Calix[6]quinone as high-performance cathode for lithium-ion battery

Weiwei Huang^{1,3†*}, Xueqian Zhang^{2†}, Shibing Zheng¹, Wenjun Zhou¹, Jian Xie³, Zhinan Yang^{2*} and Qichun Zhang^{3*}

ABSTRACT Organic quinone compounds have attracted wide attention due to their high theoretical capacities. Here, a novel cyclic macromolecular calix[6]quinone (C6Q), which possesses 6 *p*-quinone units and can provide 12 electrochemical active sites, has been applied as a promising cathode material in lithium ion batteries (LIBs). The as-fabricated LIBs exhibited an initial specific capacity as high as 423 mA h g⁻¹ ($C_{\text{theo}} = 447 \text{ mA h g}^{-1}$) at 0.1 C. After 100 cycles, the capacity of C6Q maintained at 216 mA h g⁻¹, and even after 300 cycles, C6Q still achieved a high specific capacity of 195 mA h g⁻¹ with negligible capacity fading (as compared with the 100th cycle). Due to the large capacity and wide electrochemical window, C6Q can deliver a specific energy up to 1201 W h kg⁻¹. In addition, the method of immobilizing C6Q with ordered mesoporous carbon (OMC) CMK-3 could further enhance the electrochemical performance of C6Q.

Keywords: calix[6]quinone, lithium-ion battery, organic, cathode, high-performance

INTRODUCTION

Till now, rechargeable lithium-ion batteries (LIBs) have been extensively used in the market, especially in many portable electronics [1–3]. However, conventional inorganic electrode materials face several serious issues, including huge energy consumption in preparation, high cost, and the contamination of the environment caused by excessive waste batteries [4–8]. Therefore, developing new low-cost high-performance electrode materials is considered as an important research direction for future innovative LIBs [9–14]. Specially, “organic batteries” have become a current hot topic because this type of batteries could be the next generation of environmentally friendly

batteries. Compared with the traditional inorganic electrode materials, organic electrode materials have a lot of advantages, such as high theoretical specific capacity, strong designability of molecular structures, renewable constituent elements (C, H, O, N, etc.), good reversibility, high system security, low production cost and readily degradable property [15–23]. These merits could perfectly solve most of the flaws existing in inorganic electrode materials.

Among all organic electrode materials, quinone compounds are of the most outstanding candidates due to their excellent properties [24–27]. Quinone compounds, containing conjugated carbonyls, are widely found in nature. The two-electron redox reaction endows quinones with a higher theoretical capacity compared with other organic materials. Moreover, the reduction potentials of quinones are higher than those of other organic materials. For example, *p*-benzoquinone (BQ), the basic unit of the quinone structure, has a theoretical capacity up to 496 mA h g⁻¹. Nevertheless, the high volatility and solubility [28] of quinone greatly limit its usage in LIBs. Up to now, anthraquinone (AQ) [28], dibenzothiophene (DBT) [28], calix[4]quinone (C4Q) [29–32], pillar[5]quinone (P5Q) [33,34] and several other quinones derivatives have been widely reported. Huang *et al.* [29] first applied C4Q as cathode in LIBs and found that C4Q could deliver an initial capacity of 431 mA h g⁻¹ (97% of C_{theo}) in the liquid electrolytes; however, the batteries only preserved a capacity approximating to 100 mA h g⁻¹ after five cycles. Zheng *et al.* [30] applied C4Q as an electrode in sodium-ion batteries (SIBs) and found that only 24 mA h g⁻¹ of the capacity could be observed after 10 cycles. Zhu *et al.* [33] reported the use of P5Q in LIBs with only 50% ca-

¹ College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

² State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

³ School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

[†] Huang W and Zhang X contributed equally.

* Corresponding authors (emails: huangweiwei@ysu.edu.cn (Huang W); zhinanyang@ysu.edu.cn (Yang Z); qc Zhang@ntu.edu.sg (Zhang Q))

capacity delivered after three cycles. Although all these organic electrode materials possess high theoretical capacities, their cycling performance is very poor. There are two reasons for these problems: (1) these materials are soluble in organic electrolytes, hence their capacities would continuously degrade during the cycling process [27,35]; and (2) the large interfacial resistances of quinone cathodes would result in low conductivity, resulting in poor rate performance [4,29,36]. Therefore, it is highly desirable to enhance the performance of quinone-based electrodes through some modification.

To address the solubility issue, quinone compounds can be converted into polymers or salts. For example, Song *et al.* [37] applied poly(benzoquinone sulfide) (PBQS) in LIBs and found that the as-fabricated batteries displayed an energy density of 734 W h kg^{-1} , long-term cycling stability (1000 cycles, 86%) and superior rate capability (5000 mA g^{-1} , 72%). Wang *et al.* [38] synthesized 2,5-dihydroxyterephthalic acid ($\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$) and this organic-lithium salt presented a superior electrochemical performance with an initial capacity of 223 mA h g^{-1} (93% of C_{theo}) and a capacity retention of 95% after 50 cycles. However, polymerization method could inevitably add dead mass to the active electrode material. In addition, polymerization process could be incomplete and not controllable, and the as-obtained polymers are not easy to be characterized. In addition, the output voltage of organic salts will decrease with the increase of salt groups, which leads to the decrease of energy density of batteries [37,39].

Therefore, to avoid the above-mentioned issues, we synthesized a novel calix[6]quinone (C6Q) oligomer with six *p*-quinones linked by methylene groups at the ortho-positions. Compared with C4Q, C6Q has the same theoretical specific capacity ($C_{\text{theo}} = 446 \text{ mA h g}^{-1}$) but a higher molecular weight ($M_{\text{C4Q}} = 480$, $M_{\text{C6Q}} = 720$). Moreover, the larger cavity of C6Q would allow more electrolytes to get in, which would be more favorable for lithiation/delithiation. When C6Q was applied to LIBs at 0.1 C, it exhibited a high initial capacity of 423 mA h g^{-1} , and could maintain 216 and 195 mA h g^{-1} after 100 and 300 cycles, respectively. Moreover, utilizing ordered mesoporous carbon (OMC) CMK-3 to immobilize C6Q further improved the electrochemical properties. The capacity increased to 273 mA h g^{-1} after 300 cycles. At the same time, the rate performance of C6Q was also improved.

EXPERIMENTAL SECTION

Materials preparation

C6Q was successfully prepared according to the reported

synthetic route of C4Q [40]. There were three step-reactions to convert calix[6]arene into C6Q: diazonium coupling, reduction, and oxidation. In the reduction reaction, because the intermediate was easily oxidized, an enhanced method was employed: (1) the reaction was run under inert atmosphere (e.g., N_2); (2) after the reaction, the product was harvested rapidly through centrifugation to reduce the contact time with air; and (3) oxygen-free water was used to wash the product to further avoid oxidation. The synthetic detail and the characterization of C6Q are provided in Supplementary information (SI). Employing the previous methods to fabricate C4Q/CMK-3 composites [14], the C6Q/CMK-3 immobilization mass ratios of 1:1 and 1:2 were selected for preparation. Taking C6Q/CMK-3 (1:1) as an example, under 50°C , the dispersion liquid of 100 mg CMK-3 in 6 mL *N*-methyl-2-pyrrolidone (NMP) was added into the solution of 100 mg C6Q in 8 mL NMP, the mixture was ultrasonicated for 2 h at 25°C , and then dried in vacuum at 90°C until the mass no longer reduced.

Materials characterization

Chemical structure of C6Q was confirmed by Electrospray ionization mass spectrometry (ESI-MS), Infrared spectroscopy (IR), and nuclear magnetic resonance (NMR). ESI-MS was performed with a CQ Finnigan apparatus. IR spectrum was recorded on a FTIR-650 spectrometer. The morphologies of C6Q, C6Q/CMK-3 (1:1) and C6Q/CMK-3 (1:2) were studied on scanning electron microscope (SEM) (JEOL JSM7500F) and transmission electron microscope (TEM) (Philips Tecnai-F20). The crystalline of C6Q/CMK-3 composites were studied through X-ray diffraction (XRD) in the wide 2θ range of 5° – 90° at a speed of 5° min^{-1} (D-max-2500/PC, Cu K α radiation). The characteristic peaks of samples were determined by a standard card comparison. Surface area and pore volume of CMK-3 and C6Q/CMK-3 composites were studied on a Belsorp-Mini instrument by using N_2 adsorption-desorption isotherms at 77 K.

Electrochemical investigation

The cathode slurry was prepared by employing C6Q or C6Q/CMK-3 as the active material, Ketjen Black as the conductive carbon, and polyvinylidene fluoride (PVDF) as the binder (mass ratio: 6:3:1). After sufficiently grinding, the uniform product was coated on Al foil. After being dried in vacuum oven at 60°C for 12 h, the film was cut into circular pieces (12 mm in diameter) with the electrode area mass loading of approximately 1.4 mg cm^{-2} . CR2032 coin cells were fabricated in an Ar-

filled glove box. In the coin cell, the electrolyte was 1 mol L⁻¹ LiPF₆ in a mixed solvent containing ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1, v/v), Celgard 2400 was employed as the separator, and Li tablet was used as the counter electrode. The galvanostatic discharge-charge and rate performance were tested on Land CT2001A. Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) were conducted on CHI-660E. All the assembly and test processes were carried out at 25°C.

RESULTS AND DISCUSSION

ESI-MS (Fig. S1), IR (Fig. S2) and ¹H NMR (Fig. S3) confirmed the successful synthesis of C6Q. Fig. S1 shows the charge-to-mass ratio of C6Q ($m/z = 738.3$ ($M + \text{NH}_4^+$)), which is consistent with the sum of its molecular weight (720) and NH_4^+ (18). In the infrared spectrum, two absorption peaks at 1655 and 1614 cm⁻¹ are the stretching vibration of the carbonyl group (C=O), while the peak at 1300 cm⁻¹ belongs to the absorption peak of methylene (-CH₂). The ¹H NMR spectrum of the product is shown in Fig. S3, and the integral ratio of the peaks of 6.63 (s, 12H, -CH=C-) and 3.51 (s, 12H, -CH₂-) is 1:1, which is in line with the ratio of two hydrogens in the molecule, and the chemical shifts are consistent with the reported result [41].

C6Q, C6Q/CMK-3 (1:1) and C6Q/CMK-3 (1:2) were separately assembled for charging and discharging tests. Fig. 1a is the charge-discharge schematic illustration and Fig. 1b is the CV curve of the LIBs with a sweep speed of 0.2 mV s⁻¹. The voltage range is 1.3–3.7 V. There are two reduction peaks (2.65, 2.83 V, where 2.65 V is a small shoulder peak) and two oxidation peaks (2.84, 3.35 V) respectively, manifesting that the redox process of C6Q is a two-step (12 e⁻) electrochemical reaction. In the reduction process, its active sites firstly gained 12 electrons to form anions, and then balanced by 12 Li⁺. Different from the reduction process, the delithiation process in the oxidation reaction is carried out in two steps, corresponding to two oxidation peaks in the CV curve. The shapes and peak areas of the first and second circles in CV curve are basically the same, indicating that the process is completely reversible.

Fig. 1c shows a comparison of cycle capabilities among C4Q, C6Q and C6Q composites. As we can see, under the condition of 0.1 C, the initial discharge capacity of C6Q reached 95% of the theoretical capacity (423 mA h g⁻¹), indicating that all 12 carbonyl groups of C6Q could participate in the reversible lithiation/delithiation electrode reactions. It is worth noting that the high energy

density of 1201 W h kg⁻¹ exceeds that of conventional inorganic materials. After 100 cycles, the capacity decayed to 216 mA h g⁻¹ due to the continuous dissolution of C6Q during the cycle. However, compared with C4Q, the macromolecular structure of C6Q effectively reduced its dissolution rate, which could be verified by qualitative immersion experiment. Fig. S4 compares the color change of C4Q, C6Q and C6Q composite cathodes soaked in electrolytes after 1, 15, and 30 days, and it can be found that the color change of C4Q is the most obvious, while C6Q has a slight change and C6Q/CMK-3 composites almost have no change. These results suggest that C6Q has a smaller solubility than C4Q, and CMK-3 could further reduce the dissolution rate of C6Q in traditional electrolytes. It can also be seen from Fig. 1c that the cyclic performance of C6Q was improved after immobilization of C6Q in CMK-3, where C6Q/CMK-3 (1:2) performed outstandingly with a capacity of 273 mA h g⁻¹ (63% of capacity retention) after 300 cycles. Their coulombic efficiency (nearly 100%) indicates that they have great charge/discharge reversibility (Fig. 1d). Fig. 1e, f and Fig. S5 show that the addition of CMK-3 has no influence on the electrochemical performance of C6Q, and the charge-discharge curve shape of pure C6Q is basically the same as the composites.

The rate performance of C6Q and its composites in LIBs was compared and provided in Fig. 1g. A continuous series of charging and discharging tests were performed at different rates of 0.1–1 C. From Fig. S6, we can see that the charge-discharge curves of C6Q and its composites under different current densities were basically the same. At a low rate of 0.1 C, their discharge specific capacities were the same. With the increase of current density, there were no obvious changes in charge-discharge curves. The discharging specific capacities of the composites were significantly higher than that of C6Q. When the current density was 1 C, the capacity of C6Q/CMK-3 (1:2) was the highest one; however, there was no significant difference between C6Q and C6Q/CMK-3 (1:1). The possible reason is that, under large current density, the existence of pore structure might slow down the migration process of lithium ions, thereby affecting the electrochemical reaction rate [42,43]. When the current rate recovered to 0.1 C, the composites showed much higher stable capacity than C6Q, and C6Q/CMK-3 (1:2) showed better performance. It is confirmed that C6Q/CMK-3 composite could enhance the conductivity and rate performance for LIBs.

The surface morphologies of C6Q and C6Q/CMK-3 composites were studied by SEM (Fig. 2a–d). Fig. 2a re-

Figure 1 (a) The proposed electrochemical redox of C6Q. (b) CV of C6Q at 0.2 mV s⁻¹. (c) Cyclic properties of C6Q/CMK-3 composites, C6Q and C4Q. (d) Coulombic efficiency of C6Q and C6Q/CMK-3 composites. (e) The charge-discharge curves of C6Q. (f) The charge-discharge curves of C6Q/CMK-3 (1:2). (g) Rate capability of C6Q and C6Q/CMK-3 composites.

veals that C6Q possesses olive-shaped microstructures and CMK-3 has a large specific surface area and pore volume. The pore structure and the smooth surface of CMK-3 can be seen clearly in Fig. 2b. Fig. 2c, d do not show any obvious crystal particles on the surface of CMK-3. Correspondingly, there is no characteristic dif-

fraction peak of C6Q appearing in XRD pattern (Fig. 3). The TEM and TEM-mapping performed separately for C6Q/CMK-3 (1:2) suggest that C6Q is evenly distributed in CMK-3 (Fig. 2e–h). Fig. S7 shows that after 300 cycles of charge-discharge experiment, the morphology of composite materials is almost unchanged, indicating that

Figure 2 SEM images of CMK-3 and C6Q/CMK-3 composites (a) C6Q, (b) CMK-3, (c) C6Q/CMK-3 (1:1), and (d) C6Q/CMK-3 (1:2). (e) TEM image of C6Q/CMK-3 (1:2). (f–h) TEM-mapping of C6Q/CMK-3 (1:2).

their structure is relatively stable.

The XRD patterns of C6Q and its composites are revealed in Fig. 3. C6Q has a relatively strong diffraction peak, corresponding to its great crystal structure. The peaks at 26° and 44° in the XRD pattern of CMK-3 are in line with the (002) and (100) crystal plane respectively, suggesting its graphitization structure. C6Q composites have the same peak shape as CMK-3 beyond 17° . This finding is consistent with the results of previous studies on C4Q/CMK-3 [43].

N_2 adsorption and desorption tests of CMK-3 and C6Q composites were conducted, and their testing results are shown in Fig. 4. According to Fig. 4a, CMK-3 has a large pore volume and can adsorb a large amount of N_2 . After the encapsulation of C6Q into the pore of CMK-3, the pore volume becomes smaller and smaller. Especially, when the ratio of C6Q was 50%, the adsorption amount of N_2 reached the minimum. Fig. 4b evinces that the specific surface area of CMK-3 reaches $1073.4 \text{ m}^2 \text{ g}^{-1}$, the pore volume is $1.28 \text{ cm}^3 \text{ g}^{-1}$, and the pore diameter distribution is around 3.8 nm. These results suggest that CMK-3 is an ordered mesoporous material with a large specific surface area and pore volume. As the ratio of C6Q continued increasing, the specific surface area and pore volume of C6Q decreased rapidly. The specific surface area of C6Q/CMK-3 (1:2) dropped to $270.47 \text{ m}^2 \text{ g}^{-1}$, and the pore volume changed into $0.25 \text{ cm}^3 \text{ g}^{-1}$. By further increasing the content of C6Q, the specific surface area of C6Q/CMK-3 (1:1) reached $110.87 \text{ m}^2 \text{ g}^{-1}$, and the pore volume was reduced to

Figure 3 XRD patterns of C6Q and C6Q/CMK-3 composites.

$0.13 \text{ cm}^3 \text{ g}^{-1}$. This result suggests that C6Q has been filled completely into the pore of CMK-3 at the ratio of 1:1.

C6Q/CMK-3 (1:2) composites have the best performance by studying the cyclic performance of C6Q and C6Q composites in LIBs. The EIS of C6Q and C6Q/CMK-3 (1:2) were compared, and the kinetic processes in the electrochemical reaction between them were studied. The voltage of each cell during EIS was around 3.50 V. The impedance changes of these two materials were measured after different cycles, and the results are shown in Fig. 5. The EIS of C6Q and C6Q/CMK-3 (1:2) are made up of semicircle (high frequency region) and diagonal (low frequency region). The diameter of the

Figure 4 (a) N₂ adsorption and desorption curves of CMK-3 and C6Q/CMK-3 composites. (b) Pore distribution curves and pore volume curves for CMK-3 and C6Q/CMK-3 composites.

Figure 5 The EIS during the cycle of LIBs (a) C6Q/CMK-3 (1:2), (b) C6Q. (c) The corresponding equivalent circuit.

semicircle in the high frequency region is positively correlated with the magnitude of the charge transfer resistance. The initial impedances of C6Q/CMK-3 (1:2) were significantly lower than that of C6Q. With the increase of cycle numbers, their charge-transfer impedance values rose gradually. However, the impedance values of C6Q/CMK-3 (1:2) were still lower than those of C6Q due to its lower rate of dissolution in traditional organic electrolytes.

CONCLUSIONS

In summary, we have successfully synthesized C6Q and applied it as cathode materials in LIBs with an initial capacity up to 423 mA h g⁻¹ (about 95% of theoretical capacity). The electrochemical performances of C4Q and C6Q have been compared. C6Q with a large cyclic structure possesses a more stable cycling performance, a more excellent rate performance and a less impedance compared with C4Q. After 300 cycles, the capacity of C6Q still maintained 195 mA h g⁻¹. In addition, the encapsulation of C6Q into CMK-3 not only further enhances the cycling performance of C6Q but also achieves better rate capability. Our results suggest that larger cyclic

structure in C_xQ family should be excellent candidates as cathode materials in LIBs.

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Author contributions Huang W and Zhang X wrote the paper. Zhang X conducted a series of electrochemical tests. Zheng S prepared the C6Q and performed tests such as TEM, IR, and NMR. Zhou W collected the data and analyzed the results. Xie J modified the article. Huang W, Yang Z and Zhang Q supervised the project and conceived the experiments. All authors contributed to the general discussion.

Conflict of interest There are no conflicts to declare.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Weiwei Huang obtained her BSc degree at Hebei Normal University of Science & Technology in 2005, MSc degree of inorganic chemistry at Hebei Normal University in 2008 and PhD degree of physical chemistry at Nankai University in 2011. Then, she joined Prof. Jun Chen's group at Nankai University as a postdoctoral fellow. In 2013, she joined the School of Environmental and Chemical Engineering at Yanshan University as an associate professor. She is currently studying at Nanyang Technological University as

a visiting scholar. Her research is focused on the organic electrode materials for Li/Na batteries.

Xueqian Zhang obtained his BSc degree of materials science and engineering at Yanshan University in 2017. He is currently a Master candidate under the joint guidance of Prof. Weiwei Huang and Prof. Zhinan Yang at Yanshan University. His research mainly focuses on the synthesis and preparation of organic electrode materials in Li/Na batteries and investigation of electrolytes.

Zhinan Yang obtained his BSc degree at Xi'an University of Science and Technology in 2008, and PhD degree in engineering at Yanshan University in 2013. Then, he joined the School of Mechanical Engineering of Yanshan University as a lecturer, and has been an associate professor since 2017. He worked as a visiting scholar at the University of New South Wales in Australia and the University of Cambridge in the UK. His research is focused on the advanced structural materials preparation techniques.

Qichun Zhang is an Associate Professor at the School of Materials Science and Engineering, Nanyang Technological University, Singapore. His research focuses on conjugated rich carbon materials and applications. Currently, he is an associate editor for *J. Solid State Chemistry*, Advisory board members of *Materials Chemistry Frontiers*, *Chemistry-an Asian Journal*, *Journal of Materials Chemistry C*, and *Inorganic Chemistry Frontiers*. He is also a fellow of the Royal Society of Chemistry. In 2018 and 2019, he has been

recognized as one of highly-cited researchers (top 1%) in cross-field in Clarivate Analytics. Till now, he has published more than 327 papers (H-index: 67) and filed 4 patents.

高性能锂离子电池正极Calix[6]quinone

黄苇苇^{1,3†*}, 掌学谦^{2†}, 郑仕兵¹, 周文君¹, 谢健³, 杨志南^{2*}, 张其春^{3*}

摘要 有机醌类化合物因其具有高的理论容量值而引起了人们的广泛关注. 本文合成了一种新型的环状大分子Calix[6]quinone (C6Q), 它由6个对苯醌单元组成, 可提供12个电化学位点, 是一种极具发展前景的锂离子正极材料. C6Q在0.1 C的电流密度下展示了高达423 mA h g⁻¹的初始放电比容量(理论放电比容量为447 mA h g⁻¹). 经过100圈充放电循环之后, 它的容量保持在216 mA h g⁻¹; 经过300次循环之后, 仍然拥有195 mA h g⁻¹的高容量. C6Q具有高容量和宽的电化学窗口, 因此可以提供高达1201 W h kg⁻¹的能量密度. 此外, 使用有序介孔碳CMK-3固载C6Q的方法可以进一步提高C6Q的电化学性能.