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Organic Potassium Terephthalate ($\text{K}_2\text{C}_8\text{H}_4\text{O}_4$) with Stable Lattice Structure Exhibits Excellent Cyclic and Rate Capability in Li-ion Batteries

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ABSTRACT

Terephthalate ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) moiety with stable oxidized and reduced states is widely employed as the organic anode in batteries. However, along with the dissolution problem, the representative lithium terephthalate (Li_2TP) exhibited unsatisfactory cyclic and rate capability. Herein, based on the calculated and experimental results, we demonstrated that potassium terephthalate (K_2TP) possesses superior cyclic and rate capability in Li-ion batteries. On one hand, due to the larger radius of K^+ ion, K_2TP exhibits more stable lattice architecture than Li_2TP for the better size matching between cations and anions; On the other hand, K^+ ion in K_2TP could remain electrochemical inertness even its standard redox potential (-2.931 V) is higher than Li^+ ion (-3.040 V). Meanwhile, the $\text{K}-\text{O}$ bond in K_2TP is calculated to be more ionic while the $\text{Li}-\text{O}$ bond in Li_2TP has more covalent character. The ionic $\text{K}-\text{O}$ bond of K_2TP could further enhance its dissolution resistance against non-polar electrolyte. Indeed, after its electronic conductivity and particle dispersity were improved by mixing with graphene, the modified K_2TP anode could exhibit very stable capacity of $\sim 122\text{ mAh g}^{-1}$ at 8 C for 500 cycles, which is comparable or even superior to the state-of-the-art Li-ion batteries currently reported for small organic molecules.

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1. Introduction

Organic electroactive compounds are attracting more and more attentions as the promising electrode materials for the next-generation, large-scale energy storage systems (such as Li-ion or Na-ion batteries etc.) [1–3]. Compared to the conventional inorganic counterparts composited by expensive transition metals [4,5], the naturally abundant organic electrode materials with

structural diversity and unlimited production are more easily accessible and recyclable, well enough to meet the urgent need for low cost and sustainability [6,7]. At present, various kinds of organic electrode materials have been exploited, such as radical compounds, organosulfur and carbonyl compounds etc. [8,9]. However, the universally poor electronic conductivity of organic electrode materials inherently limits the full exploitation of their electrochemically-active sites, consequently leading to the lower specific capacity than theoretical prediction. Meanwhile, the gradual dissolution of organic electrode materials into liquid electrolyte seems to be inevitable and subsequently results in continuous consumption of active materials during long-term cycling [10]. In fact, the above disadvantages can be circumvented in some way. For instance, the poor electronic conductivity can be effectively solved by nano-sizing the organic electrode materials or mixing with conductive additives [11–13]; Whereas the solubility

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can be significantly suppressed through turning the organic electrode materials into the related organic-metal salts or conjugated polymers [14,15].

On the other hand, few attentions are paid to the electrochemical stability of organic electrode materials. Basically, the local electric fields within the boundary region of electrode can reach the value as high as 10^7 V cm^{-1} [16], which positively are the main driving force to reversibly convert their electronic properties between reduced and oxidized states; Whereas in the negative aspect, the electric fields are also strong enough to alter their reactivity and then cause the unexpected side reaction, particularly some extremely-active compounds like radical intermediate(s) are usually generated [17]. Therefore, it is reasonably required that not only should organic electrode materials possess stable oxidized and reduced states, but also their correspondingly-formed intermediate(s) should be electrochemically stable. Otherwise the organic electrode materials will be consumed gradually for the critical issue of chemical decomposition [18].

Organic terephthalate ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) motif was initially exploited by M. Armand et al. as the anode in Li-ion batteries, where it is capable of accepting or losing two electrons based on its stable oxidized state [terephthalate motif] or reduced state [(cyclohexa-2,5-diene-1,4-diylidene)dimethanebis(olate) motif] [2]. Additionally, it should be aware that single-electron transfer starts in the initial stage and leads to the generation of radical intermediate, as shown in Scheme 1. Fortunately, due to the critical conjugation with benzene skeleton, the radical compound is quite stable in isolated state and can be detected by electron paramagnetic resonance (EPR) [19]. However, along with the solubility issue and poor electronic conductivity, the currently reported terephthalate salts of lithium terephthalate ($\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$, Li_2TP) and sodium terephthalate ($\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$, Na_2TP) displayed unsatisfactory cyclic and rate capability in Li-ion and Na-ion batteries, respectively [20–23]. Basically, the lattice structures of Li_2TP and Na_2TP are constructed by alternating layers of flat aromatic rings and metal cations. Apparently, the dominant contribution to their lattice stability is the electrostatic attraction/chemical bond between organic anions and metal cations [24,25]. Although the aromatic-aromatic interaction among the alternating terephthalate anions was reported to make certain contribution to the lattice packing as well as crystal stability, the electrostatic repulsion among these negatively-charged motifs could be rapidly increased and become dominant once metal cations are in vacancy [26].

Consequently, we hypothesize the unfavorable solubility and poor performance of Li_2TP and Na_2TP are both ascribed to their unstable lattice structures. On one hand, the observed dissolution indicates that the solvation of Li^+/Na^+ ions or terephthalate anions into the related liquid electrolyte may be more energetically favorable than that in solid [27]; On the other hand, the imbedded “dead” Li^+/Na^+ ions within the lattice structure are not totally inactive, especially under high rate conditions, and then their

electrochemical participation would cause further structure decomposition [28]. Previously, J. A. Kaduk systematically investigated several crystal structures of terephthalate salts [26]. And his calculations further demonstrated very crowded anion packing in the crystal structures of Li_2TP and Na_2TP due to the small radius of Li^+/Na^+ ions (0.76/1.02 Å) as well as short metal-oxygen bonds ($\sim 1.96/2.43$ Å); Whereas in potassium terephthalate ($\text{K}_2\text{C}_8\text{H}_4\text{O}_4$, K_2TP) crystal, K^+ ion has a larger radius of 1.38 Å and displays better matching size with terephthalate anion, which results in much lower van der Waals repulsion during energy minimization, and thus leads to a more stable lattice structure. At the same time, our recent work unveiled that K^+ ion is not easily reducible even its standard redox potential (-2.931 V) is higher than Li^+ ion (-3.040 V) [29]. Inspired by these results, we inferred that K_2TP should possess better cyclic and rate capability in Li-ion batteries for its more stable and spacious lattice structure, the latter of which might be more advantageous to fast insertion/deinsertion process of massive quantities of Li^+ ions [28]. Herein, we report that the fabricated Li-ion half cell based on K_2TP indeed displays better cyclic and rate capability than Li_2TP under the same conditions. More impressively, K_2TP anode could achieve very stable capacity of $\sim 122 \text{ mAh g}^{-1}$ under the high current rate of 8 C for 500 cycles when its electronic conductivity is technically improved.

2. Experimental

2.1. Materials preparation

Potassium terephthalate ($\text{K}_2\text{C}_8\text{H}_4\text{O}_4$, K_2TP) was simply synthesized by using stoichiometric amount of terephthalic acid (TPA) and KOH in deionized water, as previously reported [1]. The K_2TP /graphene composite was easily synthesized as following: Terephthalic acid and graphene (4 wt%) were firstly mixed in *N*-methyl-2-pyrrolidone (NMP) solution and then the mixture was sonicated for 1 h. After adding equivalent KOH into the mixture, the reaction proceeded under refluxing and stirring overnight. Back to room temperature, the resulting products were centrifuged, washed with ethanol and then dried at 150°C overnight. The theoretical specific capacity for K_2TP is calculated to be 220 mAh g^{-1} and 1 C refers to two-electron insertion into K_2TP in one hour.

2.2. Materials characterization

Thermogravimetric analysis was performed by using Q500 analyzer in N_2 atmosphere at the heating rate of $10^\circ\text{C min}^{-1}$ from 50 to 800°C . X-ray diffraction (XRD) measurement was carried out by using Cu $\text{K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$, X'Pert Pro MPD) with the scanning rate of $0.06^\circ \text{ s}^{-1}$ in the 2θ range of $5\text{--}60^\circ$. The simulated XRD pattern was obtained from the experimental data of K_2TP crystal by using Mercury software, and the derived 2θ values (9.09° , 27.41° , 27.51° and 36.96°), corresponding to its lattice planes of (100), (-112), (300) and (400), matched well with the experimental data (9.0° , 27.4° , 27.5° and 36.9°). Fourier transform infrared spectrometer (FT-IR, Shimadzu, IR Prestige-21) test was operated within the wavenumber range of $400\text{--}4000 \text{ cm}^{-1}$, and the related pellets were prepared by thoroughly mixing 1 wt% of the as-prepared sample with spectroscopic-grade KBr in a glove box with 99.999% Ar atmosphere. The morphology image was collected by field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N). ^1H NMR spectra were recorded on AC Bruker spectrometer (400 MHz) at room temperature by using D_2O as the solvent, and the chemical shifts were expressed in parts per million (ppm) relative to the residual H_2O .

Scheme 1. Detailed redox mechanism for organic terephthalate ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) motif.

2.3. Quantum calculations

Isolated molecules were relaxed without constraints using Gaussian 09 package [30] at the level of density functional theory (DFT). And they were optimized by the M06L hybrid functional [31] with the 6-31G(d) basis set. The solvent effect was with self-consistent reactions field (SCRF) based on the polarizable continuum model (PCM), where the dielectric constant (ϵ) was set as 33.6 from the experimental results in literature [32]. The functional of M06 [33] was applied in the single point calculations to compute molecular orbital information; and 6-311 + G* basis set was applied on all atoms.

Calculations of crystal structures were carried out with the Vienna *ab initio* simulations package (VASP), utilizing the projector augmented wave (PAW) method in conjunction with the generalized gradient approximation (GGA). The PAW cutoff radii were 0.582, 0.794, 0.804, 1.085, and 1.217 Å for H, C, O, Li, and K, respectively. Planewaves with cutoff energy at 520 eV were used as the basis set. MonkhorstPack $2 \times 6 \times 2$ k-point grid was used to sample the Brillouin zone. All possible initial structures for $\text{Li}_2\text{TP-Li}_2$ and $\text{K}_2\text{TP-Li}_2$ were achieved by adding four additional Li ions and four electrons into one unit cell of the optimized Li_2TP and K_2TP cells, respectively (note that each unit cell contains two molecules). Under the condition of keeping the symmetry of the system, the four extra Li ions were put as randomly as possible.

2.4. Cell assembling and electrochemical tests

Electrochemical measurements were carried out by using two-electrode half cells. The working electrodes were prepared by casting the slurry onto a clean copper foil, where the slurry contained the as-prepared active material (60 wt%), acetylene carbon black (30 wt%) and poly(vinylidene fluoride) binder (PVDF, 10 wt%). The counter electrode was lithium foil. The electrolyte was 1 M LiPF_6 in the mixture solvents of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio of 1:1. The separator was polypropylene (PP) membrane (Celgard 2400).

These cells were assembled in Ar-filled glove box with high purity of 99.999%. The galvanostatic cycling test was carried on a LAND facility (CT2001A, LAND electronic Co.) during the voltage window of 0.5–2.5 V. Cyclic voltammograms (CV) were tested on a CHI instrument electrochemical workstation (CHI 660C). Electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical workstation (CHI 660C), and the amplitude of the alternating-current (AC) signal was 5 mV over the frequency range of 10^{-1} – 10^5 Hz.

2.5. Inductively coupled plasma tests:

Inductively coupled plasma (ICP) emission spectrometry (Horiba JY Ultima 2) was carried out to detect the metal cations of K and Li. Both the fresh and cycled electrodes were dissolved in deionized water by sonication. Before ICP test, the cycled electrode was immersed in EC and DMC for 48 h to remove most LiPF_6 salt. Standard solutions were prepared to obtain a standard curve of peak intensity vs. ion concentration (relationship between peak intensity and the concentration of Li or K element). The concentration of Li or K element in the fresh and cycled electrodes was obtained by comparing the peak intensity of the fresh and cycled electrodes to the standard peak intensity in the standard curve. The fresh electrode contained the concentrations of 0 and 81.99 mg L^{-1} for Li and K elements, respectively; While the cycled electrode still contained K element concentration of 60.34 mg L^{-1} , as well as Li element of 5.55 mg L^{-1} . The latter Li element was mainly from the residual LiPF_6 salt, but the K-Li exchange in the LiPF_6 -based electrolyte cannot totally be ruled out during cycling.

3. Results and discussion

3.1. Synthesis and characterization of K_2TP

K_2TP was conveniently synthesized through an environmental-friendly wet chemistry method [2]. The infrared spectrum of the synthesized K_2TP was shown in Fig. S1a, where the bands located

Fig. 1. Spatial distributions of HOMO and LUMO/SOMO energy levels calculated for terephthalate anion ($\text{C}_8\text{H}_4\text{O}_4^{2-}$), its reduced state ($\text{C}_8\text{H}_4\text{O}_4^{4-}$) and the formed radical intermediate ($\text{C}_8\text{H}_4\text{O}_4^{3-}$), respectively.

at 1575 and 1382 cm^{-1} were assigned to $\nu_s(\text{COO}^-)$ and $\nu_{as}(\text{COO}^-)$ vibrations and simultaneously the broaden peaks in the range of 2500 to 3000 cm^{-1} belonging to the stretching vibration of O–H bond in terephthalic acid (TPA) disappeared in the spectrum of K_2TP . In its X-ray diffraction (XRD) pattern (Fig. S1b), the selected characteristic peaks ($2\theta = 9.0, 27.4, 27.5$ and 36.9°) of K_2TP were observed. Compared with the simulated XRD pattern derived from the experimental data of K_2TP crystal, these typical peaks could be well correlated to its lattice planes of (100), (–112), (300) and (400), respectively. The purity of K_2TP was also confirmed by ^1H NMR spectrum (Fig. S1c), where only the H signal from benzene ring ($\delta = 7.78$ ppm) was detected and no H signal from residual COOH group was detected, indicating the complete conversion of TPA. The morphology of the freshly synthesized K_2TP was observed by scanning electron microscope (SEM) and its powders exhibited distinctive thin-slice shape with micro size range of 5–20 μm (Fig. S1d). Meanwhile, K_2TP powders showed excellent thermal stability by its decomposition temperature above 550 $^\circ\text{C}$ in thermogravimetric analysis (5 wt% loss), as depicted in Fig. S2.

3.2. Quantum calculations

At first, the detailed electronic structures of terephthalate anion ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) as well as the related radical intermediate ($\text{C}_8\text{H}_4\text{O}_4^{3-}$) and its reduced state ($\text{C}_8\text{H}_4\text{O}_4^{4-}$) were calculated by quantum chemistry. As shown in Fig. 1, the capability of accepting electrons brings in the expected structure change of terephthalate anion ($\text{C}_8\text{H}_4\text{O}_4^{2-}$). Before the reduction starts, the C–C bonds in benzene ring of $\text{C}_8\text{H}_4\text{O}_4^{2-}$ moiety are almost equally distributed (*cal.* 1.40 Å in C2–C3 vs. 1.39 Å in C3–C4). As the reduction proceeds, the bond length in C2–C3 is gradually elongated from 1.43 Å of $\text{C}_8\text{H}_4\text{O}_4^{3-}$ radical to 1.47 Å of $\text{C}_8\text{H}_4\text{O}_4^{4-}$ moiety; Whereas the bond length in C3–C4 is slowly shortened from 1.39 Å ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) to 1.37 Å ($\text{C}_8\text{H}_4\text{O}_4^{4-}$). This is probably caused by the breaking of aromaticity in the reduced state ($\text{C}_8\text{H}_4\text{O}_4^{4-}$) and the formation of double bond (C=C) at C3–C4 position. Meanwhile, the deep HOMO (highest

occupied molecular orbital) energy level (*cal.* –6.44 eV) of terephthalate anion ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) indicates that it is difficult to lose electrons (be oxidized) even it is negatively charged; Whereas the high HOMO level (*cal.* –1.17 eV) of the reduced $\text{C}_8\text{H}_4\text{O}_4^{4-}$ moiety indicates that it has strong tendency to lose electrons. These results unveil that terephthalate anion can only act as the organic anode after it is charged.

On the other hand, the injected electrons are residing on the LUMO (lowest unoccupied molecular orbital) energy level of organic moiety. The deeper LUMO level is, the better electron affinity it exhibits. However, the relatively high LUMO level (*cal.* –0.77 eV) of terephthalate moiety ($\text{C}_8\text{H}_4\text{O}_4^{2-}$) manifests that strong driving force is needed for injecting electrons. Interestingly, the SOMO (single occupied molecular orbital) level of the radical intermediate ($\text{C}_8\text{H}_4\text{O}_4^{3-}$) exhibits close value (*cal.* –0.62 eV) to the LUMO level of terephthalate moiety, suggesting that the sequent two-electron reduction process may not be easily distinguished due to their close electron affinity, which could explain why usually one cathodic peak is observed in cyclic voltammogram (CV) experiments. At the same time, the positive value for the LUMO (*cal.* 0.47 eV) of the reduced $\text{C}_8\text{H}_4\text{O}_4^{4-}$ moiety implies its unstable energy level, in accordance with the usual observation of two-electron acceptance for terephthalate moiety. More importantly, the spin density of the unpaired electron in the radical intermediate ($\text{C}_8\text{H}_4\text{O}_4^{3-}$) is symmetrically distributed throughout the whole molecule and then accounts for its chemical stability. In addition, the HOMO and LUMO spatial distributions and energy levels for isolated Li_2TP and K_2TP molecules were depicted in Fig. S3, where the metal cations make very little contribution to the HOMO and LUMO orbitals. Due to the electrostatic attraction, all the energy levels are stabilized and their calculated energy values are lowered as well.

Next, the optimized packing geometry of Li_2TP and K_2TP were performed. And the calculated results match well with the reported values [26]. See detailed cell parameters in Table S1. Both Li_2TP and K_2TP are monoclinic with the space group of $P2_1/c$

Fig. 2. Calculated lattice structures for (a) Li_2TP and (b) lithiated $\text{Li}_2\text{TP-Li}_2$; (c) K_2TP and (d) lithiated $\text{K}_2\text{TP-Li}_2$, respectively.

($Z=2$). In Li_2TP , each Li atom is tetrahedrally coordinated to four O atoms and the average Li–O bond in a LiO_4 coordination sphere is *cal.* 2.00 (experimental 1.96) Å. In K_2TP , K-ion coordination is trigonal prismatic and the average K–O bond in a KO_6 coordination sphere is *cal.* 2.79 (experimental 2.81) Å. The calculated dissociation energy for removing K^+ ion from K_2TP unit cell into vacuum costs 11.2 eV; While this value is 14.0 eV for removing Li^+ ion from Li_2TP .

In order to get more insights about their lithiated structures, 243 possible initial structures with inserted Li^+ ions for Li_2TP and K_2TP were respectively chosen for structural minimization. The optimized structures with the lowest energy for the resulting $\text{Li}_2\text{TP-Li}_2$ and $\text{K}_2\text{TP-Li}_2$ were depicted in Fig. 2. After lithiation, the resulting $\text{Li}_2\text{TP-Li}_2$ and $\text{K}_2\text{TP-Li}_2$ exhibit a slightly shrunken unit cell when compared to pristine Li_2TP (–6 vol%) and K_2TP (–3 vol%) (Table S1), which is attributed to the stronger electrostatic attraction upon introduction of electrons and Li^+ ions. In the optimized lithiated structures, there are two types of Li sites in the resulting $\text{Li}_2\text{TP-Li}_2$. One type is labelled as Li1-Li4 and the other is labelled as Li5-Li8 (Fig. 2a–b). And there is only one type of Li sites in the resulting $\text{K}_2\text{TP-Li}_2$ (labelled as Li1-Li4 in Fig. 2c,d). Compared to their pristine structures, these lithiated sites labelled as Li1-Li4 can be easily regarded as the inserted Li^+ ions. In lithiated $\text{K}_2\text{TP-Li}_2$ structure, removing any K^+ ion out of K1-K4 sites from $\text{K}_2\text{TP-Li}_2$ unit cell into vacuum still costs lower energy (11.9 eV) than removing any inserted Li^+ ion (12.3 eV) therein; Whereas removing any original Li^+ ion out of Li5-Li8 sites from $\text{Li}_2\text{TP-Li}_2$ unit cell into vacuum costs higher energy (14.5 eV) than that of the inserted Li1-Li4 sites (13.7 eV). The lower dissociation energy required for K^+ ion out of K_2TP or $\text{K}_2\text{TP-Li}_2$ unit cell indicates their more ionic structure.

As confirmed in Fig. 3, K^+ ion in K_2TP indeed exhibits apparently more positive charge than that of Li^+ ion in Li_2TP , indicating K–O bond has more ionic character while Li–O bond is more covalent. Simultaneously, our commonly-used electrolytes of ethylene carbonate (EC) and dimethyl carbonate (DMC) exhibit similar polarity as Li_2TP even they contain polar carbonate moiety.

Therefore, when considering the immersion of electrode materials within liquid electrolyte as well as the “like dissolves like” rule, which describes a solute dissolves well in a solvent if they share similar polarity [34], Li_2TP would dissolve better in less polar organic electrolyte than K_2TP . This conclusion is in accordance with our observation that LiPF_6 has a better solubility than KPF_6 in the same EC/DMC solvent.

3.3. Electrochemical performance of K_2TP

Fig. 4a displayed the typical CV curves of K_2TP for the initial three cycles. It was clear that there was one reduction peak around 0.71 V during the 1st cathodic scan and then it stabilized at ~ 0.85 V in the following 2nd and 3rd cycles, which was mainly attributed to the reducing process of terephthalate moiety and the insertion of Li^+ ions. Notably, the voltage difference between the first cathodic peak and the following ones was mainly caused by the formation of solid electrolyte interface and the decomposition of electrolyte [35]. Whereas during the anodic scan, the stable oxidization peak at ~ 1.05 V suggested the oxidizing process of the formed (cyclohexa-2,5-diene-1,4-diylidene)dimethanebis(olate) moiety and the extraction of Li^+ ions from K_2TP . No other clear cathodic peak was observed. The initial three discharge-charge curves of K_2TP was shown in Fig. 4b at the current rate of 0.1 C, where the similar discharge (reducing process) and charge (oxidizing process) platforms were observed. And K_2TP anode delivered an initial discharge/charge capacity of 313/126 mAh g^{-1} , respectively.

To evaluate the rate capability of K_2TP , the following rate performance of the half cells based on K_2TP and Li_2TP was carried out under the same conditions. As shown in Fig. 4c, under different current rates, the half cell based on K_2TP exhibited superior performance than Li_2TP . At low current rates of 0.3 and 0.6 C, the discharge capacities were 120 and 105 mAh g^{-1} for K_2TP , higher than 90 and 71 mAh g^{-1} of Li_2TP . Furthermore, at high current rates of 2, 4 and 8 C, these values (92, 82 and 72 mAh g^{-1}) were still better than Li_2TP (53, 33 and 25 mAh g^{-1}). Meanwhile, the cyclic performance of Li_2TP and K_2TP was also comparably studied at

Fig. 3. The electron density surface according to the electrostatic potential of (a) ethylene carbonate (EC); (b) dimethyl carbonate (DMC); (c) Li_2TP and (d) K_2TP , respectively.

Fig. 4. (a) The initial three CV curves of K₂TP; (b) The initial three charge-discharge curves of K₂TP; (c) The rate performance of K₂TP and Li₂TP, respectively; (d) The long-term profile of K₂TP and Li₂TP for 100 cycles.

Fig. 5. SEM images for (a) pristine K₂TP electrode; (b) The 1st fully discharged K₂TP and (c) the 1st fully recharged K₂TP, respectively; (d) Their related XRD patterns (background peaks were marked with star).

0.1 C for 100 cycles. As depicted in Fig. 4d, the decaying trend of Li₂TP was significantly observed, where it delivered the capacity of 82 mAh g⁻¹ at the 100th cycle. But for K₂TP, the capacity value at the 100th cycle was 121 mAh g⁻¹, still maintaining satisfactory retention of 77% regarding to the 2nd one (157 mAh g⁻¹) and 55% to the theoretical value (220 mAh g⁻¹). Remarkably, the above results were obtained from the micro-sized K₂TP and Li₂TP particles, and the incomplete capacity achievement of bulk K₂TP was ascribed to the low kinetic transportation of Li⁺ ions and electrons.

Afterwards, the SEM images for the 1st fully discharged and recharged K₂TP anode were depicted in Fig. 5. And the SEM image of the recharged K₂TP after 20 cycles was shown in Fig. S4. Before the discharge started, the pristine K₂TP particles were easily recognized by its bulk size (Fig. 5a). After the 1st fully discharged and recharged, no significant morphology changes were observed (Fig. 5b and c). In contrast, Li₂TP showed an obvious morphology change when immersing it into EC/DMC solvents [27]. Subsequently, their related XRD patterns were simultaneously collected in Fig. 5d. After the 1st full discharge, we noticed that one characteristic peak ($2\theta = 9.0^\circ$) of K₂TP disappeared while the intensity of the other typical peak at 37.7° increased. But when K₂TP anode was fully recharged, its XRD pattern was recovered almost as the same of the pristine one. To further confirm the crystal stability of K₂TP, inductively coupled plasma (ICP) test was carried out to inspect K-Li exchange in the LiPF₆-based electrolyte [11]. And the data unveiled that K concentration in the cycled electrode did not significantly drop down when compared to the fresh one (see details in experimental section). From the above results, it can be concluded that the lattice structure of K₂TP could remain stable and intact during lithiation/delithiation process.

3.4. Electrochemical performance of K₂TP/graphene composite

Although the architectural stability of K₂TP was clearly demonstrated above, the reversible capacity achieved for the micro-sized K₂TP obviously fell behind its theoretical value (220 mAh g⁻¹), even at low current rate of 0.1 C. Apparently, the large particle size and poor electronic conductivity of K₂TP are significantly disadvantageous for the kinetic transportation of carriers, particularly for electrons [36]. Therefore, the following simple modification was carried out by making the *in-situ* formed K₂TP onto graphene matrix, since graphene additive is not only profitable for electron transportation, but also exhibits excellent particle dispersion for organic compounds due to the intermolecular π - π interaction [18]. After introducing graphene additive (4 wt% to K₂TP), the *in-situ* formed K₂TP particles were well dispersed with size range of only hundreds nanometer and also homogeneously embedded onto graphene matrix (Fig. S5a and b), which can be confirmed by the reduced XRD intensity as well as the broader diffraction peaks of the resulting composite (Fig. S5c). And the initial three discharge-charge curves of the composite still exhibited the similar behaviors like the case without graphene (Fig. S5d).

As expected, the resulting K₂TP/graphene composite displayed the enhanced reversible capacity of 215 mAh g⁻¹ at 0.1 C, due to the improved conductivity. Meantime, the capacity contribution from the added graphene in our case was calculated to be less than 10 mAh g⁻¹ (Fig. S6). More importantly, along with the better particle dispersity as well as the architectural stability of K₂TP, the resulting K₂TP/graphene composite displayed impressive rate capacity and cyclic stability. As shown in Fig. 6, under the current rates of 2 and 4 C, the capacities remained the values of 137 and 131 mAh g⁻¹, respectively. Particularly, very stable capacity of ~ 122 mAh g⁻¹ under the high current rate of 8 C was maintained for 500 cycles, which is comparable or even superior to the state-

Fig. 6. (a) The performance of the K₂TP/graphene composite at different current rates of 0.1, 0.3, 0.6, 2, 4 and 8 C, respectively; (b) The selected profile at 8 C for 500 cycles.

of-the-art Li-ion batteries based on small organic molecules (Table S2).

To further confirm the conductive functionality of graphene, the CV and electrochemical impedance spectroscopy (EIS) experiments were performed. As shown in Fig. S7, the apparent Li-ion diffusion coefficient of the K₂TP/graphene composite deduced from the CV data was larger than pristine K₂TP; Whereas the charge transfer resistance value (R_{ct}) of the composite derived from the EIS measurements was also much smaller than pristine K₂TP. Both results are in good agreement with our expectation.

4. Conclusions

In summary, owing to the stable lattice architecture, potassium terephthalate as the organic anode could exhibit outstanding cyclic and rate capability in Li-ion batteries. After the electronic conductivity and particle dispersity were improved by introducing graphene as the matrix, the resulting potassium terephthalate/graphene composite could display very stable capacity of ~ 122 mAh g⁻¹ under the high current rate of 8 C for 500 cycles, without obvious capacity decay. This fundamental finding could be of great interest in other battery systems, and the related work is ongoing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.11.079>.

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