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Pillar[5]quinone-Carbon Nanocomposites As High-Capacity Cathodes For Sodium-Ion Batteries

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ABSTRACT: New organic cathodes to replace inorganic materials for the capacity enhancement of sodium-ion batteries (SIBs) are highly desirable. In this research, we described the investigation of pillar[5]quinone (P5Q), which we determined to have a theoretical capacity of 446 mAh g⁻¹, a value that makes it a very promising candidate as a cathode in rechargeable batteries. Inspired by this value, P5Q was encapsulated into CMK-3 to form a composite, and then integrated with single-walled carbon nanotubes (SWCNTs) to generate a film that was used as the cathode in SIBs. The as-assembled SIBs showed an initial capacity up to 418 mAh g⁻¹ and maintained 290 mAh g⁻¹ after 300 cycles at 0.1 C. Even at 1 C, the capacity could still reach 201 mAh g⁻¹.

INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in various fields including electric vehicles and portable devices¹⁻⁶ since they were commercialized in 1991.⁷ However, two issues have become a bottleneck for further applications of traditional LIBs with inorganic transition metal/oxides as electrodes, namely limited lithium resources and the pollution associated with the transition metal elements used in the electrode(s). Thus, to address these two issues, it is highly desirable to (1) search for alternative ion conductors (e.g Na, K, Mg, Zn, or Al) to replace lithium, and (2) employ organic electroactive materials as electrodes in rechargeable batteries for the replacement of toxic metal/oxides.

Since sodium is at least 10 times more abundant in the earth's crust than lithium⁸⁻¹⁰ and can be easily obtained from a number of sources (rock salt from mines, sea water), it is reasonable to consider sodium as a viable alternative for lithium in rechargeable batteries. In fact, sodium-ion batteries (SIBs) have already been demonstrated to be an ideal choice for energy storage.¹¹⁻¹³ Moreover, sodium extraction results in far less pollution compared with elements such as nickel, cadmium, and lead, currently used in commercially available batteries and have been confirmed to cause hazards to the environment and human health. Thus, SIBs are an important area of research.

A critical challenge being faced with respect to the development and deployment of new electrode materials for batteries is the capacity of inorganic materials (except lithium, silicon and sulfur), which are typically small. These low capacities are an obstacle for their larger scale

applications such as large vehicles and equipment, and grid-scale applications. To solve this problem, we believe that organic compounds or organic-inorganic hybrid complexes are a good choice.¹⁴⁻¹⁹ Among various organic electroactive materials, quinones are one of the most extensively studied materials due to their numerous advantages,²⁰⁻²⁴ including environment-friendliness, renewability, designability,²⁵⁻²⁹ large specific capacity,³⁰⁻³⁶ and the unique carbonyl structure suitable for binding various metal ions. In this research, we synthesized an organic compound, P5Q, that contains a cycle array of five p-quinones linked by methylenes at the para-position (Figure 1 and S1). Although P5Q has a high theoretical capacity (446 mAh g⁻¹), and the cavity structure is beneficial to electron transport, its high solubility in liquid electrolytes makes it impractical as a cathode material in rechargeable batteries. To address this issue, a poly(ethylene glycol) (PEG)-based gel polymer electrolyte³⁷ or all-solid state electrolytes³⁸ have been employed to improve the performance of the as-fabricated rechargeable batteries.

In addition to the optimization of electrolytes,³⁹⁻⁴² modifying cathode materials is another strategy to solve the solubility issue. For instance, the solubility can be reduced through the formation of quasi solid, polymerization, or encapsulation. However, the process to prepare quasi-solid is very complicated while polymerization tends to result in dead mass and cause the loss of capacity.⁴³ By comparison, we believe that encapsulation is a simpler and easier way to be operated.

Thus, in this research, we will adopt last method to prepare our cathodes.

Figure 1. 3D structures of (a) P5Q, (b) P5QNa₁₀ drawn by Chemdraw.

Since CMK-3 has been demonstrated to possess ordered porous structure and large surface area,⁴⁴ which are favorable for the diffusion and absorption of sodium ions,⁴⁵⁻⁴⁸ it is logical for us to use CMK-3 as the encapsulating material in this research. Moreover, given that single-walled carbon nanotubes (SWCNTs) have been widely used as conductive additives to wind around the outside of encapsulating materials to form a three-dimensional conductive network among nanocomposites,⁴⁹ we believe that this feature can also offer a good conducting path for electrons in our research. By adopting this strategy, a P5Q/CMK-3/SWCNTs cathode with the initial capacity of 418 mAh g⁻¹ has been fabricated. The as-fabricated SIBs still maintained 290 mAh g⁻¹ after 300 cycles at 0.1 C.

Figure 2. Schematic of the discharge-charge of P5Q cathode and sodium-metal anode. During the discharge, electrons in sodium metal lose and pass through the separator to reach P5Q. At the same time, the carbonyl groups gain electrons and sodium ions are embedded in the carbonyl groups of P5Q. The charging process is the opposite way.

EXPERIMENTAL SECTION

Materials preparation

P5Q was prepared according to the previous report (Figure S1).⁵⁰ All reagents were purchased and directly used without further purified, except that DMSO was required to be purified with CaH₂ and distilled under vacuum before used. P5Q and CMK-3 were ultrasonically treated for 30

minutes, respectively, before blending them together. After blending, the mixture was kept ultrasonication for 2 hours before dried under vacuum at 100 °C for 10 hours.

Characterization and electrochemical measurement

The as-prepared P5Q was characterized by ¹H NMR, ¹³C NMR, and ESI-MS (Figures S3-S5). Its band gap (ΔE , eV) was studied through UV-Vis absorption spectrum (UV) and density functional theory (DFT) calculation. The fourier transform infrared spectroscopy (FTIR) of P5Q was recorded between 800 cm⁻¹ and 2400 cm⁻¹, while the XRD patterns of P5Q, CMK-3 and their composites were obtained in the wide 2 θ range of 10-80° at a sweep speed of 5° min⁻¹. Surface topography was observed through scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively. Surface area and pore volume were analyzed on a Belsorp-Mini instrument by an N₂ adsorption-desorption isotherm at 77K.

CR 2032 coin-type cells were assembled in glove box with the order of sodium plate, separator, and positive electrode made from P5Q/CMK-3 composites. Two different compositions were used to study their electrochemical performance: (1) P5Q (20 wt%), CMK-3 (40 wt%), SWCNTs (30 wt%), and Poly (vinylidene fluoride) (PVDF 10 wt%); and (2) P5Q (30 wt%), CMK-3 (30 wt%), SWCNTs (30 wt%) and PVDF (10 wt%). After grinding these mixtures together for 10 minutes, 200 μ L N-methyl-2-pyrrolidone (NMP) was added, and the mixtures were kept grinding for another 10 minutes before coating them on aluminum foil. After drying the as-fabricated films in vacuum at 60 °C for 10 hours, the cathodes were ready for test. The electrolyte was 1 M NaClO₄ in a mixed solvent containing ethylene carbonate (EC, 47.5% volume ration), dimethylcarbonate (DMC) (47.5% volume ratio) and 5% fluoroethylene carbonate (FEC). Separators in these cells were glass microfiber filters (0.7 μ m). All as-fabricated cells were run on Land CT2001A cell testing system. Cyclic voltammetry (CV) was conducted on CHI600E to observe the discharge-charge voltage range of the as-fabricated cells. All of above-mentioned cell tests were carried at 25 °C.

RESULTS AND DISCUSSION

The spectra such as ¹H NMR, ¹³C NMR, and ESI-MS of the as-prepared P5Q were consistent with the earlier report,⁵⁰ confirming the correctness of our sample. FTIR (Figure S6) showed two peaks at 1614 cm⁻¹ and 1655 cm⁻¹, which can be assigned to the telescopic vibration of carbonyl group, and one peak at 1250 cm⁻¹, which belongs to the vibration of benzene-linked methylene, further proving that P5Q has been obtained.

The DFT calculation (Figure S2) indicated that the lowest unoccupied molecular orbital (LUMO) level and the highest occupied molecular orbital (HOMO) level of P5Q were -4.23 eV and -7.66 eV, respectively. Based on these data, the energy gap of P5Q was calculated to be 3.43 eV. The LUMO value suggests that P5Q has great electron affinities and good reduction potentials.⁴⁹ These results were very close to the value calculated from UV absorption

spectrums.

XRD patterns of P5Q and its composites were provided in Figure 3. The sharp peaks in the pattern of P5Q demonstrated its good crystallinity. The broad peaks in the XRD spectrum of CMK-3 were similar to the previous report.⁴⁶ After encapsulated in CMK-3, sharp peaks of P5Q disappeared, which might be attributed to the transformation of P5Q from the crystalline state to amorphous state during the preparation of composite materials. With the increasing amount of CMK-3, the peak at 25° became broad and was in line with the previous reports.¹⁵

Figure 3. XRD patterns of P5Q, CMK-3 and P5Q/CMK-3.

Raman spectrum of P5Q (Figure 4) displayed the strong peak near 1660 cm⁻¹ and the weak peaks at 1597 cm⁻¹ and 1292 cm⁻¹, while CMK-3 showed two broad peaks at 1585 cm⁻¹ and 1323 cm⁻¹. For P5Q/CMK-3 (1:2) composites, there was no obvious characteristic peak of P5Q, however, the signal for the characteristic peak of CMK-3 was still seen obviously, which might suggest that P5Q was well encapsulated in CMK-3.

Figure 4. Raman spectra of P5Q, CMK-3 and P5Q/CMK-3.

The structure of this encapsulated material was further studied by TEM (Figure 5). TEM mapping (Figure 5a)

clearly indicated that carbon and oxygen in the composite were evenly distributed. As illustrated in Figures 5b and 5c, nano-pore structures in CMK-3 disappeared after encapsulation, which further confirmed that P5Q has already been filled in CMK-3. Figure 6 showed the surface area of CMK-3, pore volume of P5Q/CMK-3 composites, N₂ adsorption-desorption isotherms, and pore size distribution (PSD). It indicated that surface area and the pore volume of original CMK-3 were 1330 m² g⁻¹ and 1.59 cm³ g⁻¹, respectively. After encapsulation, these values decreased to 1.79 m² g⁻¹ and 0.01 cm³ g⁻¹, which further proved the success in the encapsulation of P5Q into CMK-3.

Figure 5. (a) TEM of P5Q/CMK-3 (1:2) and its TEM-mapping. (b) TEM of CMK-3. (c) TEM of P5Q/CMK-3 (1:2).

Figure 6. (a) The nitrogen adsorption-desorption isotherms and (b) the corresponding pore-size distributions of CMK-3 and P5Q/CMK-3 (1:2).

SEM studies (Figure 7) indicated that P5Q and CMK-3 possesses rod-like and bundle-like shapes, respectively. After the encapsulation, the shapes showed some changes. Figures 7c and 7d were the images of composites with two different mass ratios between P5Q and CMK-3 (1:1 and 1:2, respectively). Some spherical structures could be observed on the outer surface of the composite (1:1), which suggested that P5Q was not completely filled into CMK-3 (Figure 7c). When the ratio increased to 1:2, no spherical P5Q could be seen on the outer surface of CMK-3, indicating that P5Q has completely been filled into CMK-3. Figure 7e showed the morphology of single-walled carbon nanotubes, which can wrap the P5Q/CMK-3 composites (Figure 7f).

Figure 7. SEM images of (a) P5Q, (b) CMK-3, (c) P5Q/CMK-3 (1:1), (d) P5Q/CMK-3 (1:2), (e) SWCNTs and (f) P5Q/CMK-3 (1:2)/SWCNTs.

To study the charge and discharge window of SIBs with P5Q/CMK-3 as the cathode, cyclic voltammetry test was carried in the range of 1.50 - 4.20 V. The test results were recorded in Figure S7. There were two oxidation peaks and one reduction peak at 3.02 V, 3.83 V and 2.37 V, respectively. With the increasing cycle number, the peak area decreased without any change in the position, which suggested a good reversibility. CV curves of the composites (Figure 8a) were similar to that of pure P5Q.

Figure 8b showed the rate performance of both P5Q and the composites (P5Q/CMK-3 (1:1) and P5Q/CMK-3 (1:2)) at 0.1 C, 0.2 C, 0.5 C and 1 C. As the rate increased, the capacities of all three materials decreased. Note that the capacity of pure P5Q at each rate was always lower than that of the composites. The capacity provided by P5Q/CMK-3 (1:1) was between pure P5Q and P5Q/CMK-3 (1:2), and P5Q/CMK-3 (1:2) delivered the highest capacity. The discharge-charge cycles at different rates were shown in Figures S8b, S8d and S8f. The pure P5Q provided a discharge capacity of 148 mAh g⁻¹ at 1 C, while P5Q/CMK-3 (1:1) was 150 mAh g⁻¹ and P5Q/CMK-3 (1:2) was 201 mAh g⁻¹, where P5Q/CMK-3 (1:2) displayed the highest capacity at high rate.

The discharge capacity of P5Q and the composites under 0.1 C were recorded in Figure 8c. After 100 cycles, discharge capacity of P5Q decreased from 431 mAh g⁻¹ to 117 mAh g⁻¹ (the retention is 27%). The discharge capacity of P5Q/CMK-3 (1:1) decreased from 414 mAh g⁻¹ to 134 mAh g⁻¹ (the retention is 32%) after 300 cycles while the discharge capacity in the composites of P5Q/CMK-3 (1:2) only decreased from 418 mAh g⁻¹ to 290 mAh g⁻¹ (the retention is 69%). This result suggested that increasing the amount of CMK-3 could stabilize P5Q and reduce the fading speed of the capacity. The specific discharge-charge cycles for each ratio were provided in Figures S8a, S8c, and S8e. The cyclic stability of nanocomposites in 1:2 P5Q/CMK-3 was shown in Figure 8b and the coulombic efficiency was always maintained at around 100%, which fully proved the high cyclic stability of P5Q/CMK-3 composites. The electrochemical performance of P5Q and their composites were summarized in Table 1.

Figure 8. (a) CV curves of P5Q/CMK-3 (1:2). (b) Rate performance of P5Q and P5Q/CMK-3. (c) Discharge capacities of P5Q and P5Q/CMK-3 at 0.1 C, coulombic efficiency of P5Q/CMK-3 (1:2).

In order to further evaluate the charge transfer and electrolyte diffusion of P5Q and P5Q/CMK-3 (1:2) in SIBs, electrochemical impedance tests were carried out in the frequency range of 10⁻² - 10⁵ Hz at 2.60 V. The profiles were shown in Figures 9a and 9b. The semicircle represented the charge-transfer resistances at the electrode surface and the double-layer capacitance between the electrolyte and the cathode.^{51, 52} After 10 cycles, the impedance increased with the number of cycles, which may be attributed to the dissolution of the active material,⁵³ however, the impedance of the composite rised slowly due to that the process of CMK-3 hinders the dissolution. The final impedance of composites after encapsulation was smaller than that of the unfilled one, demonstrating that CMK-3/SWCNTs is beneficial to improve the conductivity of the nanocomposites.

Figure 9. The EIS test of (a) P5Q and (b) P5Q/CMK-3 (1:2). (c) Equivalent circuit.

Table 1. Summary of main parameters and electrochemical performance of P5Q cathode materials.

Electrode composition	Weight ratio	Electrolyte	Reversible capacity [mAh g ⁻¹] / Current rate	Capacity retention [%] (Cycle number / Current rate)	Reversible capacity [mAh g ⁻¹] / Current rate
P5Q:SWCNTs:PVDF	30:60:10	1 M NaClO ₄ in EC/DMC/FEC	431/0.1 C	~27% (100/0.1 C)	148/1 C
P5Q:CMK-3:SWCNTs:PVDF	30:30:30:10	1 M NaClO ₄ in EC/DMC/FEC	414/0.1 C	~32% (100/0.1 C)	150/1 C
P5Q:CMK-3:SWCNTs:PVDF	20:40:30:10	1 M NaClO ₄ in EC/DMC/FEC	418/0.1 C	~69% (300/0.1 C)	201/1 C

CONCLUSIONS

In summary, P5Q has been successfully prepared and employed as the cathode material (after encapsulation with CMK-3 and SWCNTs) in SIBs due to its unique carbonyl structure and high theoretical specific capacity (up to 446 mAh g⁻¹). The as-fabricated SIBs achieved an initial capacity of 418 mAh g⁻¹ and maintained 290 mAh g⁻¹ after 300 cycles at 0.1 C. Our results clearly suggest that the family of Pillar[n]quinones should be promising cathode materials in SIBs for future practical applications.

ASSOCIATED CONTENT

Supporting Information.

The synthesis of P5Q, additional experimental data and the information of P5Q molecular structure. The Supporting Information is available free of charge on the ACS Publications website.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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