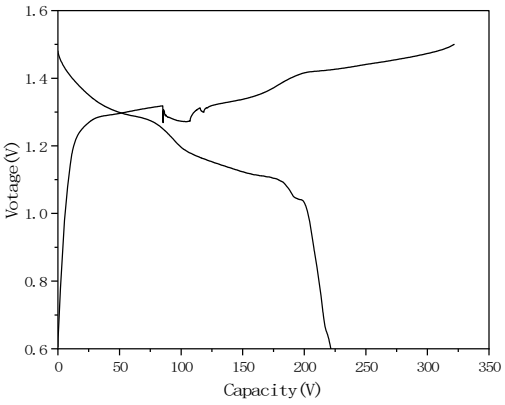


Fig.9 The cycle performance of DHP64 at 0.5 C

4. Summary

In this study, an azine derivative (dihydroxyphenazine) was synthesized using o-phenylenediamine as a raw material as an anode material for aqueous organic batteries. The influence of the electron-donating group hydroxyl group on the electrochemical properties of phenazine was explored, revealing a strong structure-electrochemical activity correlation. The introduced hydroxyl groups can significantly reduce the discharge potential from -0.80 V to -1.0 V. At the same time, compared with PZ, DHP provides a fast charge transfer channel through the intermolecular interaction of the functional group hydroxyl group, which reduces the charge transfer resistance and provides superior rate performance. Therefore, the DHP‖$Ni(OH)_2$ battery exhibits excellent electrochemical performance, including a high reversible capacity of 242.21 mA/g at 0.5 C and an energy density as high as 53.42 Wh/kg, revealing its huge potential in large-scale energy storage systems.

Acknowledgements

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