S-Doped Carbon-Coated FeS₂/C@C Nanorods for Potassium Storage

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Received: 10 January 2020 / Revised: 10 February 2020 / Published online: 22 April 2020

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Abstract

Potassium-ion batteries (PIBs) are promising scalable energy storage system; however, one of the challenges for its potential application is the huge volume variations during cycling due to the insertion/extraction of large size potassium ions. Here, we fabricated the S-doped carbon-coated rod-like FeS₂/C@C, which not only effectively alleviate the volume variations upon cycling but also can improve electrical conductivity and maintain the structural integrity. As an anode material for PIBs, the rod-like FeS₂/C@C electrodes delivered excellent rate performance (175 mA h g⁻¹ at 0.5 A g⁻¹) and stable cycle performance (262 mA h g⁻¹ after 100 cycles at 0.1 A g⁻¹). The superior excellent performance is associated with the unique structure of FeS₂/C@C. The as-synthesized FeS₂/C@C is demonstrated to be a potential anode for PIBs.

Keywords Iron disulfide · Carbon matrix · Potassium-ion batteries · Nanorods · Volume variations

1 Introduction

Lithium-ion batteries (LIBs) have been successfully commercialized during the past 2 decades. However, the uneven distribution of lithium resources in the worldwide and rarity (0.0065 wt%) in the Earth's crust largely restrict their applications [1–4]. Therefore, the alternative energy storage technologies with low cost and reliable serve life are highly desirable to LIBs [5–7]. In terms of the similar properties to Li, with the merit of the high abundance of K (2.09 wt%) and Na (2.36 wt%) in the Earth's crust, potassium-ion batteries

(PIBs) and sodium-ion batteries (SIBs) have been considered as promising energy storage system [8–14]. Although some promising results of SIBs have been achieved in the last few years, the progress of PIBs is also slow due to the larger ionic radius of K⁺ (1.38 Å) compared to that of Na⁺ (1.02 Å) [15–18]. In addition, PIBs possess several significant advantages, such as the more negative standard redox potential of K⁺/K (−2.93 V vs. standard hydrogen electrode (*E*⁰)) compared to that of Na⁺/Na (−2.71 V vs. *E*⁰), the fast ionic conductivity of K⁺ in electrolyte, and the alternative use of Al foil to Cu foil [12, 19–22]. These characteristics provide promising opportunities for PIBs to be developed as low-cost batteries with good rate performance and high energy density [23–27]. At the current stage, it is still a big challenge to select suitable electrode materials that can accommodate huge volume variations during the cycles [28].

Among kinds of available anode materials, transition metal sulfides (e.g., FeS_x, CoS_x, NiS_x, etc.) possess nature abundant and high theoretical capacity, which have been treated as promising anode materials for the next-generation PIBs. However, the partial dissolution of polysulfide intermediates and large volumetric change during the potassium insertion/extraction will result in fast capacity fading, which seriously limits their practical applications, and one effective strategy to solve the above problems is to construct the carbon materials with the nanocomposites of transition metal sulfide [25, 29]. Therefore, Xia et al. [30] reported a few layers SnS₂ nanosheets supported on reduced graphene oxide

Available online at <http://link.springer.com/journal/40195>.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s40195-020-01050-y>) contains supplementary material, which is available to authorized users.

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(SnS_2/rGO) investigated as anode material for PIBs, and the presence of rGO improved specific capacity (448 mA h g^{-1} at 0.05 A g^{-1}), rate capability (247 mA h g^{-1} at 1 A g^{-1}), and cycle performance (73% capacity retention after 300 cycles), which demonstrates that K storage performance can be remarkably promoted by subtle structure engineering. As a low-cost and low-toxic sulfide mineral, FeS_2 has been considered as a promising electrode material for PIBs [31–33]. However, the collapse of the active material structure caused by the serious volume variations during potassiation/depotassiation would lead to poor cycle performance [34–36]. Recently, Mai et al. [37] have fabricated a hollow FeS_2 nanocages@rGO composite as anode, which exhibited unsatisfactory rate capability (151 mA h g^{-1} at 0.5 A g^{-1}). Guan et al. [34] designed a composite by in situ engineering of a yolk-shell FeS_2/C structure on a graphene matrix, which delivered reasonable capacity, good rate capability (203 mA h g^{-1} at 10 A g^{-1}), and long-term stability over 1500 cycles at 10 A g^{-1} . Li et al. [38] designed a multi-layer architecture of FeS_2/C , which exhibited 295 mA h g^{-1} after 150 cycles at 1 A g^{-1} . Up to now, there are few studies relevant to FeS_2 as anode materials for PIBs, which made this material still deserved to be further investigated [37].

Herein, we have designed a rod-like structured $\text{FeS}_2/\text{C}@\text{C}$ synthesized by a solvothermal method coupled with sulfidation strategy. By the above method, the FeS_2/C composite is encapsulated in the carbon shell, which can effectively alleviate the volume expansion during the cycles, maintain the structural integrity, and improve electrical conductivity. As anode materials for PIBs, $\text{FeS}_2/\text{C}@\text{C}$ delivered a high initial discharge capacity of around 340 mA h g^{-1} at 100 mA g^{-1} and it still retained 262 mA h g^{-1} after 100 cycles. Impressively, the rate capabilities and cycling retention of $\text{FeS}_2/\text{C}@\text{C}$ anode were much better than those of FeS_2/C composite. When it comes to the FeS_2/C , a very poor cycling performance was displayed, which more strongly demonstrated the importance of the coating carbon in maintaining the cyclic stability of the material during the potassiation/depotassiation process. Moreover, this synthetic strategy of the composite is expected to be applied to other similar materials to improve the cycling stability of anode electrode materials for potassium-ion batteries.

2 Experimental

2.1 Synthesis of Rod-like Fe-MOF, $\text{Fe}_3\text{O}_4/\text{C}@\text{C}$ Composite, and $\text{FeS}_2/\text{C}@\text{C}$ Composite

Rod-like Fe-MOF: The rod-like Fe-MOF was synthesized through a solvothermal method described in the previous literature [17]. Briefly, a yellow precursor solution was prepared by dissolving $0.54 \text{ g FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.44 g fumaric

acid in 27 mL *N,N*-dimethylformamide (DMF) and stirring for 20 min. Then, a 3 mL 0.4 M NaOH aqueous solution was slowly added to the above solution. After stirring for 10 min, the resulting mixture was transferred to a 50-mL Teflon-lined stainless-steel autoclave and maintained for 24 h at 100°C . After cooling to room temperature, the mixture was washed with ethanol several times and was dried in a vacuum oven at 60°C for 12 h.

$\text{Fe}_3\text{O}_4/\text{C}@\text{C}$ composite: For the preparation of $\text{Fe}_3\text{O}_4/\text{C}@\text{C}$, 0.1 g as-obtained rod-like Fe-MOF was dispersed in 8.8 mL water by ultrasonication. Then, 0.285 g CTAB, 0.0435 g resorcinol, 3.53 mL ethanol, and $12.5 \mu\text{L}$ ammonia were added and stirred at 35°C for 30 min. Finally, $62.5 \mu\text{L}$ formalin solution was added to the above solution drop by drop. The product was continuously stirred for 6 h at 35°C and then aged at room temperature overnight without stirring. After washed with water and ethanol several times, the mixture was collected by centrifugation [39]. In addition, the obtained product was heat-treated at 150°C for 1 h and 600°C for 2 h in an Ar atmosphere.

$\text{FeS}_2/\text{C}@\text{C}$ composite: 0.1 g $\text{Fe}_3\text{O}_4/\text{C}@\text{C}$ was placed in a combustion boat and 1 g sulfur powder was placed in another one, and then, they were annealed at 500°C (heating rate of 2°C min^{-1}) for 3 h in a glass tube in an Ar atmosphere. The product was obtained after the glass tube naturally cooled to room temperature. The FeS_2/C was synthesized with the same method while without carbon coating.

2.2 Materials Characterization

Morphology and structure were evaluated by scanning electron microscopy (SEM) (Hitachi S4800) with a voltage of 5 kV and were performed by transmission electron microscopy (TEM, JEOLJEM-3010) at a beam voltage of 200 kV . Powder X-ray diffraction (XRD) patterns were analyzed by using XRD (Rigaku D/MAX-2500) at 250 mA and 50 kV with $\text{Cu-K}\alpha$ radiation. The surface area and pore size of the samples were performed by the measurements of Brunauer–Emmett–Teller (BET), which were carried out using an Autosorb-QI (Quantachrome Instruments). The carbon content was evaluated by thermogravimetric analysis (TGA, Setaram 018124) from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ in the air. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250 spectrometer) was used to reflect the bonding nature and chemical states of the composites, and the Raman spectra (RS) were carried out using a LAM HR 800 Raman spectrometer.

2.3 Electrochemical Performance Characterization

The working electrodes were fabricated from 80 wt% active material, 10 wt% acetylene black, and 10 wt% sodium carboxymethyl cellulose (CMC) dissolved in water and ethanol.

The slurry was pasted on clean Cu foil when it was well mixed and dried at 60 °C under vacuum for 12 h. The average mass loading was about 0.9 mg cm⁻². Batteries were assembled in an argon atmosphere filled glovebox (both the content of O₂ and H₂O are less than 0.1 ppm) using a K metal as a counter electrode, and the separator was glass fiber (Whatman, Grade GF/D). The electrolyte was 3 M KPF₆ in the dimethoxyethane (DME) solution. The galvanostatic measurements were tested by using a Neware Battery Testing System, and the charge and discharge ranges were 0.01–3 V. Cyclic voltammetry (CV) and electrochemical

impedance spectra (EIS) curves were collected on an IVIUM electrochemical work station.

3 Results and Discussion

The overall synthesis procedure of the rod-like FeS₂/C@C is shown in Fig. 1. Firstly, the pink rod-like Fe-MOF was obtained with FeCl₃·6H₂O and fumaric acid by a solvothermal method at 100 °C. Secondly, as-obtained Fe-MOF was covered with resorcinol formaldehyde (RF) resin to obtain the Fe-MOF@RF and with the subsequent carbonization at 150 °C and 600 °C in Ar atmosphere, and the part of Fe-MOF and the RF resin layer produced carbonization to obtain Fe₃O₄/C@C. As shown in Fig. 1, the Fe₃O₄ particles attached to the carbonized rods. Finally, the FeS₂/C@C composites were achieved by sulfidation treatment between Fe₃O₄/C@C and sulfur power at 600 °C for 3 h.

The detailed morphology and structure of the Fe-MOF, Fe₃O₄/C@C and FeS₂/C@C were observed by the field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). As shown in Fig. 2a, the Fe-MOF precursor displayed well-distributed nanorod with a diameter of around 100 nm and a length of approximately 2 μm. The morphology of Fe₃O₄/C@C is displayed in Fig. 2b, c, which shows approximately similar length of the rods with that of the Fe-MOF precursor. However, it could be seen that the outside layer of the rods was rough, which is attributed to the RF coating layer. As shown in Fig. S1a–b, the morphology of FeS₂/C shows the same rods as FeS₂/C@C. Figure 2d, e and Fig. 3a indicate that the size of FeS₂/C@C composites (diameter of around 100 nm and a length of approximately

Fig. 1 Schematic illustration of the synthesis of rod-like FeS₂/C@C

Fig. 2 a SEM images of the Fe-MOF; b, c SEM images of the Fe₃O₄/C@C; d, e SEM images; f XRD images of the FeS₂/C@C

Fig. 3 **a** SEM image, **b** TEM image, **c** HRTEM image, **d** corresponding elemental mapping of Fe, S, and C of $\text{FeS}_2/\text{C}@\text{C}$

2 μm) is also well consistent with the Fe-MOF precursor and the $\text{Fe}_3\text{O}_4/\text{C}@\text{C}$ intermediate. XRD was employed to investigate the structure of rod-like $\text{FeS}_2/\text{C}@\text{C}$. As shown in Fig. 2f, all diffraction peaks were well matched to the peaks of the pyrite (JCPDS No.71-2219) and the XRD of FeS_2/C (Fig. S2a) also corresponded to pyrite (JCPDS No.71-2219). XRD patterns (Fig. S3a) of as-prepared $\text{Fe}_3\text{O}_4/\text{C}@\text{C}$ were well matched with the Fe_3O_4 phase (JCPDS No. 75-0033).

Transmission electron microscopy (TEM) was employed in order to clearly observe the morphology and obtain detailed structure information. As displayed in low- and high-magnification TEM images (Fig. 3b), the rod-like structure was observed, which consists of small nanoparticles attached to the rod-like carbon and coated by a thin carbon layer. HRTEM image (Fig. 3c) of the FeS_2 nanoparticles exhibited a lattice distance of approximately 0.246 nm, which is matched with the (210) of FeS_2 . As shown in Fig. 3d, the energy-dispersive X-ray spectrometric (EDS) mapping images show that Fe, S mapping signals are well overlapped and mainly appear in the interior, while the C elements are distributed both in the interior and exterior, which further confirmed that FeS_2 nanoparticles were attached to the rod-like carbon and the FeS_2/C was coated with a thin carbon layer [40]. Moreover, the element mapping (Fig. S1c) confirms the existence and uniform distribution of elements Fe, S, and C in $\text{FeS}_2/\text{C}@\text{C}$.

The Raman spectroscopy is performed in Fig. 4a to further evaluate the carbon state in the $\text{FeS}_2/\text{C}@\text{C}$ and FeS_2/C , from which the D peak located at 1292 cm^{-1} and the peak at 1535 cm^{-1} related to the G peak can be clearly observed [34]. Notably, a high I_D/I_G ratio of $\text{FeS}_2/\text{C}@\text{C}$ could be

calculated as around 2.5, while the I_D/I_G ratio of FeS_2/C is around 2.1, which demonstrates the carbon with rich defects in $\text{FeS}_2/\text{C}@\text{C}$ composites [41, 42]. In order to analyze the carbon content of the $\text{FeS}_2/\text{C}@\text{C}$, TGA was carried out in air atmosphere. The result (Fig. 4b) displays the TGA curves of $\text{FeS}_2/\text{C}@\text{C}$ and FeS_2/C , which can evaluate the chemical components. The FeS_2/C shows a weight loss from 200 to 500°C , which is related to the loss of the initial carbon. The weight loss of FeS_2/C between 550 and 700°C results from the combustion of sulfur [17]. As shown in the TGA curve of $\text{FeS}_2/\text{C}@\text{C}$ composites, the first weight loss estimated to be about 40.8% from 200 to 450°C belongs to the combustion of carbon layers [42, 43], which can reveal that the content of carbon from phenolic resin in the composite is about 17.5%. The second weight loss from 500 to 700°C is related to the transition of FeS_2 to Fe_3O_4 in the air atmosphere, which is compatible with the previous report [43]. Based on the quantitative results of TGA curve of $\text{FeS}_2/\text{C}@\text{C}$ composites and the XPS results, the weight percentage of FeS_2 in $\text{FeS}_2/\text{C}@\text{C}$ can be calculated to be $\sim 56.2\text{ wt}\%$; the sulfur content in FeS_2 can be determined to be $\sim 28.1\text{ wt}\%$; the doped sulfur and the sulfur content in FeS_2 are $\sim 29.4\text{ wt}\%$; therefore, the extra amount of sulfur (1.3 wt%) can be assigned to the sulfur content in the S-doped carbon of $\text{FeS}_2/\text{C}@\text{C}$ [44–46].

The XPS was employed to detect the surface electronic states and composition of $\text{FeS}_2/\text{C}@\text{C}$. The XPS survey spectra (Fig. 4c) demonstrate the existence of Fe, C, O, and S in $\text{FeS}_2/\text{C}@\text{C}$ composite. As shown in Fig. 4d, the peaks at 707.5 eV, 720.3 eV can be indexed to $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$, respectively [47]. The observed peak at 169.0 eV shown in

Fig. 4 **a** Raman spectra, **b** TGA curves of FeS₂/C@C and FeS₂/C; **c** XPS survey spectra **d** Fe 2p, **e** S 2p, **f** C 1 s spectra of FeS₂/C@C

Fig. 4e is attributed to the SO₄²⁻ on the surface of the FeS₂ particles; and the peak at 165.1 eV is characterized for S 2p_{1/2} of doped S; the S 2p_{3/2} of doped S and S 2p_{1/2} of FeS₂ are corresponding to the peak at 163.8 eV [46]; the peak at 162.5 eV is related to S 2p_{3/2} of the FeS₂. The C 1 s spectrum in Fig. 4f can be divided into three peaks. The peaks at 284.8 eV, 286.5 eV, and 289.2 eV are assigned to C–C, C–O, and O–C=O, respectively, which were resulted from the functional group of PF⁻ derived carbon coating layer and the Fe-MOF precursor [36]. For the FeS₂/C, the result (Fig. S2b-e) exhibits the XPS of FeS₂/C, and the XPS survey spectrum (Fig. S2b) demonstrates the composition of Fe, C, O, and S in FeS₂/C composite. The result (Fig. S2c) displays the peaks at 706.5 eV and 720.2 eV, which can be assigned to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The C 1 s spectrum in Fig. S2d has two peaks at 284.7 eV and 290.1 eV, and the

one located at 284.7 eV is the characteristic peak for C–C and the other peak at 290.1 eV can be assigned to O–C=O, which is related to the Fe-MOF precursor [36]. In Fig. S2e, the observed peak at 164.7 eV can be recognized as the S 2p_{1/2} of doped S. The peak at 163.6 eV is attributed to the S 2p_{3/2} of doped S and S 2p_{1/2} of FeS₂, and the peak at 162.5 eV is related to the S 2p_{3/2} of the FeS₂ [46, 48].

Cyclic voltammetry (CV) curves are presented in Fig. 5a to illustrate the potassium storage behavior at a scan rate of 0.1 mV s⁻¹ between 0.01 and 3 V versus K⁺/K. During the first cathodic process, the observed peak at around 0.53 V could be assigned to the conversion from FeS₂/C@C and K to K₂S and Fe, as well as the formation of solid electrolyte interphase (SEI) layers on the surfaces of the electrode [49–51]. In the following cycles, the reduction peak localized at 0.58 V is related to the potassiation process. For the

Fig. 5 **a** Cyclic voltammograms of $\text{FeS}_2/\text{C}@C$ at a scan rate of 0.1 mV s^{-1} for the initial 3 cycles; **b** discharge-charge profiles of $\text{FeS}_2/\text{C}@C$ at different current densities; **c** cycling performance at 0.1 A g^{-1} and **d** rate capability of $\text{FeS}_2/\text{C}@C$ and FeS_2/C ; **e** EIS of $\text{FeS}_2/\text{C}@C$ and FeS_2/C electrodes before cycling; **f** BET nitrogen adsorption and desorption isotherms of $\text{FeS}_2/\text{C}@C$ (inset is the corresponding pore size distribution)

anodic process, the obvious peaks at around 1.96 V correspond to the depotassiation process to form K_xFeS phases [52–54]. The fine overlapping of the second and third CV curves reveals the excellent cyclability [48, 55]. As displayed in Fig. 5b, the charge-discharge curves at a current density 0.1 A g^{-1} show the matching electrochemical behavior with CV curves: two voltage platforms over the range of $0.5\text{--}0.6 \text{ V}$ and $1.9\text{--}2.1 \text{ V}$ during the charge-discharge process, respectively. The CV and galvanostatic discharge/charge curves of FeS_2/C are displayed in Fig. S3b and c, and the obvious peak located at 2.57 V corresponds to the depotassiation process to form K_xFeS phases, which were well matched the voltage platform around the range of $2.5\text{--}2.6 \text{ V}$. The result (Fig. 5c) illustrates the cycling performances and corresponding coulombic efficiency of $\text{FeS}_2/\text{C}@C$ and

FeS_2/C at a current density of 100 mA g^{-1} . It is observed that the $\text{FeS}_2/\text{C}@C$ displays a high initial disadvantage capacity of $730.58 \text{ mA h g}^{-1}$ and the corresponding coulombic efficiency is around 60%. The FeS_2/C electrode delivered the initial discharge capacity of $524.3 \text{ mA h g}^{-1}$, but the capacity dropped quickly with the increased cycle number, which demonstrates that the initial carbon cannot tolerate the volume expansion during the charge-discharge process. In contrast, $\text{FeS}_2/\text{C}@C$ electrode possesses initial carbon rod and carbon of phenolic resin carbonization production, which makes the composite possess a strong protective shell and improved conductivity. Thus, the $\text{FeS}_2/\text{C}@C$ electrode delivered excellent cycling stability (262 mA h g^{-1} after 100 cycles, the capacity retention rate is about 80%). The $\text{FeS}_2/\text{C}@C$ and FeS_2/C were investigated at different

current densities ranging from 0.05 to 0.5 A g⁻¹ and back to 0.05 A g⁻¹. As shown in Fig. 5d, the FeS₂/C@C electrodes show excellent rate capacity, which delivers capacities of 438, 375, 298, 175 mA h g⁻¹ at 0.05, 0.1, 0.2, and 0.5 A g⁻¹, respectively. It is still 407 mA h g⁻¹ when the current density decreases back to 0.05 A g⁻¹, which demonstrates the good rate performance of FeS₂/C@C. In contrast, due to the poor cycle performance of the FeS₂/C, the rate capacity is extremely low, which further demonstrates the advantage of the coating carbon.

As shown in Fig. 5e, the EIS of FeS₂/C@C and FeS₂/C was carried out. Both of the Nyquist plots are composed of a semicircle and a straight line [56]. The high-frequency semicircle indicates the SEI film resistance (R_{SEI}), and the medium-frequency semicircle is related to the charge-transfer resistance (R_{ct}), and the line in low-frequency one is corresponding to the diffusion of K⁺ [54]. It is known that the larger semicircle in the high-frequency one, the higher charge-transfer resistance (R_{ct}), which indicates that the electrical conductivity of the active materials is poor, and an ideal line in the low-frequency one is a more vertical line [57]. Through fitting with the original curve, it is clear that the FeS₂/C@C electrode displays a low R_{ct} of 786.7 Ω cm², while the FeS₂/C exhibits 2085 Ω cm², indicating that its structure is more stable during cycles and the carbon coating layer can improve the charge-transfer kinetics of the FeS₂/C@C composite [43, 48, 58], which was consistent with the rate capability. Therefore, it demonstrates the importance of the carbon coating during cycles. The diffusion resistance was obtained by calculating the slope of the fitted line in $Z' - \omega^{-1/2}$ ($\omega = 2\pi f$) curve in the low-frequency region (Fig. S3d). It is clear that the FeS₂/C@C electrode exhibited a much lower slope than FeS₂/C electrode, indicating its higher K⁺ diffusion coefficient, which is good for enhancing the electrochemical kinetics of electrodes [59].

The N₂ adsorption–desorption isotherms of FeS₂/C@C and pure FeS₂/C are shown in Fig. 5f and Fig. S2f. As it can be seen, the FeS₂/C@C processes a Brunauer–Emmett–Teller (BET) surface area of 97.466 m² g⁻¹, while the BET surface area of FeS₂/C is 72.494 m² g⁻¹. Both the FeS₂/C@C and FeS₂/C show mesopores at 3.8 nm, which could serve as fast channels and high surface area for the transport of electrolyte for improving electrochemical performance and rate capability during potassium storage process [58, 60].

4 Conclusion

In summary, a novel FeS₂/C@C composite was rationally synthesized by one-pot solvothermal, carbon coating, and sulfidation. Owing to the excellent architecture structure and protective carbon coating, the composite exhibited excellent

potassium storage. It can deliver a stable cycle performance of 262 mA h g⁻¹ after 100 cycles at 0.1 A g⁻¹ and good rate capability (175 mA h g⁻¹ at 0.5 A g⁻¹). More importantly, this facile design strategy can be also applied to the other anode materials to ensure the structural stability and exhibit superior electrochemical performance for PIBs.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Nos. 51302079, 51702138), the Natural Science Foundation of Hunan Province (No. 2017JJ1008), and the Key Research and Development Program of Hunan Province of China (No. 2018GK2031).

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