The Core-Shell Heterostructure CNT@Li$_2$FeSiO$_4$@C as a Highly Stable Cathode Material for Lithium-Ion Batteries

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Abstract

The reasonable design of nanostructure is the key to solving the inherent defects and realizing a high performance of Li$_2$FeSiO$_4$ cathode materials. In this work, a novel heterostructure CNT@Li$_2$FeSiO$_4$@C has been designed and synthesized and used as a cathode material for lithium-ion battery. It is revealed that the product has a uniform core-shell structure, and the thickness of the Li$_2$FeSiO$_4$ layer and the outer carbon layer is about 19 nm and 2 nm, respectively. The rational design effectively accelerates the diffusion of lithium ions, improves the electric conductivity, and relieves the volume change during the charging/discharging process. With the advantages of its specific structure, CNT@Li$_2$FeSiO$_4$@C has successfully overcome the inherent shortcomings of Li$_2$FeSiO$_4$ and shown good reversible capacity and cycle properties.

Keywords: Lithium-ion batteries, Cathode, Li$_2$FeSiO$_4$, Core-shell structure

Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices and electric vehicles because of the advantages of high-efficiency energy conversion, long cycling life, high energy density, and low self-discharge [1–3]. However, new generation LIBs with higher energy density, higher rate capability, and higher cycling performance are urgently needed to meet the development of electric vehicles [4–6]. It has been recognized that exploiting new cathode materials is of great significance for the development of the new generation LIBs, as the performance of LIBs is closely related to the properties of cathode materials. In the last few years, the Li$_2$FeSiO$_4$ cathode material has aroused great attention due to its inexpensive, good chemical stability and environmentally friendly. Especially, it is potential to insert/extract two lithium ions for each molecular unit having a capacity of 332 mAh g$^{-1}$ in theory [7, 8]. Yet it is hard to realize the two Li storages in practical applications, because of the low conductivity ($\sim 6 \times 10^{-14}$ S cm$^{-1}$) and the lithium-ion diffusion coefficient ($\sim 10^{-14}$ cm$^2$ s$^{-1}$) of Li$_2$FeSiO$_4$ [9–12]. Hence, it is very important to improve the electronic conductivity and lithium-ion transport ability of Li$_2$FeSiO$_4$ cathode to optimize the performance of LIBs. Many efforts have been made to solve these problems, such as synthesizing nanoscale Li$_2$FeSiO$_4$ [13–15] and coating the surface with a carbon material [16–18]. However, it often encounters two problems during the synthesis process. One problem is that it is difficult to synthesize a pure-phase Li$_2$FeSiO$_4$ product, and some accompanying impurities such as Fe$_3$O$_4$ or Li$_2$SiO$_3$ are often unavoidable, which is adverse to the practice capacity [19, 20]. The other problem is that the nanostructure of Li$_2$FeSiO$_4$ often encounters damage during the annealing treatment.

In this study, a core-shell heterostructure CNT@Li$_2$FeSiO$_4$@C cathode material has been synthesized. Compared with the reported work about Li$_2$FeSiO$_4$ cathode material, the CNT@Li$_2$FeSiO$_4$@C material exhibits the advantage of no impurity phase and structural integrity by adjusting the chemical reagent metering ratio and reaction conditions. In addition, the inner layer of CNT...
can increase conductivity. The thickness of the Li$_2$FeSiO$_4$ in the middle layer is only 20–25 nm, which benefits the Li$^+$ diffusion. And the outer amorphous carbon layer can improve conductivity and protect the internal frame structure. Therefore, the core-shell heterostructure CNT@Li$_2$FeSiO$_4@C$ exhibits a significant improvement in specific capacity, cycle stability, and rate performance.

**Methods**

**Materials and Synthesis**

The CNT@Li$_2$FeSiO$_4@C$ was fabricated by a step-by-step preparation process. First, the CNT@SiO$_2$ coaxial structure was prepared by a sol-gel coating process [21, 22]. Typically, 8 mg of CNTs was dispersed in the mixture of 80 mL of ethanol and 30 mL of deionized water, and then the mixture was sonicated for 30 min to form a homogeneous solution. Then, 2 mL of NH$_4$H$_2$O (25–28 wt.%) and 0.16 g of cetyltrimethylammonium bromide (CTAB) were added into the above solution under sonicated and kept for 20 min. The mixed solution containing 0.45 mL of tetraethoxysilane (TEOS) and 40 mL of ethanol was dripped into the above solution under magnetic stirring for more than 40 min, which was followed by stirring for 10 h. The CNT@SiO$_2$ product was obtained by centrifugation and cleaning with deionized water and ethanol. Next, the CNT@Li$_2$FeSiO$_4$ was obtained by solid-phase sintering. The aqueous solution of 0.334 g LiAc·2H$_2$O and 0.734 g Fe(NO$_3$)$_3$·9H$_2$O was successively dissolved in 30 mL ethanol under stirring for 20 min. Then, it was transferred to a vacuum dryer of 80°C for 12 h. The obtained CNT@SiO$_2$ was added to the solution and sonicated for 40 min and magnetic stirring for 20 min. Then, it was washed by centrifugation and cleaning with deionized water and ethanol. Finally, the CNT@Li$_2$FeSiO$_4@C$ was prepared by using glucose as a carbon source. 0.2 g of CNT@Li$_2$FeSiO$_4$ was dispersed by ultrasonic for 40 min in 40 mL ethanol. Then, the solution containing 0.1 g of glucose was added to the solution. The resulting solution was placed in a vacuum dryer at 80°C for 12 h and then kept at 650°C for 10 h in the argon atmosphere; as a result, the CNT@Li$_2$FeSiO$_4$ was prepared. The CNT@Li$_2$FeSiO$_4@C$ was prepared by using glucose as a carbon source. 0.2 g of CNT@Li$_2$FeSiO$_4$ was dispersed by ultrasonic for 40 min in 40 mL ethanol. Then, the solution containing 0.1 g of glucose was added to the solution. The resulting solution was placed in a vacuum dryer at 80°C for 6 h. Then, the product was calcined 400°C for 4 h in argon atmosphere to get the CNT@Li$_2$FeSiO$_4@C$ cathode material.

**Materials Characterization**

The crystalline structure of the CNT@Li$_2$FeSiO$_4@C$ and CNT@Li$_2$FeSiO$_4$ was characterized by X-ray diffraction (XRD, D2 PHASER Bruker) in the 2θ ranging from 10° to 80° with Cu-Kα radiation ($\lambda = 1.5418$ Å) radiation at 30 kV and 10 mA. The chemical elements of the materials were verified by X-ray photoelectron spectroscopy (XPS, K-ALPHA 0.5EV) system. The scanning electron microscopy (FESEM, S-4800) and transmission electron microscopy (TEM, Tecnai G2 F 20) were used to observe the structure and morphology of the materials. The distribution of element in the composite was revealed by energy-dispersive X-ray spectroscopy (EDX). The carbon content of the composite was examined by thermogravimetric analyzer (TGA) curve (STD Q600 TA) with a speed of 10°C min$^{-1}$ from RT to 800°C.

**Electrochemical Measurements**

The cathode was made by 10 wt.% polyvinylidene fluoride (PVDF), 20 wt.% acetylene black, and 70 wt.% active material dispersed in N-methyl-2-pyrrolidone (NMP) to form a consistent slurry. Then the slurry was coated onto the Al foil and dried under vacuum at 80°C for more than 12 h. The mass loading of the active material for CNT@Li$_2$FeSiO$_4@C$ and CNT@Li$_2$FeSiO$_4$ electrode was about 1.5 mg/cm$^2$. At last, the half cells were assembled in an argon-filled glove box. The battery was tested for charge and discharge using a Neware battery system over a voltage window of 1.5–4.8 V. Cyclic voltammetric (CV) measurement was carried out on a VMP3 multichannel electrochemical workstation (France, Bio-logic) at different scan rates.

**Results and Discussion**

The schematic diagram of the preparation process of the CNT@Li$_2$FeSiO$_4@C$ material is shown in Fig. 1. First, the CNT@SiO$_2$ was prepared by a simple sol-gel method. By controlling the dosage of CNT and TEOS, the purpose of accurately controlling the thickness of the Li$_2$FeSiO$_4$ layer was achieved. Second, CNT@Li$_2$FeSiO$_4$ with good crystallinity was obtained by annealing at 650°C for 10 h in argon atmosphere. Finally, the CNT@Li$_2$FeSiO$_4$ was coated with amorphous carbon only at 400°C to achieve the core-shell heterostructure CNT@Li$_2$FeSiO$_4@C$.

Figure 2a depicts the XRD patterns of CNT@Li$_2$FeSiO$_4$ and CNT@Li$_2$FeSiO$_4@C$. The diffraction peaks of Li$_2$FeSiO$_4$ are consistent with the monoclinic structure with p2$_1$/n space group. Moreover, no XRD diffraction peak of impurities (such as Fe$_3$O$_4$ and Li$_2$SiO$_3$) is observed, which confirms the purity of the obtained product. The main element and the surface valence state CNT@Li$_2$FeSiO$_4@C$ are studied by XPS (Fig. 2b–d). Figure 2b shows the full spectrum of Li$_2$FeSiO$_4$, including Li 1s, Si 2p, Si 2s, C 1s, O 1s, and Fe 2p. Figure 2c shows the Fe2p spectrum, and two peaks at 710.3 eV and 723.8 eV are attributed to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ of Fe$^{2+}$, respectively. The binding energy satellite peak at 710.4 eV is 4.6 eV lower than the binding energy satellite peak at 715.0 eV, which further indicates that only Fe$^{2+}$ exists in Li$_2$FeSiO$_4$ nanocrystals [23]. Figure 2d shows that the peak at Si 2p at 101.8 eV is substantially consistent with the peak at Si$^{2+}$ in polysiloxane, which proves the formation of orthogonal silicate structure [SiO$_4$] [24, 25].
Scanning electron microscopy (SEM) reveals the morphology and structure of CNT (Additional file 1: Figure S1A), CNT@SiO₂ (Additional file 1: Figure S1B), CNT@Li₂FeSiO₄ (Fig. 3a, b), and CNT@Li₂FeSiO₄@C (Fig. 3c, d). It is worth noting that the one-dimensional nanostructure of both CNT@Li₂FeSiO₄ and CNT@Li₂FeSiO₄@C is kept and no free Li₂FeSiO₄ particles are observed. The TG result confirms that the carbon content of CNT@Li₂FeSiO₄ and CNT@Li₂FeSiO₄@C was 16.93% and 22.69%, respectively (Additional file 1: Figure S2).

The structure of CNT@Li₂FeSiO₄ and CNT@Li₂FeSiO₄@C is further confirmed by transmission electron microscopy (TEM). The core-shell structure of CNT@Li₂FeSiO₄ can be visually discerned from Fig. 3e and f. The
Fig. 3  a, b SEM images of CNT@Li$_2$FeSiO$_4$. c and d SEM images of CNT@Li$_2$FeSiO$_4$@C.  e and f TEM images of CNT@Li$_2$FeSiO$_4$. h and i TEM images of CNT@Li$_2$FeSiO$_4$@C.; j and k HRTEM of CNT@Li$_2$FeSiO$_4$@C and CNT@Li$_2$FeSiO$_4$@C, respectively; l–o EDX elemental mappings of Fe, Si, and O.

Fig. 4  a The charge/discharge curves of CNT@Li$_2$FeSiO$_4$ electrode at the rate of 0.2 C. b the charge/discharge curves of CNT@Li$_2$FeSiO$_4$@C electrode at the rate of 0.2 C. c the cycling performance of CNT@Li$_2$FeSiO$_4$ and CNT@Li$_2$FeSiO$_4$@C electrode, and d the rate performance of CNT@Li$_2$FeSiO$_4$ and CNT@Li$_2$FeSiO$_4$@C electrode.
total diameter of CNT@Li2FeSiO4 is about 70 nm and the thickness of the outer layer Li2FeSiO4 is 20 nm. The core-shell heterostructure of CNT@Li2FeSiO4@C can be clearly confirmed in Fig. 3h and i. Moreover, Fig. 3i further shows the one-dimensional nanostructure of the CNT@Li2FeSiO4@C with a diameter of about 85 nm. The inner layer of CNT has a diameter of about 40 nm, and the middle layer of Li2FeSiO4 has a thickness of about 16–22 nm. And the thickness of the outer carbon layer is around 2 nm. Figure 3j and k shows the HR-TEM of CNT@Li2FeSiO4 and CNT@Li2FeSiO4@C, respectively. The lattice fringe with a distance of 0.27 nm coincides with the (−103) lattice spacing of the orthorhombic Li2FeSiO4. Figure 3l also shows the thickness of the outer amorphous carbon is around 1.5 nm. Figure 3m–o are elemental mapping analysis of CNT@Li2FeSiO4, which demonstrates the coexistence and uniform distribution of Fe, Si, and O elements.

The cycling performance of CNT@Li2FeSiO4 and CNT@Li2FeSiO4@C was tested on a Neware battery test system with a voltage window of 1.5–4.8 V at a current density of 0.2 C. As shown in Fig. 4a, the first discharge specific capacity of the CNT@Li2FeSiO4 is 100.8 mAh g−1 and the capacity retention after 2, 10, 50, and 150 cycles was 95.2%, 92.8%, 91%, and 78.2%, respectively. By contrast, the CNT@Li2FeSiO4@C has the charge capacity of 207 mAh g−1 and the discharge capacity of 178 mAh g−1 in the initial cycle (Fig. 4b). After 2, 10, 50, and 150 cycles, the discharge capacity retention of the CNT@Li2FeSiO4@C electrode are remained at 95.5%, 93.3%, 92.4%, and 89.3%, respectively. Obviously, CNT@Li2FeSiO4@C has much higher capacity and better cycling performance compared to CNT@Li2FeSiO4, which should be due to its much higher conductivity [26, 27]. As far as we know, the cycling characteristics of CNT@Li2FeSiO4@C in this work exhibits much better cycling performance compared with that of previous reports. For instance, porous Li2FeSiO4/C nanocomposite prepared by tartaric acid-assisted sol-gel method had an initial discharge capacity of 176.8 mAh g−1 at 0.5 C and a reversible capacity of 132.1 mAh g−1 at 1 C after 50 cycles [28]. Reduced graphene oxide modified Li2FeSiO4/C composite was synthesized by a citric-acid-based sol-gel method that could deliver a reversible capacity of 178 mAh g−1 at 0.1 C and a capacity retention of 94.5% after 40 cycles [29]. The reason for the better electrochemical properties can be summarized as the following three parts. First, the combination of CNT and Li2FeSiO4 can improve the electrical conductivity of the material. Second, Li2FeSiO4 with a thickness of only 20–25 nm benefits the diffusion of lithium ion. Last, the carbon layer coated on the outside of the Li2FeSiO4 can protect the inner structure and further improve the conductivity. In addition, the cycling performance plots of CNT@Li2FeSiO4 and CNT@Li2FeSiO4@C in Fig. 4c further validate the above statement. It can be seen that the CNT@Li2FeSiO4@C has higher cycle performance and capacity than that of CNT@Li2FeSiO4 at a current density of 0.2 C. The rate performance of CNT@Li2FeSiO4 and CNT@Li2FeSiO4@C is shown in Fig. 4d. It can be observed that the discharge capacity of CNT@Li2FeSiO4 is 98.8 mAh g−1, 81.3 mAh g−1, 78.6 mAh g−1, and 62.4 mAh g−1 at 0.2, 0.5, 1, and 2 C, respectively. While CNT@Li2FeSiO4@C cathode exhibits a much better rate performance, the discharge capacity of 167.7 mAh g−1, 125.8 mAh g−1, 94.6 mAh g−1, and 70.6 mAh g−1 is achieved at 0.2, 0.5, 1, and 2 C, respectively. These performances are better than those described in other similar reports [30–32].

The CV curves are further applied to analyze the kinetic characteristic of CNT@Li2FeSiO4@C cathode material. Figure 5a shows a CV profile of CNT@Li2FeSiO4@C at different scan rates from 0.1 to 1.0 mV s−1. The main redox couple potentials caused by the Fe2+/Fe3+ reaction are 3.1 V (anodic) and 2.7 V (cathodic), respectively, which is in accordance with the galvanostatic platform curve. It is worth noting that only one main redox couple potentials at 3.1 V (anodic) and 2.7 V (cathodic) corresponding to the Fe2+/Fe3+ reaction are observed, and Fe3+/Fe2+ redox couple is confirmed to be inexistent. And the CV result is in accordance with the dQ/dV vs. voltage data (Additional file 1: Figure S3). So we can conclude that only one Li+ per formula unit is inserted and extracted during the charge/discharge process.

In addition, the peak position of the redox peak changes a little with the increasing of scanning rate, indicating the small polarization reaction of CNT@Li2FeSiO4@C cathode material [28]. The diffusion coefficient of lithium ions in CNT@Li2FeSiO4@C can be calculated by the linear relationship between the peak current Ip(A) and the square root of the scan rate v1/2 (v1/2 s−1/2) from the CVs (Fig. 5b). Through the equation below [33, 34],

\[ I_p = 2.69 \times 10^{5} n^{3/2} A D_{Li}^{1/2} C_{Li}^{1/2} v^{1/2} \]

Here, \( n \) is the number of electrons participating in the reaction, \( A \) refers to the electrode area, and \( C_{Li} \) stands for the volume concentration of Li+ in the electrode. Figure 5b illustrates a good linear relationship between Ip and v1/2. During the anodic and cathodic reactions, the diffusion coefficients of lithium ions are \( 7.32 \times 10^{-11} \) and \( 0.64 \times 10^{-12} \) cm² s⁻¹, and these coefficients are superior to previous experimental results [35, 36]. This advantage can be attributed to the excellent electrical conductivity and ion transport efficiency of CNT@Li2FeSiO4@C during charge and discharge. Electrochemical impedance spectroscopy (EIS) was used to investigate the electrochemical performance of CNT@Li2FeSiO4@C and CNT@Li2FeSiO4. Additional file 1: Figure S4 shows
the Nyquist plots of the CNT@Li$_2$FeSiO$_4$@C and CNT@Li$_2$FeSiO$_4$ electrode. The Nyquist plots are composed of high-frequency semicircle associated with lithium-ion migration resistance ($R_{SEI}$) through the solid electrolyte interface (SEI), intermediate frequency semicircle caused by cathode electrolyte interface charge transfer resistance ($R_{ct}$), and low-frequency region tilt line corresponding to the lithium-ion diffusion in the cathode (a Warburg region) [36]. The charge transfer resistance ($76.5 \Omega$) of the CNT@Li$_2$FeSiO$_4$@C is significantly lower than that of the CNT@Li$_2$FeSiO$_4$ ($193.4 \Omega$), indicating that the electron transfer speed of CNT@Li$_2$FeSiO$_4$@C is higher.

Conclusions
In summary, we have prepared CNT@Li$_2$FeSiO$_4$@C through a very effective layer-by-layer stacking strategy. The core-shell heterostructure CNT@Li$_2$FeSiO$_4$@C improves the conductivity, enables rapid extraction/insertion of lithium ions, and relieves the structural damage. As a result, it exhibits high capacity, cycling, and rate performance. Therefore, the CNT@Li$_2$FeSiO$_4$@C cathode material has a promising prospect in the application of lithium ion battery.

Additional File

Additional file 1: Figure S1. (a) SEM image of CNT, (b) SEM of CNT@Li$_2$FeSiO$_4$. Figure S2. Thermogravimetry of CNT@Li$_2$FeSiO$_4$ and CNT@Li$_2$FeSiO$_4$@C. Figure S3. The dQ/dV vs. voltage plots of CNT@Li$_2$FeSiO$_4$@C at 0.2 C. Figure S4. The Nyquist plot of CNT@Li$_2$FeSiO$_4$ and CNT@Li$_2$FeSiO$_4$@C electrode and the equivalent circuit for electrodes.

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Authors’ Contributions
TP prepared the manuscript, and WG carried out the experiment. YGZ, YBW, KJZ, and YHW helped in the technical support for the characterizations. YL and HLY designed the experiment. All the authors discussed the results and approved the final manuscript.

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Availability of Data and Materials
All data and materials are fully available without restriction.

Competing Interests
The authors declare that they have no competing interests.

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References
1. Larcher D, Tarascon J-M (2015) Towards greener and more sustainable batteries for electrical energy storage. Nat Chem 7:19
2. Whittingham MS (2014) Ultimate limits to intercalation reactions for lithium batteries. Chem Rev 114:11414–11443
3. Luo R, Lu Y, Hou X, Yu Q, Peng T, Yan H, Liu X, Kim J-K, Luo Y (2017) Encapsulation of Se/C into ultra-thin Ni (OH)$_2$ nanosheets as cathode materials for lithium-selenium batteries. J Solid State Electrochem 21: 3611–3618
4. Lv D, Bai J, Zhang P, Wu S, Li Y, Wen W, Jiang Z, Mi J, Zhu Z, Yang Y (2013) Understanding the high capacity of Li$_2$FeSiO$_4$: in situ XRD/XANES study combined with first-principles calculations. Chem Mater 25:2014–2020
5. Luo Y, Luo J, Jiang J, Zhou W, Yang H, Qi X, Zhang H, Fan HJ, Denis Y, Li CM (2012) Seed-assisted synthesis of highly ordered TiO$_2$@α-Fe$_2$O$_3$ core/shell arrays on carbon textiles for lithium-ion battery applications. Energy Environ Sci 5:6559–6566
6. Peng T, Liu C, Hou X, Zhang Z, Wang C, Yan H, Lu Y, Liu X, Luo Y (2017) Control growth of mesoporous nickel tungstate nanofiber and its application as anode material for lithium-ion batteries. Electrochim Acta 224:460–467

Abbreviations
CNT: Carbon nano-tube; CTAB: Cetyltrimethyl ammonium bromide; CV: Cyclic voltammetric; EDX: Energy-dispersive X-ray spectroscopy; EIS: Electrochemical impedance spectroscopy; HR-TEM: High resolution-transmission electron microscopy; LIBs: Lithium-ion batteries; NMP: N-methyl-2-pyrrolidone; PVDF: Polyvinylidene fluoride; SEI: Solid electrolyte interface; SEM: Scanning electron microscopy; TEM: Transmission electron microscopy; TEOS: Tetraethoxysilane; TGA: Thermogravimetric analyzer; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction
7. Rangappa D, Murukanahally KD, Tomai T, Unemoto A, Honma I (2012) Ultrathin nanosheets of Li$_2$MnSiO$_4$ (M= Fe, Mn) as high-capacity Li-ion battery electrode. Nano Lett 12:1146–1151

8. Nytén A, Abouimrane A, Armand M, Gustafsson T, Thomas J (2005) Electrochemical performance of Li$_2$FeSiO$_4$ as a Li-ion battery cathode material. Electrochem Commun 7:156–160

9. Tan R, Yang J, Zheng J, Wang K, Lin L, Ji S, Liu J, Pan F (2015) Fast rechargeable all-solid-state lithium ion batteries with high capacity based on nano-sized Li$_2$FeSiO$_4$ cathode by tuning temperature. Nano Energy 16:112–121

10. Gao H, Hu Z, Zhang K, Cheng F, Chen J (2013) Intergrown Li$_2$FeSiO$_4$/LiFePO$_4$/C nanocomposites as high-capacity cathode materials for lithium-ion batteries. Chem Commun 49:3040–3042

11. Fu R, Li Y, Yang H, Zhang Y, Cheng X (2013) Improved performance of Li$_2$FeSiO$_4$/C composite with highly rough mesoporous morphology. J Electrochem Soc 160:A3048–A3053

12. Guo H, Song X, Zhuo Z, Hu J, Liu T, Duan Y, Zheng J, Chen Z, Yang W, Amine K (2015) Storage and effective migration of Li-ion for defected β-LiFePO$_4$ phase nanocrystals. Nano Lett 16:601–608

13. Yang G, Song H, Cui H, Liu Y, Wang C (2013) Ultrafast Li-ion battery anode with superlong life and excellent cycling stability from strongly coupled ZnO nanoparticle/conductive nanocarbon skeleton hybrid materials. Nano Energy 25:79–85

14. Su DS, Perathoner S, Centi G (2013) Nanocarbons for the development of advanced cathode materials. Chem Rev 113:5782–5816

15. Yang Y, Zhao D, Ba D, Li Y, Liu J (2018) "Carbon-glue" enabled highly stable and high-rate Fe$_2$O$_3$ nanorod anode for flexible quasi-solid-state nickel-copper/iron alkaline battery. Adv Mater Interfaces 5:1801043

16. Zhai P-Y, Zhao S-X, Cheng H-M, Zhao J-W, Nan C-W (2015) Synthesis and structural stability of Li$_{1.1}$Mn$_{0.1}$PO$_{4.1}$SO$_{4.9}$/C mixed polyanion cathode material for Li-ion battery. Electrochim Acta 153:217–224

17. Lu D, Wen W, Huang X, Bai J, Ji M, Wu S, Yang Y (2011) A novel Li$_2$FeSiO$_4$/C composite: synthesis, characterization and high storage capacity. J Mater Chem 21:9506–9512

18. Zhao Y, Wu C, Li J, Guan L (2013) Long cycling life of Li$_2$MnSiO$_4$ lithium battery cathodes under the double protection from coating of carbon and graphene network. J Mater Chem A 1:3856–3859

19. Qu L, Li M, Bian L, Du Q, Luo M, Yang B, Yang L, Fang S, Liu Y (2017) A strontium-doped Li$_2$FeSiO$_4$/C cathode with enhanced performance for the lithium-ion battery. J Solid State Electrochem 21:3659–3673

20. Deng B, Lei T, Zhu W, Xiao L, Li J (2018) In-plane assembled orthorhombic Nb$_2$O$_5$ nanorods with high-rate Li$^{+}$ intercalation for high-performance flexible Li$^{+}$ion capacitors. Adv Funct Mater 28:1704330

21. Peng T, Guo W, Zhang Q, Zhang Y, Chen M, Wang Y, Yan H, Lu Y, Luo Y (2018) Uniform coaxial CNT@Li$_2$MnSiO$_4$@C as advanced cathode material for lithium-ion battery. Electrochim Acta 291:1–8

22. Wang Y, Zhang D, Lu Y, Wang W, Peng T, Zhang Y, Guo Y, Wang Y, Hua K, Kim J-K (2019) Cable-like double-carbon layers for fast ion and electron transport: an example of CNT@NCT@MnO$_x$ 3D nanostructure for high-performance supercapacitors. Carbon 143:333–342

23. Deng C, Zhang S, Gao Y, Wu B, Ma L, Sun Y, Fu Y, Wu Q, Liu F (2011) Regeneration and characterization of air-exposed Li$_2$FeSiO$_4$. Electrochim Acta 56:7327–7333

24. Murali Gan J, Troukoff K, Manthiram A (2010) Microwavothermal synthesis of nanostructured Li$_2$MnSiO$_4$/C (M=Mn and Fe) cathodes for lithium-ion batteries. Chem Mater 22:5754–5761

25. Zhang S, Deng C, Fu B, Yang S, Ma L (2010) Effects of Cr doping on the electrochemical properties of Li$_2$FeSiO$_4$ cathode material for lithium-ion batteries. Electrochim Acta 55:8482–8489

26. Jiang X, Xu H, Liu J, Yang J, Mao H, Qian Y (2014) Hierarchical mesoporous Li$_2$Mn$_{0.5}$Fe$_{0.5}$SiO$_4$ and Li$_2$Mn$_{0.5}$Fe$_{0.5}$SiO$_4$/C assembled by nanoparticles or nanoplates as a cathode material for lithium-ion batteries. Nano Energy 7:1–9

27. Yang X-F, Yang J-H, Zaghib K, Trudeau ML, Yin YJ (2015) Synthesis of phase-pure Li$_2$MnSiO$_4$/C porous nanoboxes for high-capacity Li-ion battery cathodes. Nano Energy 12:305–313

28. Zheng Z, Wang Y, Zhang A, Zhang T, Cheng F, Tao Z, Chen J (2012) Porous Li$_2$FeSiO$_4$/C nanocomposite as the cathode material of lithium-ion batteries. J Power Sources 198:229–235

29. Zhang L-L, Duan S, Yang X-L, Peng G, Liang G, Huang Y-H, Jiang Y, Ni S-B, Li M (2013) Reduced graphene oxide modified Li$_2$FeSiO$_4$/C composite with enhanced electrochemical performance as cathode material for lithium ion batteries. ACS Appl Mater Interfaces 5:12304–12309

30. Peng Z, Mao H, Yin H, Xu C, Wang WG (2013) PEG-assisted solid state synthesis and characterization of carbon-coated Li$_2$Mn$_{0.5}$SiO$_4$ cathode materials for lithium-ion battery. Int J Electrochem Sci 8:903–913

31. Qiu H, Zhu K, Li H, Li T, Zhang T, Yue H, Wei Y, Du F, Wang C, Chen G, Zhang D (2015) Mesoporous Li$_2$FeSiO$_4$/C ordered mesoporous carbon composites cathode material for lithium-ion batteries. Carbon 87:365–373

32. Li R, Ba X, Zhang H, Xu P, Li Y, Cheng C, Liu J (2018) Conformal multifunctional titaniasil shell on iron oxide nanorod conversion electrode enables high stability exceeding 30 000 cycles in aqueous electrolyte. Adv Funct Mater 28:1800497

33. Wang W, Liang H, Zhang L, Savilov SV, N J, Li L (2017) Carbon nanotube directed three-dimensional porous Li$_2$FeSiO$_4$ composite for lithium batteries. Nano Res 10:229–237

34. Qiu H, Yue H, Zhang T, Ju Y, Zhang Y, Guo Z, Wang C, Chen G, Wei Y, Zhang D (2016) Enhanced electrochemical performance of Li$_2$FeSiO$_4$/C positive electrodes for lithium-ion batteries via yttrium doping. Electrochim Acta 188:636–644

35. Jin Y, Yang C, Rui X, Cheng T, Chen CJ (2011) V$_2$O$_5$ modified LiFePO$_4$/C composite with improved electrochemical performance. J Power Sources 196:5623–5630

36. Hu L, Yang J, Aminu IS, Kang X, Zhang W, Mu S (2015) Lithium storage properties of in situ synthesized Li$_2$FeSiO$_4$ and LiFeBO$_4$ nanocomposites as advanced cathode materials for lithium-ion batteries. J Mater Chem A 3:23368–23375

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