Graphene oxide-wrapped dipotassium terephthalate hollow microrods for enhanced potassium storage†

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Unique graphene oxide-wrapped organic dipotassium terephthalate hollow microrods were synthesised using an abundant and renewable organic resource. They exhibit enhanced potassium storage compared to bulk K₂TP, which can be ascribed to the fast K⁺ ion transfer kinetics, high electronic conductivity and short diffusion distance.

In order to realize the sustainable development of modern society, searching for efficient energy storage systems with characteristics of high capacity, long cycling life, low cost and reliable security has become an urgent issue for human beings.1,2 Lithium-ion batteries (LIBs) currently dominate the intelligent electronic device market and grid storage due to their unique energy storage properties.3–5 However, their electrochemical performance is subject to intrinsic barriers for accommodation of K⁺ ions without size concerns.6,23 KIBs exhibit attractive advantages due not only to the high abundance of potassium, but also due to the similar redox potential of K+/K (−2.94 V vs. SHE) to the Li+/Li couple (−3.04 V vs. SHE), which is around 200 mV lower than that of the Na+/Na couple (−2.71 V vs. SHE).8–10 This means that the voltage and energy density in KIBs can be higher than those in NIBs in the case of the same electrode systems. Furthermore, K⁺ has much weaker Lewis acidity than Li⁺ and Na⁺, which endows a smaller Stoke’s radius of solvated ions in liquid electrolyte, ultimately resulting in a larger transport number and higher mobility of K⁺ ions in electrolyte and at the electrode/electrolyte interface.6,11 Nevertheless, K is much more active than Li and Na, which could cause more serious accidents once K dendrites come into being while the batteries are running. Besides, the larger ionic radius of K⁺ will lead to larger polarization and volume expansion. Thus, the key to the development of KIBs is seeking suitable electrode materials to accommodate the large K⁺ ions, with high safety and a stable framework structure.

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In particular, it is worth noting that carbon anodes exhibit an average discharge plateau of 0.3 V vs. K'/K, at which the risk of dendrite formation will increase, bringing about severe safety hazards.14 Hence, there is an urgent demand to seek anodes with stable cyclability and high safety for KIBs.

Recently, organic compounds have gradually achieved immense priority over inorganic materials for their manageable structures, suitable operating voltage and abundance as well as renewability.15–22 In particular, compared with inorganic solids, which are constructed with covalent/ionic bonds, the crystal state of organic materials is mainly governed by van der Waals forces, which can provide more active sites as well as a lower energy barrier for accommodation of K⁺ ions without size concerns.5,23 However, their electrochemical performance is subject to intrinsic poor conductivity and solubility in organic electrolyte.10 On one hand, nanotechnology and conductive coatings are considered the most effective methods to enhance their conductivity. On the other hand, the solubility can be significantly retarded by turning the organic materials into their corresponding organic salts, coating with a non-active passivation layer and exploring suitable electrolytes.6,11,24–27 Dipotassium terephthalate (K₂TP) is a typical organic material with two conjugated carboxylate groups, which become stable with a two K⁺ insertion/extraction. Moreover, K₂TP possesses a suitable and constant operating potential of about −0.6 V vs. K'/K when tested as an anode for KIBs, which
can avoid the formation of K dendrites and the corresponding safety concerns.\textsuperscript{6,23,27} Recently, Li’s group revealed that K\textsubscript{2}TP with a theoretical capacity of 221 mA h g\textsuperscript{-1} and two conjugated carboxylate groups can be regarded as a potential anode for KIBs, in which it delivers a considerable capacity of 181 mA h g\textsuperscript{-1} at a rate of 0.2C.\textsuperscript{6} However, owing to its inherent poor electronic conductivity, the rate capacity and cell cyclability still need further improvement.

Herein, we synthesized graphene oxide-wrapped organic dipotassium terephthalate (K\textsubscript{2}TP@GO) hollow microrods with highly stable cycling, good rate capability, and high safety. Firstly, the electronic conductivity is greatly enhanced by graphene oxide modification. Secondly, the graphene oxide surface coating can serve as a buffer layer to probably not just alleviate the active materials’ volume expansion, but also restrain the dissolution during the discharge/charge processes.\textsuperscript{10} Thirdly, the unique hollow structure promotes K\textsuperscript{+} transportation and provides enough inner space to accommodate volume expansion during the discharge/charge processes.\textsuperscript{5–20} In Fig. 1B, and are well consistent with the standard card (JCPDS No. 00-052-2142). Owing to the integrative action of the electrostatic attraction/chemical bond between the aromatic nucleus and metal cations as well as the stable benzene skeleton with large \( \pi \) conjugation,\textsuperscript{10,28–30} K\textsubscript{2}TP exhibits good thermal stability, possessing a high thermal decomposition temperature of over 550 °C which is much higher than that of terephthalic acid (PTA) (300 °C) (Fig. S1, ESI†). Fourier-transform infrared (FT-IR) spectra are shown in Fig. 1C and the broad peak between 2400 and 3000 cm\textsuperscript{-1} is assigned to \( \nu_n(COO–) \) and \( \nu_{as}(COO–) \) vibrations in PTA. The typical absorption peaks located at 1572 and 1377 cm\textsuperscript{-1} are ascribed to the formation of K\textsubscript{2}TP.\textsuperscript{24} The morphology features of the synthesized hollow K\textsubscript{2}TP@GO microrods were observed using a scanning electron microscope (SEM) (Fig. 1D and E). Hollow K\textsubscript{2}TP@GO microrods exhibit micro sizes in the range of 5–20 μm and single hollow K\textsubscript{2}TP microrods are wrapped together by graphene oxide. The EDS element mapping results demonstrate the uniform distribution of K, C and O elements in K\textsubscript{2}TP@GO (Fig. 1F). In addition, the morphology images of bulk-shaped K\textsubscript{2}TP are displayed in Fig. S2 (ESI†).

Fig. 2A displays the cyclic voltammetry (CV) measurements of the K\textsubscript{2}TP@GO electrode, which displays redox peaks around 0.52/0.69 V (vs. K\textsuperscript{+}/K\textsuperscript{0}), corresponding to the insertion/extraction of two K-ions.\textsuperscript{12,13} Except for the first scan, reversible and stable redox behaviour is observed, suggesting the reversibility of the K\textsubscript{2}TP@GO anode. The lower reduction peak in the initial cycle can be ascribed to the formation of SEI.\textsuperscript{11} For comparison, the CV curves of bulk K\textsubscript{2}TP are depicted in Fig. S4 (ESI†). The selected discharge/charge galvanostatic cycling profiles of K\textsubscript{2}TP@GO at a current density of 200 mA g\textsuperscript{-1} are presented in Fig. 2B. The charge and discharge voltages are located at around 0.68 and 0.52 V, with a small polarization of about 0.16 V. The polarization scarcely increases until the 100th cycle. The slope below 0.3 V present in the initial discharge process, which is in accordance with the CV curves, results from the formation of SEI during the K\textsuperscript{+} insertion process.\textsuperscript{6,11} Apparently, the bulk K\textsubscript{2}TP electrode has much larger polarization, as shown in Fig. S5 (ESI†).

Fig. 2B and C illustrate the cycling performance and corresponding coulombic efficiency of K\textsubscript{2}TP@GO and bulk K\textsubscript{2}TP. As for K\textsubscript{2}TP@GO, a reversible capacity of around 212 mA h g\textsuperscript{-1} is delivered at 200 mA g\textsuperscript{-1}, with a high capacity retention of 92.3% after 100 cycles. Remarkably, it achieves a coulombic efficiency as high as 99% except for in the first several cycles. The irreversible capacity and low coulombic efficiency of the first cycle results from the formation of SEI during the discharge process.\textsuperscript{6,11,24,31} For bulk K\textsubscript{2}TP, although it delivers capacities of 483.2 mA h g\textsuperscript{-1} and 176.6 mA h g\textsuperscript{-1} in the first two cycles at the same current density, it drops dramatically and a capacity of only 28 mA h g\textsuperscript{-1} is obtained after 100 cycles.

The rate capability of K\textsubscript{2}TP@GO was also investigated at current densities varying from 50 to 1000 mA g\textsuperscript{-1}. As shown in Fig. 2E, it is worth noting that the K\textsubscript{2}TP@GO electrode exhibits discharge capacities of 296, 252, 200, 150 and 114 mA h g\textsuperscript{-1} at current densities of 50, 100, 200, 500, and 1000 mA g\textsuperscript{-1}, respectively. When the current density is set back to 50 mA g\textsuperscript{-1}, the K\textsubscript{2}TP@GO...
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Electrochemical performances of K₂TP@GO and K₂TP. (A) CV curves of K₂TP@GO in the initial four cycles were tested at a scan rate of 0.1 mV s⁻¹ ranging from 0.1 to 2.0 V. Cycle performance (B) and the corresponding coulombic efficiency (C) of K₂TP@GO and bulk K₂TP electrodes at a current density of 200 mA g⁻¹. (D) Charge and discharge curves of K₂TP@GO at a current density of 200 mA g⁻¹. (E) Rate performance of K₂TP@GO at different rates. Long cycling measurements of K₂TP@GO tested at (F) 500 mA g⁻¹ and 1000 mA g⁻¹. (H) Schematic illustration of K₂TP@GO with fast K⁺ and electronic transportation and unique hollow structure with a graphene oxide wrapped layer.

The superior rate capability of K₂TP@GO is attributed to the high transport rate of K⁺ and improved electronic conductivity (Fig. S10–12, ESI†). In summary, the graphene oxide-wrapped layer and hollow structure can effectively enhance the electronic conductivity, accelerate K⁺ transfer kinetics, improve structure stability and decrease the volume expansion, leading to the superior K⁺ storage properties of K₂TP@GO (Table S1, ESI†).

In order to elucidate the potassium storage mechanism of K₂TP@GO, we performed electrochemical in situ XRD measurements (Fig. 3A and Fig. S13, ESI†). Two diffraction peaks located at ~21.9° and ~27.3° can be clearly observed, corresponding to the (102) and (−112) planes of K₂TP, respectively. Obviously, the two diffraction peaks indicate the same evolution of crystal structure during cycling. Upon the initial discharge process, the peaks weakened and gradually disappeared, indicating the transformation from a crystalline to an amorphous state (K₂TP → K₄TP)24. Nevertheless, when charged to 2.0 V, the peaks
reappeared during the depotassiation process (K₂TP $\rightarrow$ K₄TP). Similar behaviour is also observed in the following cycles. For the other three peaks, the changes (enhancement and broadening) during the first two cycles may be attributed to the volume expansion/contraction of the electrode, and no significant changes occur in subsequent cycles. The intensity of the volume expansion/contraction of the electrode, and no broadening) during the first two cycles may be attributed to the potassium storage mechanism of K₂TP@GO hollow microrods [28, 29], displaying a reversible conversion between the K₂TP phase and the K₄TP phase during K⁺ insertion/extraction processes.

In conclusion, we synthesized graphene oxide-wrapped hollow potassium terephthalate microrods as highly efficient anodes in KIBs. K₂TP@GO hollow microrods display a high reversible capacity of 212 mA h g⁻¹ at 200 mA g⁻¹, compared with bulk K₂TP. More impressively, a stable capacity of 160 mA h g⁻¹ can be maintained at a high current density of 500 mA g⁻¹ after 400 cycles. The superior K⁺ storage properties are ascribed to fast K⁺ transfer kinetics, high electronic conductivity and a robust hollow structure. In addition, the potassium storage mechanism of K₂TP@GO hollow microrods was revealed. During the potassiation process, the crystalline phase of K₂TP gradually transformed into amorphous K₄TP. This work investigates the rational design of K₂TP hollow microrods with enhanced K⁺ storage performance and may stimulate further study of organic materials in KIBs.

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Conflicts of interest

There are no conflicts to declare.

Notes and references


