

Cite this: *Chem. Sci.*, 2019, 10, 2048

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A nonaqueous potassium-ion hybrid capacitor enabled by two-dimensional diffusion pathways of dipotassium terephthalate†

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Nonaqueous potassium-ion hybrid capacitors (KIHCs) are faced with limited redox reaction kinetics of electrodes for accommodation of large-sized K^+ . Here, dipotassium terephthalate (K_2TP) is applied as an organic negative electrode to provide comparable reaction kinetics with a non-faradaic activated carbon (AC) positive electrode to boost the electrochemical performance of KIHCs. It is revealed that the large exchange current density and fast two-dimensional (2D) diffusion pathways of K^+ in K_2TP determined by density functional theory (DFT) calculations ensure its fast redox reaction and transport kinetics. The as-constructed KIHC presents both high energy and power densities of 101 W h kg^{-1} and 2160 W kg^{-1} based on the mass of the two electrodes (41.5 W h kg^{-1} and 885.2 W kg^{-1} based on the mass of the two electrodes and electrolyte), respectively, and a superior capacity retention of 97.7% after 500 cycles. The excellent electrochemical performance is attributed to the fast kinetics, good structural flexibility, and small volume change (9.4%) of K_2TP upon K^+ insertion/extraction, and its good compatibility with the AC positive electrode in 1,2-dimethoxyethane (DME)-based electrolyte. This will promote application of organic materials in hybrid capacitors and the development of KIHCs.

Received 9th October 2018
Accepted 10th December 2018

DOI: 10.1039/c8sc04489a

rsc.li/chemical-science

Introduction

Nonaqueous hybrid capacitors have recently attracted extensive research interest, and are generally composed of battery-type negative electrodes and electric double-layer capacitor (EDLC)-type positive electrodes.^{1,2} They are endowed with the advantages of both high energy density of batteries and high power density and long lifespan of EDLCs.^{3–6} The equilibrium potential of K^+/K is -2.88 V in propylene carbonate (PC), which is lower than that of Li^+/Li (-2.79 V) or Na^+/Na (-2.56 V), providing wider operating voltage windows;⁷ K^+ has a smaller Stokes' radius (3.6 \AA) than those of Li^+ and Na^+ in PC (4.8 and 4.6 \AA) due to its weaker Lewis acidity, suggesting its high mobility, that is, high ionic conductivity of K^+ in electrolytes.⁸ The abundance of K resources in the Earth's crust is comparable to that of their Na counterparts and about three orders of magnitude higher than that of their Li counterparts, endowing

it with potentially low cost and sustainability.^{9,10} Therefore, developing nonaqueous potassium-ion hybrid capacitors (KIHCs) is highly desirable. However, KIHCs are plagued by poor kinetics of redox reactions and diffusion of large-sized K^+ in the bulky electrode materials, which are usually much slower than the non-faradaic capacitive sorption of ions in EDLCs, and construction of KIHCs is faced with a materials challenge.

Carbon-based materials are attractive negative electrode candidates for K^+ storage, but their low redox potentials and rate capability preclude their usage in KIHCs.^{5,6,11–14} Alloys and conversion-reaction-type negative electrode materials exhibit high capacity, but their large volume change during charge and discharge induce decaying performance.^{15–19} Organic materials with structural flexibility enable fast K^+ diffusion and redox response, and have been attempted in potassium-ion batteries (KIBs).^{20–24} Chen *et al.* demonstrated the feasibility of 3,4,9,10-perylene-tetracarboxylic acid-dianhydride for K^+ storage.²⁰ However, its capacity retention is only 66.1% after 200 cycles, which is attributed to its dissolution in electrolytes. Li's group has revealed that organic carboxyls are stable in electrolytes, and their redox potentials are between 0.5 and 1.0 V vs. K^+/K , far from the deposition potential of K.²⁵ This can effectively circumvent the formation of K dendrites, and thus will promote safety, especially in high-rate devices. However, although they have been explored in Li-ion and Na-ion batteries,^{26,27} organic materials for KIHCs and the correlation of their molecular

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8sc04489a

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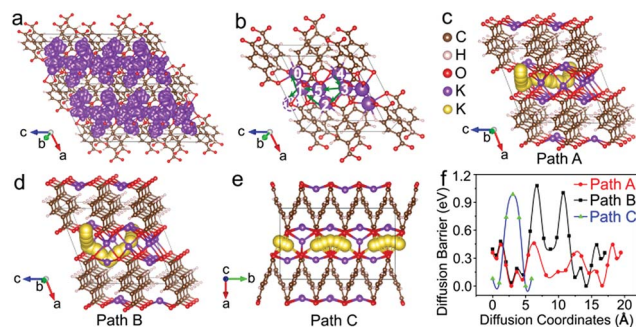


Fig. 4 (a) Trajectories of K⁺ in K₄TP obtained by MD simulation at 2000 K for 10 ps; (b) designed K⁺ diffusion path A (4 → 3 → 5 → 1 → 0), B (4 → 3 → 2 → 1 → 0), and C (1 → 1') in K₄TP; (c) path A of K⁺ diffusion; (d) path B of K⁺ diffusion; (e) path C of K⁺ diffusion; and (f) energy profiles of K⁺ migration in path A, B and C. K⁺ is displayed in different sizes and colors in (a–e) for clarity.

respectively. In path A of Fig. 4c, the diffusion barrier was calculated to be 0.46 eV, which is the minimum. Moreover, the diffusion barrier of K⁺ migrating from position 1 → 0 and 4 → 3 was calculated to be as low as 0.08 eV, which favors facile migration between these positions. Path B in Fig. 4d and path C in Fig. 4e present higher diffusion barriers of 1.08 and 0.98 eV, respectively. The calculated energy profiles along the three pathways are comparatively shown in Fig. 4f. It is obvious that path A has overall low energy barriers and is the optimal diffusion pathway for K⁺. This guarantees outstanding ionic conductivity and contributes to the excellent electrochemical performance, especially high rate capability. According to an empirical estimation criterion, a migration barrier of 0.525 eV corresponds to a typical ionic diffusivity of 10⁻¹² cm² s⁻¹ at room temperature, and a 0.06 eV increase/decrease in the migration energy leads to an order of magnitude decrease/increase in the ionic diffusivity.³⁴ Thus, the 0.46 eV diffusion barrier results in a diffusion coefficient of ~10⁻¹¹ cm² s⁻¹, matching well with the experimental D_{K⁺} in K₂TP of 1.32 × 10⁻¹¹ cm² s⁻¹.

Capacitive adsorption/release of PF₆⁻ onto/from the surface of the AC positive electrode is investigated by elemental mapping. When the KIHC was fully charged, fluorine and phosphorus can be clearly detected as shown in Fig. S14a[†] with atomic ratios of 1.49% and 0.68% with respect to carbon, respectively, suggesting that PF₆⁻ is adsorbed on the AC surface from the electrolyte. After discharge, the atomic ratios of fluorine and phosphorus are dramatically decreased to 0.23% and 0.07%, respectively, in Fig. S14b[†] indicating release of PF₆⁻ from the AC surface into the electrolyte. The reversible charge storage stems from reversible adsorption and release of PF₆⁻ in EDLs of the AC positive electrode.

Fig. 5a presents the rate capability of the KIHC at different current densities. Capacities of 43.5, 41.3, 35.9, 32.1, 28.2, and 23.9 mA h g⁻¹ are obtained at current densities of 20, 40, 100, 200, 400, and 1000 mA g⁻¹, respectively. The selected charge/discharge curves are depicted in Fig. 5b. The sloping plateaus are clearly observed in the charging/discharging process, and are in good agreement with CVs in Fig. 1d. The cycle life of the

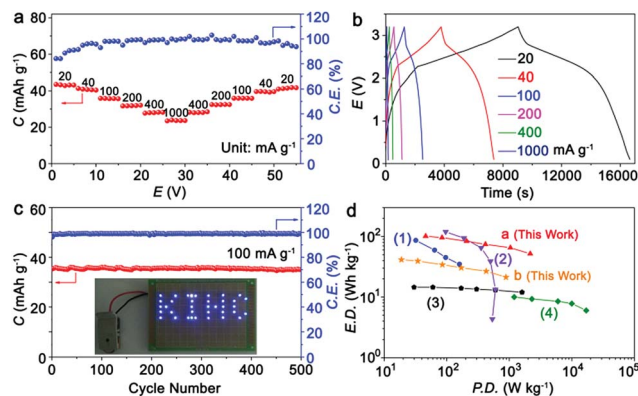


Fig. 5 (a) Rate capability; (b) charge/discharge curves at different rates; (c) cycling performance of the KIHC at 100 mA g⁻¹ for 500 cycles; and (d) Ragone plots of the KIHC at K₂TP//AC, and other reported KIHCs, a KIB, and an EDLC. (1) Soft carbon//K_{0.7}Fe_{0.5}Mn_{0.5}O₂ (KIB), ref. 12; (2) soft carbon//AC (KIHC), ref. 6; (3) graphite//AC (KIHC), ref. 5; (4) AC//AC (EDLC), ref. 35. The current density, capacity, power density and energy density are all based on the total mass of active materials in both electrodes. Exceptionally, plot b is based on the mass of both electrodes and the electrolyte.

KIHC is displayed in Fig. 5c. After 500 cycles, the capacity retention is 97.7% and the coulombic efficiencies are close to 100%, implying superior cycling stability of the KIHC. The logo “KIHC” in a pattern of light-emitting diodes is powered by one single KIHC as shown in the inset of Fig. 5c, indicating its potential for application. The KIHC delivered a high energy density of 101 W h kg⁻¹ at a power density of 46 W kg⁻¹ based on the total mass of active materials in both electrodes, as shown in Fig. 5d. Remarkably, a moderate energy density of 52 W h kg⁻¹ can be achieved even at an exceptionally high power density of 2160 W kg⁻¹, demonstrating a good balance between energy and power density. Its overall gravimetric performance is higher than that of many recently reported potassium-ion based capacitors and batteries, such as soft carbon//K_{0.7}Fe_{0.5}Mn_{0.5}O₂ (KIB),¹² soft carbon//AC (KIHC),⁶ graphite//AC (KIHC),⁵ and AC//AC (EDLC).³⁵ Besides, taking the electrolyte into account, the KIHC of K₂TP//AC possesses a little lower energy density (41.5 W h kg⁻¹) than 54 W h kg⁻¹ of Ni–Cd batteries but a much higher power density of 885.2 W kg⁻¹ vs. 125 W kg⁻¹ of Ni–Cd batteries.³⁶ This is due to the fast kinetics of capacitive behavior of the carbon electrode and redox reactions of K₂TP, and shows the advantage of hybrid capacitors.

Conclusions

In summary, a high-performance KIHC was successfully constructed using a K₂TP organic negative electrode and AC positive electrode with DME-based electrolyte. It works with redox reaction of K₂TP *via* reversible transformation of conjugated carboxyls and enolates and capacitive sorption of PF₆⁻ in EDLs of AC. DFT calculations indicate a small volume change of 9.4% during discharge/charge of K₂TP, thanks to the flexibility of the terephthalate motifs. It is found that the π-stacking aromatic organic layer and the K–O inorganic layer are responsible for



electron conduction and K^+ diffusion, respectively. The 2D diffusion pathways of K^+ have the lowest diffusion barrier of 0.46 eV, and ensure facile K^+ diffusion to match with the non-faradaic capacitive kinetics of the AC positive electrode. The KIHc demonstrates a high energy density of 101 W h kg^{-1} , high power density of 2160 W kg^{-1} based on the mass of the two electrodes, and long lifetime with a capacity retention of 97.7% after 500 cycles. These are attributed to the fast kinetics and high exchange current density of the organic electrode of K_2TP and its small volume change during discharge/charge. This investigation reveals promising applications of KIHcs for large scale electric energy storage, and will promote the development of organic functional materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the National Natural Science Foundation of China (21603108 and 21673243), the Fundamental Funds for the Central Universities, and the NSFC-RGC Joint Program (51761165025) is acknowledged.

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