Insoluble polyanionic anthraquinones with two strong ionic O–K bonds as stable organic cathodes for pure organic K-ion batteries

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ABSTRACT A new organic cathode namely potassium 2,6-dihydroxyanthraquinone (AQ26OK, theoretical capacity (C_T) = 169 mA h g⁻¹) is synthesized and fully characterized for K-ion batteries. AQ26OK is called polyanionic organic cathode because it has a polyanionic organic skeleton (–2 valent) and two strong ionic K–O bonds. Consequently, the polyanionic AQ26OK is hardly soluble into most organic liquid electrolytes. In half cells (0.3–3.4 V vs. K⁺/K) using 1 mol L⁻¹ KPF₆ in dimethoxyethane, AQ26OK delivers a highly stable specific capacity of 201 mA h g⁻¹ @ 50 mA g⁻¹ over 450 cycles (4-month test) and realizes ~106 mA h g⁻¹ for 3200 cycles at 500 mA g⁻¹. Using the reduced state (K₄TP) of potassium terephthalate (K₂TP) as the organic anode, the resulting K₄TP || AQ26OK organic potassium-ion batteries can display a highly stable average discharge capacity of 135 mA h g⁻¹_{cathode} over 250 cycles at 100 mA g⁻¹ and ~47 mA h g⁻¹ for 1000 cycles at 500 mA g⁻¹ during the working voltage of 0.01–3.1 V. To the best of our knowledge, AQ26OK is among the best stable cathodes reported for K-ion batteries.

Keywords: potassium 2,6-dihydroxyanthraquinone, insoluble organic cathodes, polyanionic character, ultra-stability, organic K-ion batteries

INTRODUCTION

Potassium-ion (K-ion) batteries (PIBs) have gradually attracted intensive attention for low-cost and large-scale electrochemical energy storage based on the following two prominent advantages: very abundant K resource and similar electrochemical properties with Li-ion batteries

[1–6]. However, it is difficult to electrochemically store K⁺ ions due to their large radius (1.38 Å for K⁺ ion vs. 0.76 Å for Li⁺ ion). For example, during the repeated intercalation and deintercalation of K⁺ ions in a redox process, inorganic electrode materials face serious crystal-structure transformation (such as lattice expansion). Consequently, most inorganic electrode materials in PIBs exhibit poor rate performance and short cycle lifespan, particularly for inorganic cathodes [7–10]. Currently, it seems impossible to simultaneously fulfill the key parameters such as energy density, power density (rate performance) and long lifespan (cycle stability) for inorganic cathodes in PIBs. For instance, several prussian-blue-based inorganic cathodes can show high energy density above 300 W h kg⁻¹ [11,12], but their cycle lifespan is far from practical usage.

In recent years, the low-cost organic redox-active compounds as electrode materials have been proved to electrochemically and reversibly store large-radius K⁺ ions in PIBs [13,14]. The key feature for organic electrode materials is that they possess enough-large void space in organic solid/crystal state [15–20]. For example, most organic compounds are interacted by van der Waals forces and so the distance between two π - π molecule planes is usually as large as 3 Å. Consequently, organic electrode materials open the new horizon for their applications in PIBs. However, the neutral small-molecule organic materials, particularly for organic cathodes, are seriously soluble in organic liquid electrolytes for all kinds of non-aqueous batteries according to the “like dissolves

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like” principle [21]. As a result, the dissolution problem becomes the main obstacle for the practical usage of organic electrodes in PIBs, particularly for the battery cycle lifespan. Although the development of insoluble organic polymer electrodes is also an effective strategy, attention should be carefully paid to the synthetic routes and structural characterizations for insoluble organic polymer electrodes (such as purity and degree of polymerization).

Luckily, there are other ways out to prevent the dissolution problem for organic electrode materials. In our previous study, we initially proposed that polyanionic organic cathodes could be a very effective way to solve the dissolution problem for small-molecule organic electrodes. The typical character for polyanionic organic cathodes is that they possess multiple strong ionic O–M bonds ($M=Na$) within the large π aromatic skeleton. Notably, the parent aromatic skeleton is usually in the polyanionic-charge state. Although some organic salts with multiple ionic bonds are reported such as $K_2C_6O_6$ and $Na_2C_6O_6$ [22,23], their organic aromatic moieties are too small and thus cannot resist the corrosion of organic liquids. According to the “like dissolves like” principle, the multiple ionic O–M bonds will enhance the dissolution of polyanionic organic cathodes into aqueous solution, but advantageously prevent the dissolution into non-aqueous solution. Following this simple principle, we initially unveiled that 9,10-anthraquinone (AQ)-2,6-disulfonate ($Na_2AQ26DS$, theoretical capacity (C_T) = 130 mA h g^{-1}) with two ionic O–Na bonds could be one representative of the polyanionic organic cathodes. Indeed, $Na_2AQ26DS$ could exhibit excellent stability in Na-ion half cells, particularly in ether-based electrolytes [24]. For example, $Na_2AQ26DS$ could deliver an impressive long-cycle lifespan over 9 months at 50 mA g^{-1} , keeping a discharge capacity of 94 mA h g^{-1} @1200th cycle using $1\text{ mol L}^{-1}\text{ NaPF}_6$ in 1,2-dimethoxyethane (DME) [25]. Subsequently, we found that $Na_2AQ26DS$ could also deliver good cycle stability in K-ion half cells using $1\text{ mol L}^{-1}\text{ KPF}_6$ in DME [26]. Regrettably, the interesting and useful concept so-called polyanionic organic cathodes seems not be widely accepted. At the same time, the currently reported polyanionic organic cathodes for PIBs are very scarce. In particular, there are very limited cases of long-lifespan inorganic/organic cathodes reported for PIBs [16].

In this paper, we design and report a new polyanionic organic cathode for PIBs for the first time. This new polyanionic organic cathode, namely potassium 2,6-dihydroxyanthraquinone (AQ26OK, theoretical specific capacity (C_T) = 169 mA h g^{-1}), has two strong ionic O–K

bonds within the poorly soluble AQ skeleton. The molecule design is based on the following considerations: (i) the replacement from sodium sulfonate group ($-(SO_3)ONa$) of the previously reported $Na_2AQ26DS$ by potassium hydroxide group ($-OK$) can promote the theoretical specific capacity of AQ26OK; (ii) the ionic-bond replacement from $-ONa$ group by $-OK$ group can avoid the ion-exchange confusion when using K-ion-based electrolytes in PIBs; (iii) K–O bond is the much stronger ionic bond than Na–O bond and thus can still ensure the insolubility of AQ26OK in most organic liquid electrolytes.

Expectantly, AQ26OK is found hardly soluble in most organic liquid electrolytes, particularly in the ether-based electrolytes. Similar to the case of $Na_2AQ26DS$ in Na-ion cells, AQ26OK exhibits 2-electron redox mechanism in PIBs for bearing the key redox-active organic AQ core, thus delivering a high C_T of 169 mA h g^{-1} . Featuring its insolubility, AQ26OK can show the highly impressive cycling stability and long lifespan in PIBs. In half cells, AQ26OK delivers a highly stable specific capacity of 201 mA h g^{-1} at a low current density of 50 mA g^{-1} for 450 cycles using $1\text{ mol L}^{-1}\text{ KPF}_6$ in DME. And this test in half cells can last for as long as 4 months at least. Furthermore, we fabricate K-ion full cells by using the reduced state (K_4TP) of potassium terephthalate (K_2TP) as the organic anode [27]. Notably, there are currently very few successful examples of organic K-ion full cells [28]. Satisfactorily, the resulting $K_4TPIAQ26OK$ organic PIBs (OPIBs) display a highly stable average discharge capacity of $135\text{ mA h g}^{-1}_{\text{cathode}}$ for 250 cycles at a low current density of 100 mA g^{-1} and $\sim 47\text{ mA h g}^{-1}$ for 1000 cycles at a high current density of 500 mA g^{-1} . And no significant capacity decay is observed during the test of full cells. As far as we know, the cycle stability and long lifespan of AQ26OK is currently among the best results for K-ion half/full cells reported to date [16].

EXPERIMENTAL SECTION

General information

All reagents were commercially available and used without further purification. Ketjen black (KB) was from Lion Co., Ltd., and carbon nanotubes (CNTs) were from XFnano Co., Ltd. The morphology images for the electrode samples were collected by field-emission scanning electronic microscopy (SEM; Hitachi, S3400N). ^1H nuclear magnetic resonance (^1H NMR) spectrum was measured on a Bruker AV II 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectra were collected on a Bruker Alpha spectrometer. The electrochemical im-

pedance spectroscopy (EIS) was measured by a CHI instrument electrochemical workstation in the frequency range of 0.05–10⁵ Hz.

Synthesis of AQ26OK

The synthesis of AQ26OK was following a similar procedure recently reported by our group [29]. A mixture of 2,6-dihydroxyanthraquinone (AQ26OH) (480 mg, 2 mmol) and potassium *tert*-butoxide (*t*-BuOK) (560 mg, 5 mmol) in 40 mL anhydrous tetrahydrofuran (THF) was heated at 80°C under N₂ for one day. After cooling to room temperature, the reaction mixture was filtrated and washed with THF and ethanol to remove excess reactants and organic impurities. Finally, AQ26OK was obtained and dried at 120°C overnight. The product was a red crystal with a satisfactory yield of 94% (596 mg, 1.88 mmol).

AQ26OK electrodes

The AQ26OK electrodes were prepared as follows: (i) 60 mg of AQ26OK, 20 mg of KB and 10 mg of CNTs were added to petroleum ether, followed by wet milling for about 1 h; (ii) 10 mg of poly(vinylidene fluoride) (PVDF) as the binder in THF was mixed with AQ26OK and conductive carbons; (iii) the slurry was casted on Al foil, dried in a vacuum oven at 120°C for 24 h and finally punched into Al disk (diameter (*d*) = 12 mm). The neat loading mass of AQ26OK on Al electrode was in the range of 1.5–2.2 mg cm⁻².

K₄TP electrodes

The reduced state (K₄TP) of K₂TP was employed as the starting organic anode. The K₂TP electrodes were at first prepared as follows [28]: (i) 24 mg of Super P and 12 mg of CNTs were added into ethyl alcohol (200 mL) and 72 mg of K₂TP was dissolved in 10 mL of H₂O. (ii) After Super P and CNTs were ultrasonically treated in ethyl alcohol for 30 min, the solution of K₂TP was added into the ethanol mixture by back titration for about 15 min. (iii) After standing overnight, the composite of K₂TP@Super P and CNTs was filtered to remove the solvent and then dried in vacuum at 80°C for one day. (iv) The anode electrodes were prepared by casting the slurry onto a clean copper round disk (*d* = 12 mm), where the slurry contained K₂TP (60 wt%), carbon additive (Super P, 20 wt%; CNTs, 10 wt%) and PVDF (10 wt%). (v) The neat loading mass of K₂TP on Cu foil was ~2 mg cm⁻². The as-prepared electrodes were dried in a vacuum oven at 120°C for 8 h. After the construction of half cells, the K₂TP-based half cells were discharged to

0.2 V. And then K₄TP of the reduced state could be *in-situ* formed from K₂TP on Cu foil in half cells.

K-ion half cells

In half cells, the counter electrode was K foil; the electrolyte was 1 mol L⁻¹ potassium hexafluorophosphate (KPF₆, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) in DME and the separator is Whatman glass fiber. All cells were assembled in the Ar-filled glovebox. Cyclic voltammograms (CVs) were measured at a scan rate of 0.05 mV s⁻¹ between 0.5 and 3.0 V using a CHI instrument electrochemical workstation (CHI 660C). The galvanostatic charge–discharge test was performed on a Land test system (CT2001A, China). The AQ26OK cathode voltage cutoffs were appropriately set between 0.3 and 3.4 V (vs. K⁺/K). And the K₂TP anode voltage cutoffs were set at 0.2–2.0 V (vs. K⁺/K).

K-ion full cells

The preparation process was the same as that for half cells mentioned above. The electrolyte was 1 mol L⁻¹ KPF₆ in DME. In full cells, the cathode and anode in half cells were cycled twice to remove the unwanted side products, respectively. Afterwards, the K₂TP-based half cells could offer the reduced-state K₄TP as a starting anode, while the AQ26OK-based half cells could offer AQ26OK of oxidized state as a starting cathode. The loading mass ratio of K₄TP:AQ26OK was about 1.2:1 (N/P ratio). The voltage range was set to be 0.01–3.1 V for full cells after many optimizations.

RESULTS AND DISCUSSION

Synthesis and characterization

The organic synthesis of AQ26OK was quite similar to the Na-ion analogues mentioned above. As shown in Fig. 1, AQ26OK could be easily and feasibly synthesized from AQ26OH and potassium *t*-BuOK through an acid–base neutralization reaction, along with a high yield of 94% (see details in the EXPERIMENTAL SECTION). It should be emphasized that the very strong non-aqueous base of *t*-BuOK is very important for the complete neutralization reaction under the consideration of the weak

Figure 1 The synthetic route for AQ26OK.

acidic –OH group in AQ26OH, rather than the common base of KOH.

To prove the complete deprotonation of AQ26OH, the organic structure of AQ26OK was initially examined by ^1H NMR spectroscopy in the solvent of dimethyl sulphoxide ($\text{DMSO}-d_6$). As shown in Fig. 2a, there were only three obvious types of H signals from anthraquinone skeleton, and the integral intensity ratio for the three types of H signals was close to 1:1:1. For comparison, there was a distinct active H signal of –OH group (~ 11 ppm) in the NMR spectrum of AQ26OH (Fig. S1). The ^1H NMR data for AQ26OK were as follows: 7.63 (d, $J = 8.8$ Hz, 2H), 6.76 (d, $J = 2.0$ Hz, 2H), 6.34 (dd, $J_1 = 8.6$, $J_2 = 2.0$ Hz, 2H). Secondly, the structure of AQ26OK could be further verified by FT-IR spectrum. As shown in Fig. 2b, the strong characteristic peak located at $\sim 3301\text{ cm}^{-1}$ assigned to the stretching vibration of O–H bond in AQ26OH was no longer observed in AQ26OK. Additionally, the tiny absorption from the vibration of H_2O in AQ26OK could still be detected. Overall, the NMR and FT-IR results were the powerful and clear evidences for the successful synthesis of AQ26OK [30].

Subsequently, it was urgent to test the solubility of AQ26OK against different organic liquid solvents. Expectantly, AQ26OK was hardly soluble in most electrolytes. As shown in Fig. 3, the red-color AQ26OK solid was mostly soluble in H_2O due to its salt character. Meanwhile, AQ26OK was found slightly soluble in the carbonate-type electrolytes such as propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC). Encouragingly, AQ26OK exhibited neglectable or no solubility in ether-type electrolytes such as DME

and 1,3-dioxolane (DOL). On the other hand, similar to most anthraquinone-based electrode materials previously studied [31], AQ26OK should be able to deliver 2-electron redox mechanism in PIBs and thus can possess a high C_T of 169 mA h g^{-1} (Fig. 4).

Cyclic voltammogram

It was important to confirm the redox behavior of AQ26OK in PIBs. So CVs were tested for AQ26OK in K-ion half cells. The fabrication details for half cells were described in the EXPERIMENTAL SECTION. And the electrode composition in half cells was 60 wt% AQ26OK, 30 wt% carbon additives and 10 wt% binder, where the initially chosen carbon additives were KB and CNTs with the weight ratio of 2:1 and the binder was PVDF. Due to its insolubility in ether-type electrolytes, the electrolyte was 1 mol L^{-1} KPF₆ in DME. The multi-scanned CV curves during the voltage range of 0.5–3.0 V for AQ26OK are shown in Fig. 5a. Delightfully, AQ26OK could display highly reversible redox behaviors in half cells. In the potassiation (reduction) scans, there was only one clear reduction peak located at $\sim 1.1\text{ V}$ (vs. K^+/K) for AQ26OK. And in the back depotassiation (oxidation) scans, only one oxidation peak at the relatively high potential of 1.5 V could be observed. Obviously, the redox peaks originated from the intercalation/deintercalation processes of K^+ ions into/from the anthraquinone moiety (Fig. 4). Additionally, the decreased reduction current observed during multiple scans (from 1st to 3rd) was strange and the behind reason was currently unclear, maybe due to the capacity decay before reaching balance. To get insight about the morphology of the composited electrode, the

Figure 2 (a) ^1H NMR spectroscopy of AQ26OK. (b) FT-IR spectra for AQ26OK and AQ26OH, respectively.

Figure 3 Solubility test for AQ26OK in common organic electrolytes.

Figure 4 The two-electron mechanism proposed for AQ26OK in PIBs.

SEM image for the AQ26OK-cathode composition is also shown in Fig. 5b. Small particles with the size of hundreds of nanometers could be observed for the AQ26OK-cathode electrode composition.

Half cells

The galvanostatic charge–discharge test was carried out for AQ26OK in the K-ion half cells. And AQ26OK could indeed exhibit satisfactory charge–discharge potentials and specific capacity using the electrolyte of 1 mol L^{−1} KPF₆ in DME. The selected charge–discharge curves of AQ26OK are shown in Fig. 6a, where the clear discharge platform was located at ~1.2 V and the charge platform was around 1.6 V. And the charge–discharge over-potential (ΔE) for AQ26OK was 0.4 V. Notably, the low

redox potentials of AQ26OK were caused by the addition of two electron-donating –OK groups, which could enrich the electron density of AQ skeleton and promote its energy level of the lowest unoccupied molecular orbital (LUMO) [31]. As a result, the redox potentials of AQ26OK were the lower than that of the AQ parent. In the first charge–discharge cycle, the discharge capacity was observed to be as large as 399 mA h g^{−1} and the back charge capacity was 325 mA h g^{−1}, along with the coulombic efficiency (CE) of 81%. Notably, the abnormal phenomenon of large capacity in the 1st cycle might be due to the part formation of a solid-electrolyte interface (SEI), and the capacity contribution from the highly reactive K-metal anode could not be totally ruled out. After the second charge–discharge cycle, the discharge capacity of AQ26OK stabilized at 209 mA h g^{−1} and the charge capacity was 235 mA h g^{−1} with an improved CE value of 89%. In addition, it was a common sense that the carbon additives (KB and CNTs) were slightly redox-active and thus could make capacity contribution to the observed value. Herein, the capacity contribution from carbons was estimated to be around 45 mA h g^{−1} in Fig. S2 [32]. After the carbon value was subtracted, the C_T of AQ26OK (169 mA h g^{−1}) could be well achieved. On the other hand, it was noticeable that the CE value could not reach 100% during the initial several cycles (Fig. 6b). As proved by the control cells with only the carbons in Fig. S2, the low-CE phenomenon probably originated from the counter K electrode and/or the electrolyte, rather than AQ26OK material. Accordingly, the energy density for AQ26OK in half cells was estimated to be 251 W h kg^{−1} (209 mA h g^{−1} × 1.2 V).

Interestingly, with the increased cycle number, the CE

Figure 5 (a) CV curves of AQ26OK in half cells. The scan rate was 0.05 mV s^{−1} and the voltage window was 0.5–3.0 V. (b) SEM image for the AQ26OK-cathode composite.

Figure 6 (a) The selected charge–discharge curves of AQ26OK at 50 mA g^{-1} . (b) The long-term cycling profile of AQ26OK at 50 mA g^{-1} . (c) The rate performance of AQ26OK. (d) The long-term cycling profile of AQ26OK at 500 mA g^{-1} .

value for AQ26OK in half cells could gradually reach 100%. More importantly, AQ26OK could show impressive cycle stability in the ether-based electrolytes. As shown in Fig. 6b, AQ26OK in half cells could deliver an impressive lifespan as long as 4 months at low current densities, maintaining a highly stable average specific capacity of 201 mA h g^{-1} at 50 mA g^{-1} during 450 cycles. Notably, the cycle lifespan in Fig. 6b was actually disturbed by the test temperature. At the same time, the rate performance of AQ26OK was evaluated in Fig. 6c. And the discharge capacities were observed to be 206/195/187/168/147/131 mA h g^{-1} at the test current densities of 50/100/200/300/400/500 mA g^{-1} , respectively. When the test current was back set to be 50 mA g^{-1} , the discharge capacity could be recovered to 199 mA h g^{-1} . The long-cycle stability of AQ26OK at high current densities was also tested in Fig. 6d, and AQ26OK could deliver a highly stable average capacity of 106 mA h g^{-1} during 3200 cycles at the high current density of 500 mA g^{-1} . As shown in Table 1, the integrated performance of AQ26OK is among one of the best stable cathodes in K-ion half cells.

Electrode kinetics

Subsequently, to get more insights about the K-ion kinetics for AQ26OK in half cells, the galvanostatic intermittent titration technique (GITT) test was carried out. In order to obtain a stable status during GITT test, the assembled half cells were firstly charged/discharged at 20 mA g^{-1} for one cycle before the GITT measurement. Afterwards, in order to reach voltage equilibrium, the cell was discharged and charged with a pulse current of 20 mA g^{-1} for 3 min between rest intervals for 13 min. The test potential range was 0.3–3.4 V. Finally, K-ion discharge diffusion coefficient (D) based on the GITT results could be calculated using the following widely used equation [36]:

$$D_{\text{K}^+} = \frac{4}{\pi} \left(\frac{V_{\text{M}} m_{\text{B}}}{M_{\text{B}} S} \right)^2 \left(\frac{\Delta E_{\text{S}}}{\tau (dE_{\text{r}}/d\sqrt{\tau})} \right)^2 \approx \frac{4}{\pi \tau} \left(\frac{m_{\text{B}}}{S_{\text{B}} \rho_{\text{B}}} \right)^2 \left(\frac{\Delta E_{\text{S}}}{\Delta E_{\text{r}}} \right)^2 (\tau \ll L^2/D_{\text{K}^+}), \quad (1)$$

where V_{M} is AQ26OK molar volume ($\text{cm}^3 \text{ mol}^{-1}$); M_{B} is AQ26OK molar mass (g mol^{-1}); S is the contact area between the electrode and electrolyte (cm^2); m_{B} is the active

Table 1 The summary for the long-lifespan cathodes selected for K-ion half cells

Cathode ^a	C_T (mA h g ⁻¹)	Number of cycles	C_p (retention) ^b	Ref.
AQ26OK	169	450 (50 mA g ⁻¹)	193/209 (92%)	This work
PTCDA	131	550 (20 mA g ⁻¹)	98/113 (89%)	[16]
AQDS	130	1000 (390 mA g ⁻¹)	84/102 (80%)	[33]
K _{0.65} Fe _{0.5} Mn _{0.5} O ₂	211	350 (100 mA g ⁻¹)	71/91 (78%)	[34]
K ₂ [(VOHPO ₄) ₂ (C ₂ O ₄)]	108	500 (200 mA g ⁻¹)	60/90 (67%)	[35]

a) PTCDA = perylene-3,4,9,10-tetracarboxylic dianhydride, AQDS = sodium anthraquinone-1,5-disulfonate; b) the practical capacity observed for the last cycle *versus* the peak value (capacity retention is based on the last cycle relative to the peak value).

Figure 7 (a) GITT curves for AQ26OK in K-ion half cells. (b) The calculated K-ion D based on GITT curves. (c) EIS spectra for AQ26OK electrodes before and after 450 cycles.

loading mass (g); S_B is the effective area of the electrode (1.13 cm²); ρ_B is the density of the active mass in the electrode, which was calculated by m_B , S_B and L_B (electrode thickness, 57.60 μm) (inset of Fig. 7a); $dE_\tau/d\sqrt{\tau}$ is the slope of the linearized proportional of E_τ during the K-inserting or K-extracting process of duration time τ (s). ΔE_s is the potential charge after every equilibrium process; ΔE_τ is the transient potential change during a single titration step [37]. The collected charge–discharge GITT curve is shown in Fig. 7a. And in Fig. 7b, the K-ion D for AQ26OK in 0.3–3.4 V was calculated to be in the range from 2.8×10^{-9}

to $9.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ($D_{\text{average}} = 2.73 \times 10^{-8}$); while the K⁺ charge D for AQ26OK was from 2.0×10^{-10} to $6.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ($D_{\text{average}} = 1.49 \times 10^{-8}$). Remarkably, the average K-ion D for AQ26OK was obviously higher than those of most reported cathodes ($\sim 10^{-12}$ to $10^{-9} \text{ cm}^2 \text{ s}^{-1}$), as summarized in Table S1. Meanwhile, the EIS for AQ26OK was also carried out in Fig. 7c. The charge–transfer resistance values (R_{ct}) of the AQ26OK electrodes in K-ion half cells before ($R_{ct} = \sim 115 \Omega$) and after 450 cycles ($R_{ct} = \sim 128 \Omega$) were relatively small. And the small resistance increments ($\sim 13 \Omega$) might indicate the high stability of AQ26OK in

ether-based electrolytes [38].

Full cells

Finally, due to the superb performance of AQ26OK in K-

ion half cells, we constructed OPIBs by using AQ26OK (1.3 mg cm^{-2}) as the organic cathode and the reduced state (K_4TP) of potassium terephthalate (K_2TP , $C_T = 225 \text{ mA h g}^{-1}$, 1.6 mg cm^{-2}) as the organic anode [27].

Figure 8 (a) The configuration of our OPIBs based on K_4TP anode and AQ26OK cathode. (b) The charge-discharge curves of the OPIBs at 50 mA g^{-1} . (c) The cycle profile at 50 mA g^{-1} . (d) The rate performance of the OPIBs. (e) The long-cycle profile at 500 mA g^{-1} .

Table 2 The summary of non-aqueous K-ion full cells reported to date

Cathode anode ^a	Voltage (V)	Capacity retention ^b	Ref.
AQ26OK (SM) K ₄ TP (SM)	0.01–3.1	86%@250th cycle (100 mA g ⁻¹) 81%@1000th cycle (500 mA g ⁻¹)	This work
PTCDI-DAQ (SM) K ₄ TP (SM)	0.2–3.2	62%@300th cycle (100 mA g ⁻¹)	[28]
PTCDA (SM) soft carbon (I)	0.8–3.2	65%@3000th cycle (600 mA g ⁻¹)	[16]
PPTs (P) K ₄ TP (SM)	0.1–3.2	64%@100th cycle (100 mA g ⁻¹)	[39]
K _{1.92} Fe[Fe(CN) ₆] _{0.94} ·0.5H ₂ O (I) K ₂ TP (SM)	1.5–3.8	90%@60th cycle (65 mA g ⁻¹)	[40]
K _{0.22} Fe[Fe(CN) ₆] _{0.805} ·4.01H ₂ O (I) Super P (I)	1.0–3.8	93%@50th cycle (100 mA g ⁻¹)	[41]
K _{0.65} Fe _{0.5} Mn _{0.5} O ₂ (I) Hard carbon (I)	0.5–3.5	75%@100th cycle (100 mA g ⁻¹)	[34]

a) SM = small-molecule cathode; P = polymer cathode; I = inorganic cathode; b) the capacity retention of the last cycle *versus* the peak value (current density).

The cell configuration of our OPIBs is shown in Fig. 8a and the fabrication details are provided in the EXPERIMENTAL SECTION. Notably, the electrolyte was still 1 mol L⁻¹ KPF₆ in DME. And most carbonate-based electrolytes only led to poor results. As shown in Fig. 8b, the charge–discharge curves of the AQ26OK || K₄TP OPIBs show very clear and flat platforms in the voltage window of 0.01–3.1 V, where the average discharge voltage was around 0.6 V and the average charge voltage was about 0.9 V. Regrettably, the low working voltage of AQ26OK || K₄TP OPIBs was ascribed to the low redox potential of AQ26OK cathode. And the specific capacity of OPIBs was calculated based on AQ26OK mass. In the first charge–discharge cycle, the discharge capacity was observed to be 126 mA h g⁻¹ and the charge capacity was 167 mA h g⁻¹ with the CE of 75%. Afterwards, the AQ26OK || K₄TP OPIBs could deliver the maximum discharge capacity of 145 mA h g⁻¹ at the second cycle. Accordingly, the energy density for the AQ26OK || K₄TP OPIBs was estimated to be 87 W h kg⁻¹ (145 mA h g⁻¹ × 0.6 V) for cathode mass. Nevertheless, our AQ26OK || K₄TP OPIBs could realize an ultra-stable average discharge capacity of 135 mA h g⁻¹ during 250 cycles at the low current density of 100 mA g⁻¹, with nearly 100% CE value (Fig. 8c). Therefore, the capacity retention for the AQ26OK || K₄TP OPIBs was as high as 86% and the capacity loss for every cycle was only ~0.06%. The rate performance of the OPIBs was carried out in Fig. 8d. And the observed discharge capacities were ~142/105/95/81/64 mA h g⁻¹ at the current densities of 100/200/300/400/500 mA g⁻¹, respectively. When the current density was back to 100 mA g⁻¹, the discharge capacities stabilized at ~132 mA h g⁻¹. Impressively, the AQ26OK || K₄TP OPIBs also exhibited a highly stable average capacity of ~47 mA h g⁻¹ at the high current density of 500 mA g⁻¹ during 1000 cycles (Fig. 8e),

with the capacity retention of 81%. As shown in Table 2, the stability of our AQ26OK || K₄TP OPIBs is currently among the best ones for the reported PIBs.

CONCLUSIONS

In summary, a new insoluble polyanionic anthraquinone, namely AQ26OK (169 mA h g⁻¹) was reported as an organic cathode for ultra-stable K-ion batteries. In half cells using ether-based electrolytes, AQ26OK could deliver high cycle stability and long lifespan over 4 months. In all-organic K-ion full cells using K₂TP as the organic anode, the resulting full cells could realize the very stable capacities of 135 mA h g⁻¹ during 250 cycles (100 mA g⁻¹) and 47 mA h g⁻¹ for 1000 cycles (500 mA g⁻¹). Our work has made a forward step for the development of stable OPIBs.

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一种新型不溶多阴离子有机正极材料在全有机钾离子电池中的应用

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摘要 有机小分子电极材料普遍会溶解在电解液中. 本文报道了一个新型有机小分子化合物蒽醌-2,6-二羟基钾(AQ26OK, 理论比容量: 169 mA h g^{-1})作为钾离子电池的正极材料. AQ26OK在大 π 共轭蒽醌的基础上含有2个强的O-K离子键, 使得有机框架为-2价. 因此, AQ26OK可以称为多阴离子有机电极材料. AQ26OK在醚类电解液中基本不溶, 从而在钾离子电池中展现出较高的循环稳定性. 在半电池中(0.3–3.4 V), 使用 1 mol L^{-1} KPF₆乙二醇二甲醚作为电解液, AQ26OK在 50 mA g^{-1} 的小电流下可以达到 201 mA h g^{-1} 的比容量, 且可以稳定循环超过450圈(寿命至少4个月); 其在大电流(500 mA g^{-1})下可以达到 106 mA h g^{-1} 的比容量且循环3200圈. 在使用对苯二甲酸钾还原态(K₄TP)作为有机负极的全有机钾离子电池中, 此K₄TP || AQ26OK有机钾离子电池(0.01–3.0 V)在小电流(100 mA g^{-1})下可以稳定循环超过250圈且平均放电比容量约为 135 mA h g^{-1} ; 其在大电流(500 mA g^{-1})下循环1000圈的平均比容量约为 47 mA h g^{-1} . AQ26OK是目前钾离子电池有机正极中最稳定的材料之一.