A novel low-cost and environment-friendly cathode with large channels and high structure stability for potassium-ion storage

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ABSTRACT Potassium-ion batteries (KIBs) are promising candidates for large-scale energy storage due to the abundance of potassium and its chemical similarity to lithium. Nevertheless, the performances of KIBs are still unsatisfactory for practical applications, mainly hindered by the lack of suitable cathode materials. Herein, combining the strong inductive effect of sulphate and the feasible preparation of Fe²⁺-containing compounds in oxalate system, a compound with novel architecture, K₄Fe₃(C₂O₄)₃(SO₄)₂, has been identified as a low-cost and environmentally friendly cathode for stable potassium-ion storage. Its unique crystal structure possesses an unprecedented two-dimensional framework of triple layers, with 3.379 Å interlayer distance and large intralayer rings in the size of 4.576×6.846 Å. According to first-principles simulations, such a configuration is favorable for reversible K-ion migration with a very low volume change of 6.4%. Synchrotron X-ray absorption spectra and X-ray diffraction characterizations at different charging/discharging states and electrochemical performances based on its half and full cells further verify its excellent reversibility and structural stability. Although its performance needs to be improved *via* further composition tuning with multi-valent transition metals, doping, structural optimization, etc., this study clearly presents a stable structural model for K-ion cathodes with merits of low cost and environmental friendliness.

Keywords: potassium-ion cathode, Fe-based polyanionic compound, low cost, environment friendly

INTRODUCTION

Due to the limited Li resources and their geographic unevenness, lithium-ion batteries (LIBs) can hardly satisfy large-scale energy storage fields for renewable energy sources such as solar, wind, etc., where the cost and environmental influence should be considered even in the sacrifice of energy densities to a certain extent [1–4]. Among potential alternatives, potassium-ion batteries (KIBs) are attracting intense academic and technological interest due to the abundance of potassium and its chemical similarity to lithium over sodium [5–7]. For KIB technologies, several families have been explored as anode materials with high capacity and long cyclability, including intercalation-type, conversion-type, and alloying type materials [8–16]. In comparison, the development of ideal cathode materials, such as Prussian blue analogues (PBAs), oxides, polyanions, and organics [17–22] are sluggish. For instance, despite of enormous investigations on PBAs, of which the three-dimensional (3D) open framework structure is promising for K-ion storage, the preparation of defect-free and water-free PBAs is difficult, which deteriorates the electrochemical performance of PBAs in terms of kinetics, Coulombic efficiency (CE), and cycling life [23–26].

Recently, polyanionic compounds have gradually at-

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tracted more attention owing to their favorable working potentials, rigid structural frameworks for K ion movement and high stability against organic solvents. Especially, polyanions based on iron are more competitive than others, thanks to its large abundance and environmental friendliness [27,28]. Besides, the selection of polyanionic groups is also critical to constructing a high-performance polyanionic cathode. Sulphate group (SO_4^{2-}) is known to possess the strongest inductive effect on the d orbitals of transition metals, contributing to high working potentials. Whereas, the sulphate system tends to generate Fe^{3+} -containing products in the presence of even trace amount of oxygen or moisture [29,30]. Such Fe^{3+} -containing materials are electrochemically unfavorable since the practical cathode in secondary batteries needs to provide charge-carrier ions for the whole system, and should originally be in a discharged state, i.e., Fe^{2+} state. Consequently, various strategies have been developed to control iron state during synthesis, for instance, applying reductive atmosphere, introducing reductive agents, etc. After evaluating the reductive behavior of several candidates, we found oxalate group ($\text{C}_2\text{O}_4^{2-}$) has excellent capability to form Fe^{2+} -containing compounds [31,32]. Therefore, combining the merits of sulphate and oxalate groups is promising to construct low cost and high-performance polyanionic cathodes for K-ion storage.

Following above guidelines, we performed tentative exploration in the mixed sulphate-oxalate systems, resulting in a new iron-based polyanionic compound, $\text{K}_4\text{Fe}_3(\text{C}_2\text{O}_4)_3(\text{SO}_4)_2$ (KFOS). Interestingly, its unique crystal structure contains triple octahedral FeO_6 layers bridged by lateral sulphate and longitudinal oxalate, with K ions located at inter- and intra-layer interstices. To the best of our knowledge, such a triple-layered framework as a K-ion host has never been reported before. Our first principle calculations suggest its configuration is excellent for reversible K-ion migration due to the structural stability and intrinsic electronic structures, and the exploration on reaction mechanism further reveals its highly reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reactions and structural stability. In our preliminary experiments, this polyanionic cathode showed a steady discharge capacity of $\sim 80 \text{ mA h g}^{-1}$ at 100 mA g^{-1} for 500 cycles, and a K-ion full cell was successfully constructed combining this cathode with soft carbon (SC) anode, which exhibited excellent cycling stability with ignorable capacity decay over 200 cycles. Although its capacity could be improved by further composition modification, doping, and structural optimization, it provides a novel structure model for K-ion cathodes with low cost and environmental friendliness.

EXPERIMENTAL SECTION

Materials

Potassium sulfate (K_2SO_4 , 99%+), ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 99.5%), oxalate dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 99%+) and ethanol (99%+) were purchased from Alfa Aesar. Ketjenblack EC600JD was purchased from Lion Corporation in Japan. *N*-methyl-2-pyrrolidone (NMP), carbon-coated Al foil (thickness, 18 μm), and Al foil (thickness, 25 μm) were purchased from Shenzhen Kejingstar Technology Co., Ltd. Propylene carbonate (PC, 99.95%), ethylene carbonate (EC, 99.95%), dimethyl carbonate (DMC), potassium molecular sieve and battery-grade potassium hexafluorophosphate (KPF_6 , 99.5%) were provided by Dodochem. Potassium block (K, 99%) and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) were purchased from Aladdin Reagent. Glass microfiber separators (Whatman Grade GF/D) were purchased from GE Healthcare Life Sciences. All chemicals were used directly as received.

Synthesis

KFOS crystallites were synthesized by a hydrothermal method. K_2SO_4 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were sealed in a Teflon-lined autoclave with 1.00 g distilled water in the molar ratio of 1:3:1 (1 for 1 mmol). The reaction went on under auto-generated pressure by keeping autoclaves in a 200°C oven for five days. The oven was then turned off until cooling down to room temperature. The resulting products were repeatedly washed with distilled water and ethanol to remove by-products, and then dried at a vacuum environment overnight. SC was facilely synthesized by thermal polymerization of PTCDA for 4 h at 900°C with a heating rate of $10^\circ\text{C min}^{-1}$.

Characterization

Optical images of the KFOS crystallites were taken by a Leica DVM6M video microscope with ultra-depth-of-field. A transparent orange KFOS crystallite in the size of $0.2 \times 0.3 \times 0.6 \text{ mm}^3$ was chosen to collect single crystal X-ray diffraction (XRD) data on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The face-indexed absorption correction was carried out based on the XPREP program. The structure was then solved by direct methods and refined using SHELX-2014 incorporated in the WinGX program. All atoms were refined anisotropically. Powder XRD patterns were performed on the finely ground polycrystallites on a

Rigaku diffractometer (MiniFlex600, 40 kV and 15 mA) using Cu K α radiation. Scans were taken over the range of 3°–90° with a 2θ step of 2° min^{−1}. *Ex-situ* XRD analyses of recollected cathodes at different states, after being washed with DMC to remove electrolyte and dried overnight, were conducted on the same XRD detector at a 2θ step of 2° min^{−1} over the range of 10°–40°. For transmission electron microscopy (TEM) characterization, a sheet from a single crystallite was prepared by an FEI Scios Focused Ion Beam/Field Emission (FE)-TEM at an accelerating voltage of 30 kV under a selective etching process, and positioned on a Cu grid. The energy dispersion X-ray spectra (EDS) of TEM were conducted by a JEOL JEM-3200FS FE-TEM equipped with an Oxford Instruments EDS analyzer. Thermal stability was characterized on hand-ground crystallites of about 8 mg by simultaneous thermogravimetric and differential scanning calorimetry (TG-DSC) using a STA449F3 thermal analyzer (Netzsch, Germany), from room temperature to 800°C under a flow of air at a rate of 10°C min^{−1}. Residual of TG-DSC analysis was checked by powder XRD as stated above.

Electrochemical test

The electrochemical performance of the KFOS/K half-cell was studied in CR2032 coin-type cells assembled in Ar-filled glove box (MIKROUNA) with water and oxygen levels ≤ 0.1 ppm. To improve KFOS's conductivity, hand-ground samples were ball-milled with Kejtenblack carbon (3:1 w/w) for 3 h. Subsequent powder was then ground with PVDF (85%:15% w/w) by hand, followed by the addition of several drops of NMP solvent until forming a homogeneous slurry. The slurry was coated onto a carbon-coated Al foil, dried at 80°C in vacuum overnight and punched into circular sheets, with diameters of 10 mm and loading mass of ~ 1.5 mg cm^{−2}. The glass fiber sheets of 16 mm in diameter were directly employed as separator and potassium metal foils served as counter electrodes in half-cells. KPF₆ (1 mol L^{−1}) in EC+PC, DMC+EC, DME+PC ($v/v = 1:1$) were tested as electrolyte, among which EC+PC turned out the most compatible one. Afterward, cells were constructed with EC+PC electrolyte. Galvanostatic charge-discharge (GCD) measurements were carried out on a battery test system (NEWARE CT-4008) using diverse voltage ranges and current densities. Cyclic voltammetry (CV) was performed on an Autolab (PGSTAT302N, Switzerland) electrochemical workstation. The full battery was assembled using KFOS cathode and SC as the anode, with the same separator and electrolyte as in half-cells. GCD was performed in a voltage range of 1.5–4.5 V. The ca-

capacity of the full cell was calculated based on the mass of active cathode material.

Synchrotron-based X-ray measurements

X-ray absorption near-edge spectra (XANES) and extended X-ray absorption fine-structure (EXAFS) of Fe K-edge data of the samples were collected at SUT-NANO-TEC-SLRI XAS beamline (BL5.2), Synchrotron Light Research Institute (SLRI), Thailand. A beam energy of 1.2 GeV generates the synchrotron radiation source at the storage ring and the beamline photon source covers an energy range of 40 to 1040 eV at the resolving power of 10,000. Typical loading of KFOS in each cathode was 5–8 mg cm^{−2}.

Theoretical calculations

Computer simulations were performed with spin-polarized density functional theory as implemented in the Vienna *ab initio* simulation package with projector-augmented-wave method. The plane-wave cutoff energy of 450 eV was applied. The Perdew-Burke-Ernzerhof functional with the Hubbard *U* correction⁶⁷ was adopted for the exchange correlation energy. An effective *U* value of 4.0 eV was applied to correct the onsite Coulomb repulsion of Fe 3d electrons. The Brillouin zone was sampled with a 3 $\times$ 4 $\times$ 3 Γ -centered *k* mesh to keep the reciprocal spacing of all calculations with supercells of K_{16−*x*}Fe₁₂(C₂O₄)₁₂(SO₄)₈ ($16 \geq x \geq 4$) less than 0.03 Å^{−1} and the criteria for energy convergence was set to be 10^{−5} eV.

RESULTS AND DISCUSSION

The synthesized KFOS crystallites exhibit orange color and most of them are in the size of several millimeters (Fig. 1a). According to Sheltx refinement [33] on single crystal XRD data, it crystallizes in *P*₂₁/*c* space group with *a* = 13.6775(7) Å, *b* = 5.4935(3) Å, *c* = 12.7483(6) Å, and $\beta = 97.770(4)^\circ$. The crystallographic data and selected atom coordination are listed in Tables S1, S2. Interestingly, the structure exhibits a 2D framework consisting of puckered triple-layered FeO₆ octahedra, which has not been reported before. FeO₆ octahedra are connected by sulphate groups along *b*-axis and oxalate groups in *ac*-plane, and the triple-layer framework contains one layer of Fe(SO₄)(C₂O₄)_{1/2}, one layer of Fe(C₂O₄), and another layer of Fe(SO₄)(C₂O₄)_{1/2}, denoted as L1, L2, and L3, respectively (Fig. 1b). L1 and L3 are identically 2D, with FeO₆ octahedra connected by SO₄ along *c*-axis and by C₂O₄ along *b*-axis (Fig. S1a). Meanwhile, L2 is composed of 1D FeO₆ bridged by C₂O₄ along *b*-axis (Fig. S1b).

Figure 1 Characterizations of KFOS crystallites. (a) In-depth optical image. (b) Structure of the single crystal XRD. (c) Powder XRD. (d) TEM-EDS mapping of component elements. (e) Artemis fitting of Fe K edge EXAFS. (f) TG-DSC.

Two crystallographic iron sites are identified in KFOS: Fe1 in L1 and L3 is bonded to oxygen atoms of two bidentated oxalate groups and two edge-sharing sulphate groups, Fe2 in L2 shares oxygen with four oxalate groups (Fig. S2). The K cations are located half in cavities formed within triple layers (K1, between L1 and L2, or between L2 and L3) and half in interlayers (K2). Noticeably, the cavities of triple layers run along *b* axis, with a cross-section of 4.576×6.846 Å, obviously larger than the interstitial sites of 3.2 and 4.6 Å in PBAs. Meanwhile, the interlayer distance is about 3.440 Å, at the same level as in layered oxide cathodes. Therefore, both K1 and K2 shall be movable in the framework. The detailed coordination

and local environments of Fe and K ions are given in Figs S3, S4.

Powder XRD pattern of the hand-ground sample matches well with that deduced from the single crystal XRD (Fig. 1c and Fig. S5), confirming the phase and high purity of the synthesized KFOS. TEM image and the corresponding EDS mappings on a KFOS sheet prepared by focused ion beams demonstrate the even distribution of K, Fe, S, O, and C elements through the whole crystallite (Fig. 1d). As most polyanionic cathode materials containing Fe(II) are sensitive to air and moisture conditions [29,30,34–36], a pristine sample was exposed in air for two weeks and then checked by synchrotron-based

X-ray absorption spectroscopy (XAS). The fitting of Fe EXAFS by Artemis program [37] based on the structural model from single crystal XRD turns out quite well (Fig. 1e, Table S3), demonstrating KFOS can be stably stored in air. TG-DSC curves show the KFOS is stable until 300°C (Fig. 1f), then it starts to decompose into Fe_2O_3 and K_2SO_4 , evidenced by XRD analysis on the residual powder (Fig. S6).

Motivated by the encouraging crystal structure of KFOS and its stability against air and heat, we evaluated its ability of K-ion storage. Supposing the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction dominates the electrochemical process, three quarter of potassium in KFOS shall be removable. In the first-principles simulations based on density functional theory (DFT) [38–40], the removal of corresponding K-ions leads to a similar but contracted unit cell, with a slight volume change of 6.4%, even smaller than that of LIB cathode LiFePO_4 (7.8%) (Fig. 2a, b) [41]. In terms of atomic structures, although all Fe–O bonds experience a shrinkage upon depotassiation, with an average value of 9.3%, the orientation of FeO_6 octrahedra keeps almost unchanged, implying the stiffness of the framework (Fig. 2c). Besides, the calculated electronic density of

states reveals that the top of the valence band consists predominantly of Fe 3d states in original KFOS (Fig. 2d). Upon depotassiation, the spin-up orbitals shift to deeper levels, while the spin-down orbitals move to higher levels above Fermi energy, allowing electron loss to its nearest anions. The simulations clearly illustrate that the extraction/(re)-insertion mechanism involves intrinsic $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox, and indicate its high structural reversibility as a cathode for K-ion storage. Noteworthy, the capacity could be improved to $\sim 140 \text{ mA h g}^{-1}$ if all K-ions are moveable, with part of iron oxidized to Fe^{4+} or replaced with ions of multi-changeable electrons such as Mn.

Encouraged by the DFT calculations, electrochemical properties of KFOS were further investigated using prototype coin cells. Pristine KFOS was first ball-milled with conductive carbon to form a uniform mixture (Fig. S7), similar to other polyanionic electrode materials [42,43]. Galvanostatic cycling experiments were performed on half cells using a fixed rate of 100 mA g^{-1} to evaluate the best voltage window and the most compatible electrolyte. After examining several measurement conditions, 1.7–4.5 V and 1 mol L^{-1} KPF₆ in PC + EC (1:1 v/v) were verified be the optimal combination. The up threshold of

Figure 2 First principles calculations of KFOS. (a) Unit cell of potassiated and depotassiated KFOS, (b) the corresponding cell parameters and volume change, and (c) atomic structures of Fe environments. (d, e) Partial density of states projected onto the Fe 3d orbitals.

4.5 V likely determined by carbonate electrolyte but not the KFOS, which restrained redox reactions and therefore limited the obtained capacity stated in detail below. Although the Coulombic efficiencies (CEs) were relatively low ($< 85\%$) in the initial several cycles, possibly due to side reactions and activation process to form solid-electrolyte interface [44,45], it kept increasing as cycling proceeded and eventually stabilized at $>99\%$. Other voltage windows and electrolytes either failed to allow sufficient K-ion desertion/insertion or resulted in a rapid capacity decay or cell failure (Fig. S8). Following electrochemical studies of KFOS are therefore focused on the potential window of 1.7–4.5 V using 1 mol L^{-1} KPF₆ in PC + EC (1:1 v/v) as electrolyte.

Fig. 3a presents a typical stabilized GCD curve at a current density of 100 mA g^{-1} . A discharge capacity of about 80 mA h g^{-1} was obtained. Although no clear plateaus can be observed, there is an obvious trend of flattening in the curve between 3.0 and 4.0 V. CV curve

shows that two main oxidation reactions occurred in the charging process, centered at 3.4 and 3.9 V, respectively, while the corresponding reduction oxidation reactions exhibited a broad envelope between 3.0–3.7 V in the discharging process (Fig. 3b). The polarization of 0.3–0.4 V in KFOS cathode is relatively low compared with other KIB cathodes [24,46]. Reversible discharge capacities of around 85, 70, 64, 58 and 54 mA h g^{-1} were obtained at 100, 200, 300, 400, and 500 mA g^{-1} , respectively, and the polarization was almost unchanged with increasing current densities (Fig. 3c). Besides, the capacity could recover to its initial value as the current density increased-decreased over and over again, proving its great rate performance (Fig. 3d). The GCD curves at the 200th, 300th, 400th and 500th cycles are well overlapped with decreasing polarization (Fig. 3e, Fig. S9). The medium discharged voltage of the KFOS was 2.9 V initially and got stable at $\sim 3.2 \text{ V}$ with a persistent charging/discharging curve (Fig. 3f and inset). Moreover, a capacity of

Figure 3 Electrochemical characterization of KFOS as the cathode in K-ion half cells. (a) Charge/discharge curve at the current density of 100 mA g^{-1} . (b) CV curve. (c) Charge/discharge curves at varied current rates (100, 200, 300, 400 and 500 mA g^{-1}), and (d) rate capacities. (e) Charge/discharge curves at 200th, 300th, 400th and 500th cycles of a cell at 100 mA g^{-1} . (f) Progressive medium discharge voltages in cycling test. The inset shows the time-voltage curve of the last 40 cycles. (g) Long-term cycling performance.

80 mA h g⁻¹ was obtained after 500 cycles (Fig. 3g), demonstrating its impressive cycling stability. It should be noted that the capacity and stability of the KFOS cathode at >4.5 V are still needed to be explored, waiting for further development of high-voltage electrolyte systems such as sulfone solvent, ionic liquids, etc.

To investigate the working mechanism of KFOS cathode for K-ion storage, we carried out synchrotron XAS of iron K-edge at different charging/discharging states to unveil the valance state and local environments of Fe

during charge/discharge [47–49]. Fig. 4a shows the time-resolved XANES in one cycle. Upon charging, the edge gradually shifted to higher energies and reaches the maximum in fully charged sample, indicating the oxidation of Fe²⁺ to Fe³⁺. A reverse shift was obviously observed on discharged samples, and the XANES of samples at the initial and final states of one cycle matched well with each other, demonstrating the good reversibility of iron state during cycling (Fig. S10). The environments of Fe atoms at different states were further analyzed by *k*²-

Figure 4 The working mechanism of KFOS in K-ion storage. (a) Mapping of Fe K edge XANES in a cycle. (b, c) EXAFS of Fe in charging and discharging. (d) *Ex-situ* XRD patterns in a cycle, and enlarged pattern in (e) 18°–22° and (f) 27°–33°.

weighted Fourier transform of EXAFS. The first peak within 1–2 Å range arose from the nearest O correlation, in accordance with KFOS crystal structure. As depicted in Fig. 4b, during the charging process, the first peak of EXAFS gradually moved to the lower radius, indicating the inter-atomic distance of Fe–O was shortened. The sample at 4.5 V featured the shortest Fe–O bond. While during the discharging, the first peak of EXAFS shifted to the longer radius (Fig. 4c), illustrating the Fe–O bond was elongated progressively. The evolution of Fe–O bond during the whole process is in accordance with the alteration of $\text{Fe}^{2+}/\text{Fe}^{3+}$, and the recovery of Fe–O bond after cycling discloses the reversibility of the process.

Further, *ex-situ* XRD characterizations were performed on KFOS samples at different stages to detect its structural stability. Because of ball milling treatment of the pristine samples and grinding effect during the cell cycling process, recollected KFOS particles have been downsized to a great extent, resulting in the weakened and broadened XRD peaks (Fig. 4d). However, from the enlarged patterns at 18° – 22° and 27° – 33° (Fig. 4e–f), the diffraction peaks at 19.5° , 28.2° , 29.5° and 31.0° , corresponding to (300), (104), (204) and (213) planes, respectively, migrated to larger degrees upon charging, and returned to original degrees on discharging. According to Bragg principles, it elucidates that the lattice of KFOS sample went through a contraction-expansion evolution during the charging/discharging process. Moreover, the similarity of whole XRD patterns and the recovery of the

pattern after a cycle again verify the excellent structure stability of the KFOS cathode.

Our group has previously reported the synthesis and electrochemical study on $\text{KFeC}_2\text{O}_4\text{F}$ [24]. Compared with it, the current study exhibits following features: first, with the aim of using oxalate to obtain iron(II) compound in sulfate system, a mixed polyanionic compound was successfully obtained, which provides new synthesis routine in the preparation of iron(II) compound. Second, the structure of KFOS is distinctively 2D, whereas the other are 3D. Third, although the obtained capacity in this study is less than that in $\text{KFeC}_2\text{O}_4\text{F}$, considering the K-rich nature of KFOS, it is possible to obtain an even higher capacity up to $\sim 140 \text{ mA h g}^{-1}$ via strategies such as replacing iron with multi-valent ions such as Mn or V to allow multi electrons migration. Meanwhile, compared with the existing polyanionic KIBs cathodes, the cycling stability of KFOS is among the best (Table S4).

A proof-of-concept K-based full cell was further configured by pairing this KFOS cathode with an SC anode. The characterization of SC (Fig. S11) confirmed the sample is as expected. Fig. 5a schematically illustrates its working mechanism. Upon charging, K ions are extracted from KFOS cathode and migrate into the SC anode, and a reverse process happens during discharging. Such a full cell at 4.5-V-charged state is capable of power more than ten LED bulbs (Fig. 5b). Fig. 5c displays the performance of the full cell at different current densities. The capacity was fully rebounded when the current density

Figure 5 Full cell characterization. (a) Schematic illustration of the configuration and mechanism of the constructed K-ion full cell. (b) LED bulbs powered by two full cells. (c) Rate performance. (d) Charge/discharge curves at 10th, 50th, 100th and 200th cycles of a full cell at 200 mA g^{-1} . (e) Long-term cycling performance.

decreased to the initial 200 mA g⁻¹, demonstrating the high stability of the cell at high rates. In addition, over 73% capacity was maintained when the current density increased from 200 to 1000 mA g⁻¹, illustrating its excellent rate capability. Moreover, in the test of life span, the GCD curves of 10th, 50th, 100th and 200th cycles exhibited high resemblance and persistent polarization (Fig. 5d), and the cell was very stable after 200 cycles with a capacity retention close to 100% (Fig. 5e), indicating its promising potential for stable K-ion storage in large-scale applications with low cost and environmental friendliness.

CONCLUSIONS

In summary, a new polyanionic compound KFOS was developed as a promising host for K-ion storage. Its unique crystal structure features a novel 2D triple-layered framework comprising wide interlayers and vast intralayer channels for K ion migration, which has never been reported previously. Benefiting from its reversible Fe²⁺/Fe³⁺ redox reactions and high structural stability, in our preliminary test, it delivers a reversible capacity of 85 mA h g⁻¹ in 1.7–4.5 V with an average discharge voltage of around 3.2 V and 94% capacity retention after 500 cycles. Moreover, by coupling this cathode with SC anode, we successfully assembled a full K-ion cell with good rate performance and excellent cycling stability over 200 cycles, suggesting KFOS is a stable K-ion host. By further investigations using high-voltage electrolytes, optimization of its component and structure, for instance, replacing iron with multi-valent transition metals Mn, a trace amount of doping, and surface modification to stabilize Fe⁴⁺, its capacity could be enhanced. Considering its advantages in easy preparation, rich resources, environmental friendliness, and excellent stability, the present study provides a feasible cathode for KIBs with the merits of low cost and environmental friendliness.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details, cif file for KFOS, etc. are available in the online version of the paper.

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一种新型廉价、环境友好、结构稳定且具有大离子通道的钾离子电池正极材料

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摘要 得益于钾的地壳丰度及其与锂的化学相似性, 钾离子电池有望应用于大规模储能领域. 目前, 钾离子电池的性能尚不能满足实用需求, 主要原因在于缺乏合适的正极材料. 基于硫酸根的强诱导效应和草酸体系制备亚铁化合物的优势, 本文制备了一种新型廉价、环境友好且稳定的储钾正极材料 $\text{K}_4\text{Fe}_3(\text{C}_2\text{O}_4)_3(\text{SO}_4)_2$. 其独特的二维层状晶体结构具有 $3.379 \text{ \AA}$ 的层间距, 且层内具有 $4.576 \times 6.846 \text{ \AA}$ 的大环. 根据第一性原理计算, 该结构有利于钾离子的可逆迁移, 且体积变化仅为 6.4% . 不同充放电态样品的同步辐射X射线吸收光谱和XRD、半电池以及全电池的电化学表征证实了其优异的电化学可逆性和结构稳定性. 通过成分调控、掺杂、结构优化等策略, $\text{K}_4\text{Fe}_3(\text{C}_2\text{O}_4)_3(\text{SO}_4)_2$ 正极材料的电化学性能有望进一步提升. 因此, 本工作为廉价、环保的储钾正极材料提供了一种新的稳定晶体模型.