

Benzene-bridged Phenanthraquinone as Organic Cathode for Li-ion and Na-ion Batteries

Di Li, Wu Tang, Cong Fan*

School of Materials and Energy, University of Electronic Science and Technology of China (UESTC), Chengdu, P. R. China

Email address:

uestc_lidi@qq.com (Di Li), tang@uestc.edu.cn (Wu Tang), fancong@uestc.edu.cn (Cong Fan)

*Corresponding author

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Abstract: Organic electrode materials are widely applied for metal (lithium and sodium)-ion batteries (LIBs and SIBs) due to their structural diversity and redox reversibility. Molecule-aggregation organic electrodes in principle possess the “single-molecule-energy-storage” capability for metal-ion rechargeable batteries. Nevertheless, the small-molecule organic have serious solubility problems in traditional commercial electrolyte, which limited the application in rechargeable batteries. Besides dissolution issue, the effect of possible solvent co-intercalation in liquid electrolytes also devalues the true performance of organic electrodes due to the weak Van der Waals forces among organic molecules. Herein, an organic small-molecule cathode called benzene-bridged phenanthraquinone (BBP) with two phenanthraquinones are exploited as the highly stable organic cathode in LIBs and SIBs. Consequently, BBP can deliver high stable capacity above 67 and 57 mAh g⁻¹ during a long cycle time in both batteries (500 mA g⁻¹). In LIBs and SIBs, the resulting BBP can deliver a peak discharge capacity of 130 and 159 mAh g⁻¹ cathode with an average voltage of 2.3 and 1.8 V. Meanwhile, the BBP can remain 79% and 88% capacity retention (133 and 126 mAh g⁻¹) at 500 mA g⁻¹ in LIBs and SIBs, respectively. And BBP delivers the capacities of 130 and 144 mAh g⁻¹ for 50 cycles at 100 mA g⁻¹ in LIBs and SIBs.

Keywords: Na-ion Battery, Li-ion Battery, Small-molecule Organic Cathode

1. Introduction

Lithium-ion batteries (LIBs) have been extensively used in many energy storage areas due to the high energy density [1-3]. But the resource scarcity and maldistribution of lithium (Li) have become great barriers to obstruct the sustainable development of LIBs [4-6]. On one hand, sodium (Na) and Li in the same main family element which main they have the similar electrochemistry property (Li: 3.04 V, Na: 2.71 V vs. standard hydrogen electrode) and energy storage mechanism; One the other hand, the Na resources are very rich compared with Li. Therefore the both LIBs and sodium-ion batteries (SIBs) are attracted attention for more and more researchers. However, the development of SIBs are still in the primary stage. One of the key issue is the cathode materials of SIBs are not stable enough. So it is necessary to develop stable cathode.

Organic materials have many advantages such as:

biodegradable, low carbon emissions, structural designability and low cost [7-10]. Therefore, in recent years, organic materials have attracted more and more attentions as cathode in LIBs and SIBs. But they are still facing some technical barriers which limited its using in LIBs and SIBs. For example, the discharge potential is lower than 2.0 V and poor cycle stability. In 2015, Manikoth M. Shaijumon and co-workers reported polyimide as cathode and sodium terephthalate as anode applied in SIBs. The cell delivers the capacities of 48 mAh g⁻¹ after 20 cycled [11]. And in 2020, Yong Lei employed polyimide and soft carbon as cathode and anode in SIBs, respectively. The cells discharge potential is around 1.5 V, after 30 cycled, the capacities are 100 mAh g⁻¹ [12]. Nowadays, the research of organic small-molecule cathode is still limited.

The high solubility of organic small-molecule in traditional organic electrolyte is the main obstacle to their application in rechargeable batteries. To solve this problem, there are some solutions have reported in recent researches. From the

perspective of technical improvement, solid/semi-solid batteries are the most effective solution to decrease solubility of small-molecule organic in traditional organic electrolyte. Honma reported a semi-solid LIBs which using Derivatives of 1,4-benzoquinone as cathode and electrolyte. Compare with traditional batteries, the cycle stability has significantly improved [13]. However, the interface problems and low ionic conductivity in this battery limit the development of all solid state batteries.

From the perspective of molecular engineering, the method to reduce the solubility of small-molecule organic in traditional organic electrolyte is to polymerize groups with redox activity. For example, a vulcanized polymer of 1,4-benzoquinone and 9,10-anthraquinone has been synthesized by Song *et al.* and adopt it as cathode in LIBs and SIBs. The batteries show satisfactory cycle stability and considerable specific capacity [14, 15]. But in polymers, the degree of polymerization and polymer purity are difficult to guarantee, which will limited the application of polymerization in organic small-molecule. In another way, increase the molecular weight of organic small-molecule can also reduce their solubility in organic electrolyte, and promote its application in rechargeable batteries. This strategy has great research value.

In this work, an organic small-molecule benzene-bridged phenanthraquinone (BBP) has been synthesized as cathode for LIBs and SIBs. The electrochemical properties in LIBs and SIBs are tested by various test methods. The electrochemical properties of phenanthraquinone (PQ) cathode has also compared with BBP in both type batteries. The BBP delivers capacities of 130 and 144 mAh g⁻¹ for 50 cycles at 100 mA g⁻¹, and remain 79% and 88% capacity retention (67 and 57 mAh g⁻¹) at 500 mA g⁻¹ after 1500 cycled in LIBs and SIBs, respectively.

2. Experiment

2.1. Raw Material

All the materials are purchased through commercial channels and do not need further purification. 3-Bromo-9,10-phenanthredione, phenanthraquinone (PQ), 1,4-phenylenebisboronic acid, anhydrous potassium carbonate (K₂CO₃), tetrakis(triphenylphosphine)palladium, 1,4-dioxane (diox), sodium hexafluorophosphate (NaPF₆), bis(trifluoromethane) sulfonimide lithium salt (LiTFSI), 1,2-dimethoxyethane (DME), 1,3-dioxolane (DOL), polyacrylonitrile copolymer (La133) come from Aladdin Biochemical Technology Co., Ltd.; Keqin black (KB) and carbon nanotubes (CNTs) come from XFNANO Co., Ltd.

2.2. Synthesis of BBP

A Schlenk tube is charged with 3-Bromo-9,10-phenanthredione (574 mg, 2 mmol), 1,4-phenylenebisboronic acid (330 mg, 1 mmol), anhydrous potassium carbonate (K₂CO₃, 1.38 g, 10 mmol), tetrakis(triphenylphosphine) palladium (10 mg), 1,4-dioxane (20 ml)

and deoxidized deionized water (10 ml) under N₂ atmosphere. The mixture is firstly heated at 110°C for 2 days and then cooled to room temperature. 50 ml deionized water and 30 ml ethyl alcohol is added in the mixture and then directly filtered. The remaining solid was washed with dichloromethane (DCM) to remove impurities. The obtained BBP is a yellow powder with a high yield more than 90%.

2.3. Cells Fabrication and Measurement

The BBP (or BQ)-ased electrodes are fabricated by 60 wt% BBP (or BQ), 20 wt% KB, 10 wt% CNTs and 10 wt% La133. The mixture powder is ground for 1 h and then add deionized water to prepare slurry. Make the slurry paint covers the Al foil evenly. The neat loading mass of BBP (or BQ) on Al foil is above 2 mg cm⁻². The electrolytes are 3 M LiTFSI in DME/DOL=1/1 and 1 M NaPF₆ DME for LIBs and SIBs, respectively. The separator is Whatman glass fiber. All cells (CR2032) are assembled in Ar-filled glove box, and choice Li foil and Na foil as counter electrode in LIBs and SIBs, respectively. The charge-discharge measurements of cells are conducted on Land test system (CT2001A, China) at voltage range of 1.2-3.2 V for LIBs and 0.7-3.4 V for SIBs. Cyclic voltammetry (CV) and AC impedance (EIS) tests are recorded using CH Instruments (CHI1400). CV tests are carried out in scan rate 0.1 mV s⁻¹ at voltage range of 1.2-3.2 V for LIBs and 0.7-3.4 V for SIBs. EIS tests are carried out at AC amplitude of 5 mV in the range of 100 KHz to 10 MHz.

3. Results and Discussion

3.1. Synthesis and Characterization

As show in Figure 1a, BBP can be synthesized from 3-bromo-9,10-phenanthraquinone and 1,4-phenylenedicarboxylic acid by one-step Suzuki reaction. Similar reactions have been widely reported. The mass spectrum of BBP is shown in Figure 1b. The mass spectrum peaks are near 491, which is basically consistent with the theoretical relative molecular weight (491) of BBP.

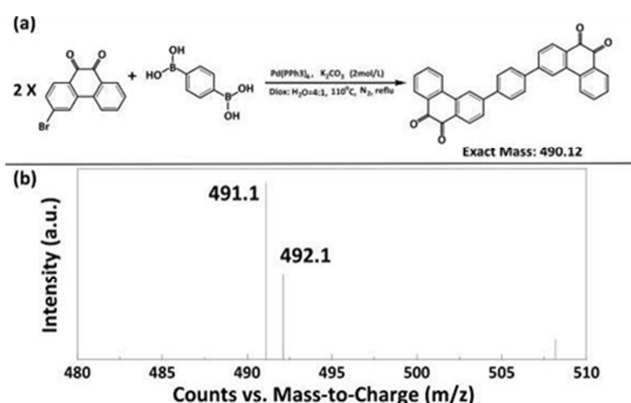


Figure 1. (a) Schematic diagram of BBP synthesis route; (b) The mass spectrum of BBP.

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By synthesizing organic small-molecule PQ into oligomer BBP, the solubility of BBP in organic electrolyte is dramatically decrease. As show in Figure 2, the PQ-based electrodes are obviously dissolved in electrolyte (1 M NaPF₆ in DME and 3 M LiTFSI in DME/DOL=1/1). But the BBP-based electrodes are almost undissolved in the same electrolyte.

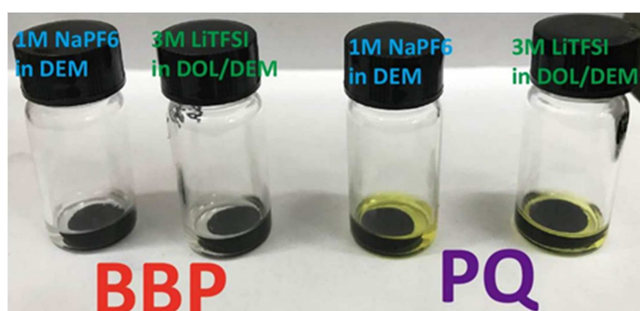


Figure 2. Solubility test of BBP and PQ in electrolyte.

3.2. Electrochemical Process

The electrochemical process of PQ and BBP in LIBs and SIBs are shown in Figure 3. As present in Figure 3(a), there are four electron transfers during electrochemical process of BBP, which contributed 219 mAh g⁻¹ theoretical specific capacity. And there are two electron transfers during electrochemical process of PQ as show in Figure 3(b).

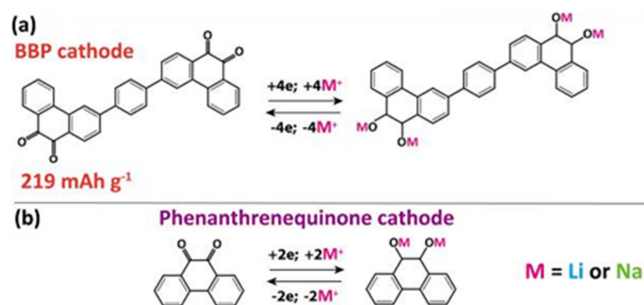


Figure 3. (a) The Electrochemical process of BBP; (b) The Electrochemical process of PQ.

Subsequently, CV test is carried out for LIBs and SIBs with BBP-based electrode, as shown in Figure 4. Both LIBs and SIBs showed reversible redox peaks. In LIBs there are two couples of redox peaks located at 2.9/2.7 V and 2.5/2.2 V. And in SIBs, there are also two redox couples at 2.5/2.3 V and 1.9/1.7 V, respectively. The appearance of two couples of redox peaks is consistent with the symmetry of BBP molecule, indicating that the process of four electron transfer is carried out in two steps. A similar situation has been observed in other phenanthraquinone-based organic cathode [16].

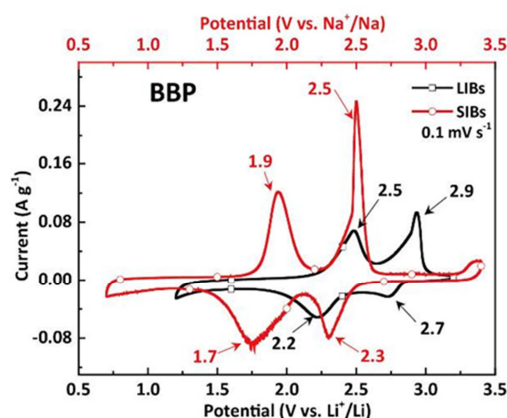


Figure 4. CV curve of BBP in LIBs and SIBs (scanning speed is 0.1 mV s⁻¹, LIBs are 1.2-3.2 V, SIBs are 0.7-3.4 V).

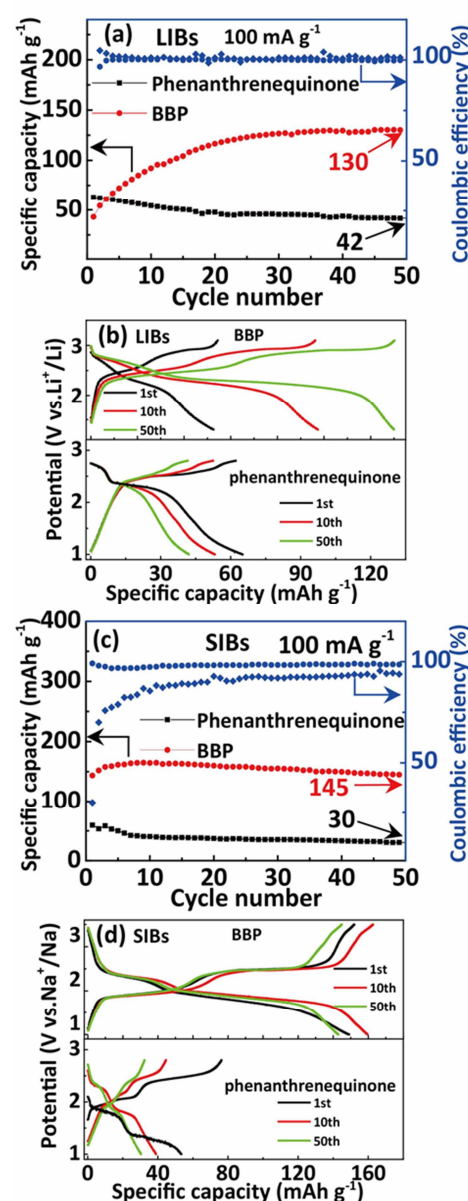


Figure 5. (a) The cycle performance; (b) Charge-discharge curves of BBP and PQ based LIBs; (c) The cycle performance; (d) Charge-discharge curves of BBP and PQ based SIBs.

3.3. Batteries Performance

The cycle performance (current density: 100 mA g^{-1}) of BBP-based LIBs and SIBs are shown in Figure 5. It can be seen from Figure. 5a and Figure. 5c that the specific capacity of PQ decreases rapidly with the increase of cycle number at the low current density (100 mA g^{-1}) in LIBs and SIBs. While the specific capacity of BBP remains 130 and 145 mAh g^{-1} in LIBs and SIBs after 50 cycles. The charge-discharge curves of both batteries are shown in Figure 5b and Figure 5d. It is observed that BBP has more obvious voltage platform than PQ in both batteries (LIBs discharge median voltage: 2.3 V ; SIBs discharge median voltage: 2.4 V), and is more stable. The results shows that the cycle stability of small-molecule organic in the battery will be improved after reducing the solubility of small-molecule organic in the electrolyte. Which means after the soluble small-molecule organic are synthesized into oligomers, their application of organic cathode in the battery field will be greatly expanded.

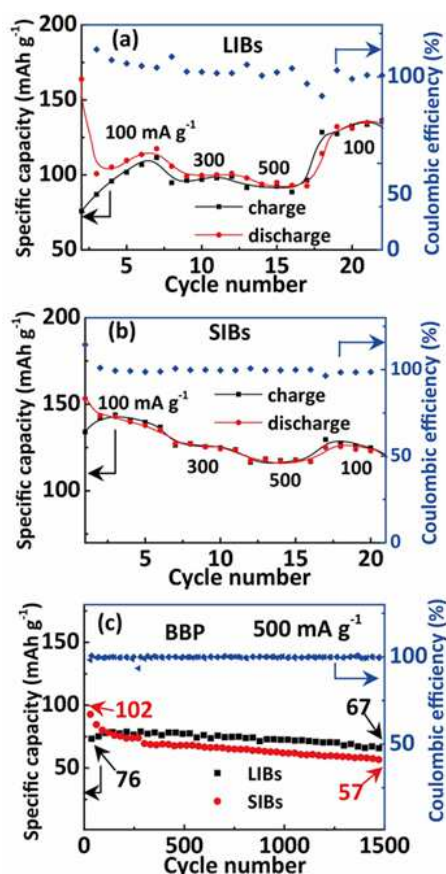


Figure 6. The rate performance of (a) LIBs and (b) SIBs; (c) The cycle performance on the current density of 500 mA g^{-1} of LIBs and SIBs.

The rate performance of BBP-based LIBs and SIBs are given in Figure 6a and Figure 6b. Which show that the specific capacities are $114/100/95$ and $140/125/118 \text{ mAh g}^{-1}$ on the current density of $100/300/500 \text{ mA g}^{-1}$ of LIBs and SIBs, respectively. On the current density of 500 mA g^{-1} , the LIBs and SIBs remain specific capacities 67 and 57 mAh g^{-1} after 1500 cycles.

It can be seen that the cycle performance of BBP-based LIBs is slightly better than SIBs. In order to explore the reason, LIBs and SIBs are testing AC impedance test (EIS) before and after cycling. And scanning electron microscopy (SEM) was used to observe the morphological changes of the two type batteries before and after cycling. It can be seen from Figure. 7a and Figure. 7b that after 50 cycles, the internal resistance of SIBs increases significantly, while the internal resistance of LIBs basically unchanged. Which is one of the reason of cycle performance of LIBs are better than SIBs. At the same time, it can be seen from the SEM picture that after 50 cycles, the holes and gaps in the SIBs are significantly more than those in the LIBs. The increase of holes and pores also leads to the theatrical increase the internal resistance of the batteries, which degrades the cycle stability of both cell.

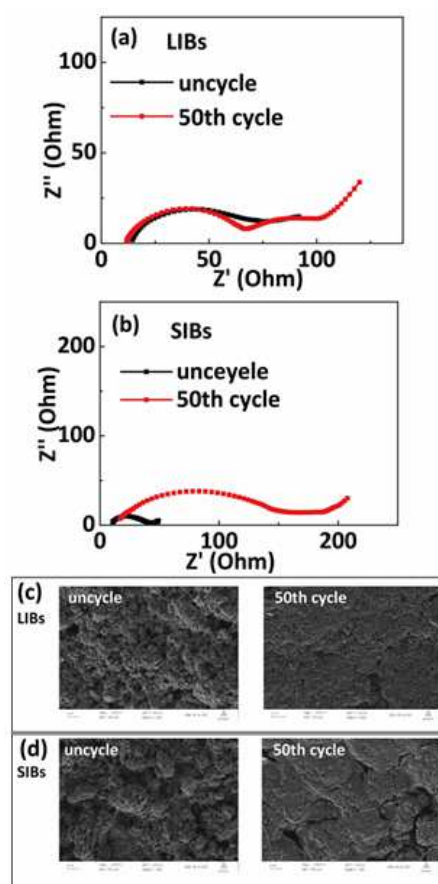


Figure 7. The Nyquist plots of the (a) LIBs and (b) SIBs; The SEM images of (a) LIBs and (b) SIBs.

4. Conclusion

In this work, BBP was synthesized. It was proved that the dissolution of small-molecule organic in organic electrolyte could be effectively inhibited by increasing their molecular weight through oligomerization. The electrochemical performance of oligomer BBP and PQ in LIBs and SIBs have been compared. The results show that the cycle stability and discharge platform of BBP are much better than PQ, which

imply the effectiveness of this strategy. In the BBP-based LIBs, the specific capacity remain 130 mAh g⁻¹ after 50 cycles on current density of 100 mA g⁻¹, and 67 mAh g⁻¹ after 1500 cycles on current density of 500 mA g⁻¹. In BBP-based LIBs, the specific capacity remain 145 mAh g⁻¹ after 50 cycles on current density of 100 mA g⁻¹, and 57 mAh g⁻¹ after 1500 cycles on current density of 500 mA g⁻¹. There are still need to do more work in deeper research on this type of cathode.

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