Direct growth of an economic green energy storage material: a monocrystalline jarosite-KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid as a superior lithium-ion battery cathode†

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The exploration of new inexpensive rechargeable batteries with high energy-density electrodes is a key to integrate renewable sources such as solar and wind, and address sustainability issues. Herein, a facile and scalable method is developed to prepare a two-dimensional earth-abundant jarosite-KFe$_3$(SO$_4$)$_2$(OH)$_6$-rGO hybrid via a solution-phase oxidation process at elevated temperature. In this synthesis, single-layer graphene sheets serve as both structure-directing agents and growth platforms to directly grow monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates with unique hexagonal shapes, forming a KFe$_3$(SO$_4$)$_2$(OH)$_6$-rGO hybrid. As a cathode for lithium batteries, the hybrid structure exhibits a high reversible capacity of 120.5 mA h g$^{-1}$ after 100 cycles at a specific current of 2C and thus retains 88% of the maximum capacity. The monocrystalline jarosite-KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates/rGO hybrid exhibits a discharge capacity of 143.6, 113.9, 98.2, 83.9 and 65.9 mA h g$^{-1}$ at 1, 2, 5, 10, and 20C, respectively, and retains a specific capacity of 134.4 mA h g$^{-1}$ when the specific current returns from 20C to 1C, displaying an excellent rate capability. At a high rate of 10C, the jarosite-KFe$_3$(SO$_4$)$_2$(OH)$_6$/rGO composites maintained 70.7 mA h g$^{-1}$ after 300 cycles with a capacity retention of 78.2%, indicating remarkable cycling stability even at a high rate. Compared with KFe$_3$(SO$_4$)$_2$(OH)$_6$ particles, the KFe$_3$(SO$_4$)$_2$(OH)$_6$/rGO nanocomposites exhibit remarkably prolonged cycling life and improved rate capability. Therefore, the earth-abundant jarosite-KFe$_3$(SO$_4$)$_2$(OH)$_6$/rGO hybrid demonstrates great potential for application as a high-performance cathode material in new-generation lithium-ion rechargeable batteries.

Introduction

Rechargeable lithium-ion batteries (LIBs) have emerged as the most popular energy source for portable devices in the past two decades, owing to their advantages of light weight and high efficiency in delivering energy.$^{1-6}$ However, current LIBs still suffer from limited energy density and cycling ability as well as high cost.$^7-9$ Therefore, further improvements are required to expand their applications to a larger field, especially in the field of renewable energy sources (wind and solar) for balancing intermittency with user demands.$^{10-11}$ Energy storage devices with high energy density and low cost are urgently needed to satisfy such a large-volume market.$^{14,15}$

Searching for novel electrode materials that are economic, safe and have high-capacity is crucial to the development and breakthrough of realizing high-performance green LIBs.$^{16,17}$ So far, a series of studies have been carried out to explore such cathode materials to substitute commercial expensive and hazardous LiCoO$_2$.$^{18,19}$ Among a variety of alternative cathode materials, polyaniionic ("XO$_4"$, $X = P, Si, Mo, S, W, etc.$) compounds have received tremendous attention due to their high theoretical capacities, low cost, high thermal stability through strong X-O bonding, better safety and environmental friendliness.$^{20,21}$ Iron based polyaniionic compounds have been extensively studied due to the reasonably high voltage of the Fe$^{2+}$/Fe$^{3+}$ redox couple, earth-abundant resources and safety. Examples include LiFePO$_4$,$^{22}$ LiFeSiO$_4$,$^{23}$ FePO$_4$,$^{24}$ Li$_2$FePO$_4$$O_7$,$^{25}$ LiFeBO$_3$ (ref. 26) and so on. Among these materials, iron-based sulfates have rarely been reported, since Manthiram and Good-enough discovered the insertion of lithium ions in the framework of NASICON type Fe$_3$(SO$_4$)$_3$ in 1989.$^{27}$ Recently, iron based hydrosulfates, particularly jarosite KFe$_3$(SO$_4$)$_2$(OH)$_6$ and NaFe$_3$(SO$_4$)$_2$(OH)$_6$, have been investigated as potential cathode materials for LIBs.$^{28}$ For example, Gnanavel et al. discovered that

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the insertion of lithium into the jarosite hydroxysulfate NaFe3-
(SO4)2(OH)6 leads to amorphous phase Li2+xNaFe3(SO4)2(OH)6 (0 < x < 0.5) via a biphase mechanism. The unique topotactic reversible reaction can be used to explain the electrochemical process of jarosite-type hydroxysulfate, indicating its energy storage capability.29 Moreover, Ding et al. used a template-
assisted redox method to synthesize jarosite KFe3(SO4)2(OH)6 nanosheets that deliver a large specific capacity of 117 mA h g⁻¹ at 0.2C and about 80 mA h g⁻¹ at 10C after 50 cycles, showing excellent rate capability and capacity retention.30 Jarosite KFe3(SO4)2(OH)6 found in natural acid minerals, is a stable and acid-resisting material with a rhombohedral crystal structure that is made up of linear tetrahedral–octahedral–tetrahedral [T–O–T] sheets with potassium located between them at 12-fold coordinate. Small cations like lithium ions or sodium ions can intercalate and deintercalate between the layers in spite of the presence of K⁺ ions.31–33 In theory, there are three lithium ions that can be intercalated and deintercalated in per formula of KFe3(SO4)2(OH)6 crystal structure in the potential range of 1.5–4 V vs. Li/Li⁺, via reduction/oxidation between Fe³⁺ and Fe²⁺, corresponding to a theoretical capacity of 166 mA h g⁻¹, which makes it a promising cathode material for LIBs.35

Meanwhile, two-dimensional nanostructured electrode materials attract more and more attention due to their enlarged surface area and shortened diffusion length, resulting in increased active contacts and accelerated Li⁺ and electron transport.34 Moreover, it is believed that two-dimensional nanostructures can effectively sustain high lithium insertion/deinsertion strain, maintain structural integrity and lead to a better cycling stability.35 However, reported 2D nanostructures are mostly composed of simple metal oxides, hydroxides and metal sulfides. It remains a challenge to fabricate 2D nanostructures based on complex compounds with well-defined morphology and crystallinity.

Graphene, as a typical two-dimensional nanomaterial with the advantages of light weight, high electrical conductivity, high mechanical strength and flexibility, is deemed as an ideal single-atom-thick substrate for the growth of active nanomaterials, especially for two-dimensional active materials since they display an analogous structure to that of graphene.36–38 Successful efforts have been devoted to preparing various 2D electrode materials hybridized with graphene for improving electrochemical storage properties. For example, Cheng et al.39 reported self-assembled V2O5 nanosheets/reduced graphene oxide (rGO) hierarchical nanocomposites, delivering a discharge capacity of 102 mA h g⁻¹ after 160 cycles at 2C and showing good cycling stability at high specific current. Moreover, Chang et al.40 synthesized MoS2/graphene nanosheet composites by using a one-step in situ solution phase method. The MoS2/graphene nanosheet composites exhibit an extraordinary capacity up to 1300 mA h g⁻¹ after 50 cycles at 100 mA g⁻¹, displaying excellent energy storage capability. Such improved performances are attributed to the unique two-dimensional structure and high electrical conductivity of graphene, and intimate interaction between active materials and graphene.40 Though nanosheets/ nanoplates on graphene oxide nanosheets have been reported,41 it is still highly desirable to synthesize monocrystalline nanoplates of complex compounds on single-layer graphene with high electrical conductivity, considering that a plate-on-sheet (KFe3(SO4)2(OH)6/graphene) nanostructure is beneficial for lithium ions and electrons to access their surface, consequently enabling a fast conversion reaction.

Herein, we prepare a monocrystalline jarosite-KFe3(SO4)2-
(OH)6-nanoplates/rGO hybrid via a facile and scalable solution-phase oxidation process at elevated temperature. In a typical synthesis, the single-layer graphene oxide sheet serves as both the structure-directing agent and growth platform for the direct growth of monocrystalline KFe3(SO4)2(OH)6 hexagonal nanoplates. In this way, monocrystalline KFe3(SO4)2(OH)6 hexagonal nanoplates are chemically bonded with graphene oxide via the oxidation of ferrous ions and the reduction of the graphene oxide. Finally, a KFe3(SO4)2(OH)6-nanoplates/rGO hybrid is achieved. In this hybrid structure, the merits of monocrystalline KFe3(SO4)2(OH)6 nanoplates can be effectively combined with the excellent electrical conductivity of graphene, yielding a cathode material with high energy density and low cost. Therefore, it is anticipated that the as-prepared KFe3(SO4)2-
(OH)6/rGO composites would display excellent rate capability and long cycling life.

**Experimental**

The first step is to grow monocrystalline KFe3(SO4)2(OH)6 nanoplates on single-layer graphene oxide nanosheets. First, 10 mg single-layered GO sheets (ACS material) were sonicated in 30 ml deionized water for one hour. Then, in a typical synthesis, potassium nitrate (0.20 g) and ferrous sulfate (1.68 g) were added and dissolved in it. After stirring for 10 min, 10 µl H2SO4 (98%) were added dropwise into the solution. Afterwards, the solution was sealed and stirred at a constant temperature of 80 °C for 12 h in a water bath. Finally, grey precipitates were collected by centrifuging and were rinsed with deionized water and alcohol several times alternatively.

The second step is the further reduction process of graphene oxide in hydrazine hydrate solution. 20 µl hydrazine hydrate was dissolved in 200 ml deionized water, followed by adding KFe3(SO4)2(OH)6@rGO prepared in the previous step. The obtained mixture was stirred for 10 h at room temperature (25 °C). Then the as-prepared KFe3(SO4)2(OH)6@rGO product was collected by centrifuging and was rinsed with deionized water and alcohol several times alternatively.

For comparison purposes, bulk KFe3(SO4)2(OH)6 powders were prepared according to the literature.42 In this synthesis, potassium nitrate (0.2 g) and iron sulfate (1.18 g) were dissolved in 0.01 M H2SO4 aqueous solution (100 ml) under magnetic stirring. The above mixed solution was then stirred at 80 °C for 12 h. The obtained suspension was collected by centrifuging and was rinsed with deionized water and alcohol several times alternatively.

**Characterization**

Crystallographic structures of the obtained products were determined by Rigaku MiniFlex X-ray diffraction (XRD)
measurements with Cu Kα radiation in a 2θ range from 10° to 80° at room temperature. The surface morphology, particle size and energy dispersive spectra (EDS) were studied using a FEI Quanta 3D FEG field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) images and selected area electron diffraction patterns (SAED) of the KFe3(SO4)2(OH)6-nanoplates/rGO composites were taken using a JEOL HRTEM (JEM-1400 electron microscope) with an acceleration voltage of 120 kV. The chemical states were analyzed via X-ray photoelectron spectroscopy (XPS) using an AXIS165 spectrometer using a twin-anode Al Kα (1486.6 eV) X-ray source with the charge neutralization function being turned on.

Electrochemical measurements

The cathode was composed of the as-prepared (monocrystalline KFe3(SO4)2(OH)6) nanoplates/rGO composite, or bulk KFe3(SO4)2(OH)6, and acetylene black as well as poly(tetrafluoroethylene) (PTFE) binder mixed at a weight ratio of 7 : 2 : 1 in deionized water followed by drying. The mass loading of each cathode electrode is 2.43 mg. The cathodes were then assembled into CR2032-type coin cells in an argon filled glove-box using lithium foil as the anode and Celgard-2320 membrane as the separator; the electrolyte was 1 M LiPF6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) and diethylene carbonate (DEC) in a volumetric ratio of 1 : 1 : 1. The coin cells were aged for 12 h before electrochemical measurements to ensure full electrochemical intercalation of lithium. Galvanostatic charge/discharge measurements were performed using an eight-channel battery analyzer (MTI Corporation) in a voltage range of 1.5–4.0 V versus Li+/Li. Cyclic voltammetry (CV) measurements were performed with an electrochemical workstation (CHI 6504C) in a voltage range of 1.5–4.0 V versus Li+/Li. Cyclic voltammetry (CV) measurements were carried out using a three-electrode cell with a LiPF6/EC/DMC/DEC electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were conducted by applying an AC potential of 5 mV amplitude in the frequency range from 0.01 to 100 kHz.

Results and discussion

Fig. 1 shows a schematic illustrating the synthesis procedure of the monocrystalline KFe3(SO4)2(OH)6-nanoplates/rGO hybrid via oxidation of ferrous ions and reduction of GO. In this process, Fe2+ cations derived from FeSO4 favorably bind with the oxygen-containing groups on the single-layered graphene oxide sheets via electrostatic interactions. Upon heating the mixture to 80 °C, Fe2+ cations gradually oxidized to Fe3+ cations while accelerating the hydrolysis leading to an acidic environment of the solution, while GO is reduced simultaneously. In this process, the surface functional groups of graphene oxide sheets as reaction active sites provide preferred nucleation sites for the growth and crystallization of KFe3(SO4)2(OH)6, enabling good dispersion of KFe3(SO4)2(OH)6 nucleated nanoparticles on the graphene platform, as confirmed by the ex situ SEM image (Fig. S1a†). After 3 hours of reaction, tiny nucleated nanoparticles of KFe3(SO4)2(OH)6 are uniformly distributed on the graphene nanosheets. When the reaction time is prolonged to 5 hours, the nucleated nanoparticles grow larger and are firmly attached on the graphene nanosheets. Afterwards, small particles pre-coated on graphene nanosheets diffuse and recrystallize into single-crystalline nanoplates with well-defined hexagonal shapes. For comparison purposes, KFe3(SO4)2(OH)6 powders are also synthesized without graphene oxide nanosheets. Without the graphene oxide nanosheets as substrates to direct the growth of KFe3(SO4)2(OH)6, the small nucleated particles of KFe3(SO4)2(OH)6 tend to aggregate and grow into large particles. The synthesis process of the monocrystalline KFe3(SO4)2(OH)6-nanoplate@rGO hybrid is also confirmed by XPS results in Fig. 2. Fig. 2a reveals the presence of carbon, potassium, sulfur, oxygen and iron in the KFe3(SO4)2(OH)6-nanoplate@rGO hybrid sample. Fig. 2b and c depict the high-resolution XPS spectrum of Fe 2p and C 1s of the monocrystalline KFe3(SO4)2(OH)6-nanoplates@rGO hybrid, bulk KFe3(SO4)2(OH)6 and graphene oxide, respectively. Fig. 2b confirms that Fe in both the KFe3(SO4)2(OH)6-nanoplates@rGO hybrid and bulk KFe3(SO4)2(OH)6 only exists in the form of Fe3+, as proved by the characteristic peak of Fe3+ at 718 eV together with two Fe 2p peaks at 717 and 720 eV, confirming that iron is oxidized by graphene oxide. In addition, it is clearly seen in Fig. 2c that the first peak at 283 eV (A) corresponds to the sp2 aromatic C–C bond, and the peak at 285 eV is related to the C–O group, whereas the other two peaks at 287 and 290 eV are due to the C≡O peak and K 2p, respectively. Therefore, it is confirmed that GO is partially reduced by ferrous ions and further reduced into rGO as evidenced by the disappearance of the C≡O peak and the lower intensity of C–O peaks in KFe3(SO4)2(OH)6@GO and KFe3(SO4)2(OH)6@rGO samples. The crystal structures of the monocrystalline KFe3(SO4)2(OH)6-nanoplates@rGO hybrid and KFe3(SO4)2(OH)6 bulk are determined by XRD. The XRD pattern in Fig. 2d is identified as rhombohedral KFe3(SO4)2(OH)6, which matches well with those of the standard XRD patterns of rhombohedral jarosite KFe3(SO4)2(OH)6 (JCPDF card no. 01-071-1777), with lattice parameters of a = 7.29 Å, b = 7.29 Å, c = 17.16 Å, and R3m space group, confirming the purity of the products of monocrystalline KFe3(SO4)2(OH)6 nanoplates and KFe3(SO4)2(OH)6 bulk. It is noted that there are no obvious diffraction peaks from rGO due to its low content.

Fig. 3 shows SEM images of the monocrystalline KFe3(SO4)2(OH)6-nanoplate@rGO hybrid and bulk KFe3(SO4)2(OH)6. Fig. 3a and b show the SEM images of the monocrystalline KFe3(SO4)2(OH)6-nanoplates@GO hybrid at high and low magnifications, respectively, revealing well-defined hexagonal
monocrystalline KFe₃(SO₄)₂(OH)₆ nanoplates with an average width of ~800 nm and a thickness of ~100 nm. Moreover, the monocrystalline KFe₃(SO₄)₂(OH)₆ nanoplates are bonded on the flexible single-layer graphene sheets, indicating the close interaction between them. Moreover, the single-layer graphene nanosheets overlap with each other, forming a three-dimensional conducting network for fast electron transport pathways. In contrast, the bulk KFe₃(SO₄)₂(OH)₆ aggregates and is composed of irregular micron-sized KFe₃(SO₄)₂(OH)₆ particles as shown in Fig. 3c and d. Such a distinct difference in the morphology and size of the two KFe₃(SO₄)₂(OH)₆ products highlights the important role of graphene nanosheets as substrates directing the growth of monocrystalline KFe₃(SO₄)₂(OH)₆ nanoplates. Due to strong interactions with the dense functional groups and defects on the surface of graphene nanosheets, the nucleated KFe₃(SO₄)₂(OH)₆ precursor on the graphene nanosheets tends to transform into monocrystalline KFe₃(SO₄)₂(OH)₆ nanoplates with well-defined shapes instead of aggregating into irregular bulks with a large size. To further study the elemental composition and distribution of the KFe₃(SO₄)₂(OH)₆@rGO hybrid, EDS mapping is performed. It is clearly observed in Fig. 4 that the monocrystalline KFe₃(SO₄)₂(OH)₆@rGO hybrid is made of C, O, Fe, S, and K elements. All the elements are distributed homogeneously in the selected area, indicating the uniformity of the as-prepared KFe₃(SO₄)₂(OH)₆@rGO hybrid. Moreover, the content of carbon is found to be about 9.6% in weight, corresponding to 9.6 wt% rGO in the sample.

In order to further identify the morphology and crystallinity of the monocrystalline KFe₃(SO₄)₂(OH)₆@rGO hybrid sample, TEM coupled with electron diffraction capability is performed as shown in Fig. 5. It can be seen in Fig. 5a that
monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates are firmly bonded on the graphene sheets. Fig. 5b displays a TEM image of two individual monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates, revealing their well-defined hexagonal shapes. And the electron diffraction pattern obtained from a single KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplate (Fig. 5c) confirms the rhombohedral monocrystalline nature of the KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplate. Fig. 5d shows a schematic showing the hexagonal monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates grown on the graphene nanosheets.

To evaluate the electrochemical performances of all the samples, coin cells made of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid and bulk KFe$_3$(SO$_4$)$_2$(OH)$_6$ are assembled and cycled in a voltage range of 1.5–4 V versus Li$^+$/Li. As a novel cathode material for LIBs, the cyclic voltammetry (CV) profile of KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO is obtained at a scan rate of 0.1 mV s$^{-1}$ in a potential region of 1.5–4 V to explore the lithium insertion/extraction behaviors. Fig. 6a displays the CV curves of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid, showing two characteristic anodic peaks at 2.488 and 2.186 V and two cathodic peaks occurring at 2.578 V and 3.068 V, in the first potential sweeping cycle, which are ascribed to the intercalation and deintercalation of lithium ions into the layers of the KFe$_3$(SO$_4$)$_2$(OH)$_6$ crystal structure. In subsequent cycles, intercalation of lithium ions takes place at 2.585 V and 2.308 V vs. Li/Li$^+$. Such a peak shift is attributed to a biphasic mechanism that occurs in the first discharge process. Fig. 6b displays the charge and discharge characteristics of the
The KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid delivers an initial capacity of 67.9 mA h g$^{-1}$, and a maximum capacity of 90.4 mA h g$^{-1}$ in the 65th cycle, retaining 70.7 mA h g$^{-1}$ after 300 cycles with a capacity retention of 78.2%, indicating excellent cycling stability at high charge/discharge rates. In contrast, the bulk KFe$_3$(SO$_4$)$_2$(OH)$_6$ delivers an initial capacity of 67.0 mA h g$^{-1}$ at the same rate and rapidly decays to less than 30 mA h g$^{-1}$ after 50 cycles. The high capacity, long cycling life and excellent rate capability of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid can be attributed to the stable crystal structure of jarosite style KFe$_3$(SO$_4$)$_2$(OH)$_6$, the morphology of two-dimensional nanoplates, and bonding between graphene sheets and monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates grown on them, which facilitates fast electron transport since electrons can be efficiently conducted back and forth from monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates to the reduced graphene sheets.

To examine the kinetics of the electrodes, EIS tests were carried out on the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid and KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk before and after 300 electrochemical cycles. The EIS technology is one of the most powerful tools to study electrochemical reactions, such as the processes occurring at the electrode/electrolyte interfaces and Li$^+$ intercalation/de-intercalation processes in the interior of cathode/anode materials. In the equivalent circuit, $R_\text{ct}$ represents the ohmic resistance of the electrode system, including the electrolyte and the cell components. $R_\text{s}$ represents the charge transfer resistance. $CPE$ and $Z_w$ are the double layer capacitance and the Warburg impedance, respectively. Fig. 7a and b exhibit the Nyquist plots of the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid and KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk before and after 300 cycles, respectively. All the Nyquist plots are composed of depressed semicircles in the medium-frequency region followed by a slanted line in the low-frequency region. Compared with the KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk (423 $\Omega$), the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid shows a much lower resistance of 84.6 $\Omega$, indicating that the reduced graphene sheets and the unique nanoplate composite structure indeed enhance the electron transport and modify the kinetics of the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid sample. Additionally, compared with the KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid and KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk before and after 300 cycles at 2C.

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**Fig. 6 (a) CV curves and (b) galvanostatic charge–discharge profiles of the first three cycles of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid. (c) Cycling performances of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid and bulk KFe$_3$(SO$_4$)$_2$(OH)$_6$ at 2C. (d) Rate performances of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid at rates ranging from 1C, 2C, 5C, 10C, 20C to 20C then back to 1C, its discharge capacity recovers to 134.4 mA h g$^{-1}$ at once and maintains a good capacity retention in the following cycles, showing much better rate capability than that of the KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk (40.3 mA h g$^{-1}$). Fig. 6e shows the long cycling performances of the two samples when charged/discharged at a very high rate of 10C for 300 cycles. The KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid delivers an initial capacity of 67.9 mA h g$^{-1}$, and a maximum capacity of 90.4 mA h g$^{-1}$ in the 65th cycle, retaining 70.7 mA h g$^{-1}$ after 300 cycles with a capacity retention of 78.2%, indicating excellent cycling stability at high charge/discharge rates. In contrast, the bulk KFe$_3$(SO$_4$)$_2$(OH)$_6$ delivers an initial capacity of 67.0 mA h g$^{-1}$ at the same rate and rapidly decays to less than 30 mA h g$^{-1}$ after 50 cycles. The high capacity, long cycling life and excellent rate capability of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid can be attributed to the stable crystal structure of jarosite style KFe$_3$(SO$_4$)$_2$(OH)$_6$, the morphology of two-dimensional nanoplates, and bonding between graphene sheets and monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates grown on them, which facilitates fast electron transport since electrons can be efficiently conducted back and forth from monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates to the reduced graphene sheets.**

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**Fig. 7 AC impedance plots of the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid and KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk before and after 300 cycles at 2C.**
bulk, the slope of the plot from the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid is increased distinctly in the low-frequency range, suggesting that the $R_{ct}$ of the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO composite is much lower than that of the KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk. To evaluate electrochemical kinetics of these electrodes, the Li-ion diffusion coefficients of different electrodes are calculated using the equation $D = 0.5RT/\pi n^2 A_s C_f$, where $R$ is the gas constant, $T$ is the temperature, $A$ is the area of the electrode surface, $F$ is Faraday’s constant, and $C$ is the molar concentration of Li ions. The calculated lithium diffusion coefficient values of the monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid and bulk KFe$_3$(SO$_4$)$_2$(OH)$_6$ are $1.35 \times 10^{-10}$ and $2.34 \times 10^{-11}$ cm$^2$ s$^{-1}$, respectively. It can be seen that the lithium diffusion coefficient of the monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid is approximately one order of magnitude higher than that of bulk KFe$_3$(SO$_4$)$_2$(OH)$_6$. Moreover, after 300 cycles, the KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk shows an increased $R_{ct}$ resistance of 600 Ω and an obvious decrease of the slope of the slanted line in the low-frequency region, indicating the increased ohmic resistance of the electrode and charge transfer resistance. In comparison with the sample before 300 cycles, the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO composite shows a $R_{ct}$ resistance slightly decreased to 52.0 Ω and the closed slope of the slanted line, indicating stable kinetics of the electrochemical reaction. Furthermore, ex situ SEM images of the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO composite and the KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk electrode after 300 cycles. It can be seen that the oxide nanoplates in the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO hybrid sample maintain their hexagonal morphology perfectly and remain firmly attached to the reduced graphene sheets instead of disintegrating and pulverizing even after 300 cycles. In comparison, though the shape of the KFe$_3$(SO$_4$)$_2$(OH)$_6$ bulk is preserved after 300 cycles when cycled at 2C, the size of the bulk is significantly reduced, possibly caused by severe pulverization during cycling. Some small impurity particles around the monocrystalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoplates are also observed and are considered as carbon black particles and binder.

Based on the above results, the high capacity as well as excellent rate capability and good cycling stability of KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO composites are attributed to the following reasons. First, the direct growth of monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoparticles on the single-layer graphene sheets ensures chemical bonding between the active nanomaterials and the conducting graphene network, and thus facilitates efficient charge transport since charge carriers can be conducted back and forth from the monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoparticles to the current collector effectively and rapidly through the highly conducting single-layer graphene network. Moreover, monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoparticles directly grown on the graphene sheets are well-dispersed via graphene-nanoplate interactions, efficiently avoiding aggregation and benefiting the rate capability and cycling life of the oxide. In addition, compared with the micron-sized bulk counterpart, the two-dimensional nanoparticles provide many more active reaction sites for the intercalation and deintercalation of lithium ions and a much shortened distance for lithium ion diffusion and electron transportation, and thus significantly improve the rate capability of the electrode.

Compared with KFe$_3$(SO$_4$)$_2$(OH)$_6$-based cathodes reported previously, the KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO composite in this work shows significantly prolonged cycling performance and improved rate capability, when cycled at 10C and even at a rate as high as 20C. Additionally, compared to syntheses of popular cathodes such as LiFePO$_4$ (ref. 46) and LiMn$_2$O$_4$, the jarosite KFe$_3$(SO$_4$)$_2$(OH)$_6$@rGO composite can be obtained via a facile low-cost solution-phase oxidation process without using any high-temperature sintering, which is ideal for large-scale production.

Conclusions

A simple and scalable approach is developed to synthesize a monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid via a solution-phase oxidation process at elevated temperature. With single-layered graphene sheets as structure-directing agents and growth platforms, monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$ nanoparticles with well-defined hexagonal shapes are directly grown on the reduced graphene sheets. Because of the unique structure of the KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid and the bonding between KFe$_3$(SO$_4$)$_2$(OH)$_6$ and rGO that provide a high surface area, efficient charge transport pathways and excellent structural flexibility for accommodating volume change during cycling, the as-prepared monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid shows significantly improved rate capability and long cycling life compared to micron-sized KFe$_3$(SO$_4$)$_2$(OH)$_6$ aggregates synthesized without graphene. When the charge/discharge rate is as high as 10C, the monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid exhibits a high reversible capacity of 70.7 mA h g$^{-1}$ after 300 cycles. In addition to the earth-abundant resources of KFe$_3$(SO$_4$)$_2$(OH)$_6$, the monocristalline KFe$_3$(SO$_4$)$_2$(OH)$_6$-nanoplates@rGO hybrid prepared via such a simple and cost-effective synthesis process demonstrates excellent electrochemical performance and will thus be a promising cathode material for large-scale energy storage systems.

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Notes and references