Accepted Manuscript

Porous Ni₃S₄/C aerogels derived from carrageenan-Ni hydrogels for high-performance sodium-ion batteries anode

Ruiqi Guo, Daohao Li, Chunxiao Lv, Yu Wang, Huawei Zhang, Yanzhi Xia, Dongjiang Yang, Xiaoliang Zhao

PII: S0013-4686(19)30003-9

DOI: <https://doi.org/10.1016/j.electacta.2019.01.011>

Reference: EA 33414

To appear in: *Electrochimica Acta*

Received Date: 20 November 2018

Revised Date: 27 December 2018

Accepted Date: 1 January 2019

Please cite this article as: R. Guo, D. Li, C. Lv, Y. Wang, H. Zhang, Y. Xia, D. Yang, X. Zhao, Porous Ni₃S₄/C aerogels derived from carrageenan-Ni hydrogels for high-performance sodium-ion batteries anode, *Electrochimica Acta* (2019), doi: <https://doi.org/10.1016/j.electacta.2019.01.011>.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Porous Ni₃S₄/C Aerogels Derived from Carrageenan-Ni Hydrogels for High-performance Sodium-ion Batteries Anode

Ruiqi Guo^a, Daohao Li^a, Chunxiao Lv^a, Yu Wang^a, Huawei Zhang^b, Yanzhi Xia^a, Dongjiang Yang^{a,c} and Xiaoliang Zhao^{a*}

^aSchool of Environmental Science and Engineering, State Key Laboratory of Bio-fibers and Eco-textiles, Shandong Collaborative Innovation Center of Marine Bio-based Fibers and Ecological Textiles, Qingdao University, Qingdao 266071, P. R. China.

^bCollege of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, P. R. China.

^cQueensland Micro- and Nanotechnology Centre (QMNC), Griffith University, Nathan, Brisbane, Queensland 4111, Australia.

Corresponding author: E-mail: xlzh86@163.com (X. Zhao)

Abstract

Nickel sulfide (Ni_3S_4) has been recognized as one of the most advanced anode materials for sodium-ion batteries (SIBs) on account of its cost effectiveness, commendable redox reversibility and high theoretical capability. However, like other metal sulfide (MS) anodes, the Ni_3S_4 suffers from poor cycle life and inferior rate capability owing to large volume changes during the repeated Na^+ de/insertion process and unsatisfied electronic conductivity. Herein, we fabricated porous Ni_3S_4 /carbon aerogels (Ni_3S_4 /CAs) using carrageenan-Ni hydrogels as the precursor via the pyrolysis route. The sulfate groups located uniformly and confinement for Ni^{2+} ions in carrageenan double-helix structures converted into uniform Ni_3S_4 nanoparticles (NPs) embedded in porous carbon through the decomposition. Remarkably, the as-prepared Ni_3S_4 /CAs-1 sample as the anode material for SIBs exhibits a high reversible capacity of 297 mAh g^{-1} at a current density of 1 A g^{-1} after 100 cycles. This work develops a facile way to synthesize Ni_3S_4 /CAs as a promising anode material for SIBs from marine biomass resources.

Keywords: Ni_3S_4 /Carbon Aerogels, Carrageenan-Ni Hydrogels, Anode Material, Sodium-ion Batteries Anode.

1. Introduction

Sodium-ion batteries (SIBs) have become increasingly attractive energy storage device to substitute for lithium-ion batteries (LIBs) due to their low economical cost, metal activity and natural abundance of sodium [1]. However, Na^+ ions with a large radius can't be intercalated into typical graphite anode materials. The electrode materials have been deemed to the main challenge which restricts the practical application of SIBs. Ideal electrode materials can accommodate Na^+ ions via insertion/extraction to the interlayers with a high capacity and long cycle life [2,3]. Hence, developing anode materials with outstanding performance and excellent durability to meet the recent progress of communication devices and electronics is urgent [4].

Transition metal sulfides (TMS) [5], such as FeS [6,7], CoS [8], and NiS [9,10] with the merits of cost effectiveness and high activity, are considered as promising anode materials [11]. Among them, Ni_3S_4 drew attention by virtue of commendable redox reversibility and high theoretical capability. However, Ni_3S_4 materials suffered from unsatisfied electronic conductivity, poor cycle life and inferior rate capability owing to large volume changes during the repeated Na^+ de/insertion process [12-15]. To address these problems, it is an effective strategy to disperse nano-sized TMS particles into a carbon matrix. Based on this, many special morphologies with high specific surface have been designed, such as nanospheres [16], anotubular [17,18] and nanorod [19,20]. These distinctive structures can evidently increase the specific surface area and shorten Na^+ ions diffusion distance. In addition, these composites can

enhance their electrochemical property since carbonaceous materials reinforce electrical conductivity and restrain the volume expansion of composites during the charge/discharge cycling [21]. Up to now, various strategies have been designed to construct TMS nanoparticles (NPs) and carbonaceous composites as conductive substrates. For example, Pan *et al.* [22] obtained CoS_2 @MCNFs material with a high specific capacity and excellent cycle life through electrospinning method. Jin *et al.* [23] fabricated a high-performance anode material by growing MoS_2 onto multi-walled carbon nanotubes via hydrothermal treatment. However, these traditional synthesis methods were far from large-scale application owing to its high cost and complex process. Thus, it is still a challenge to find simple and cost-effective method to construct high-performance TMS/C anode materials.

Herein, we utilized abundant and renewable carrageenan as the precursor to prepare Ni_3S_4 /carbon aerogels (CAs) as SIBs anode materials. Carrageenan as a type of seaweed biomass is composed of alternating disaccharide repeating sulfate groups units. Specifically, the added Ni^{2+} ions can interact with sulfate groups belonging to different double-helix, generating carrageenan- Ni^{2+} hydrogels [24-26]. On one hand, carrageenan- Ni^{2+} hydrogels can generate the porous aerogel structure with a high surface area after freeze-drying process. On the other hand, the sulfate groups located uniformly and confinement for Ni^{2+} ions in carrageenan double-helix structures converted into uniform Ni_3S_4 NPs embedded in porous carbon. While evaluated as anode materials in SIBs, the prepared Ni_3S_4 /CAs-1 sample exhibited a reversible capacity of 297 mAh g^{-1} after 100 cycles at 1 A g^{-1} . The excellent properties can be

contributed to the porous carbon network architecture derived from aerogels. It offers a buffer space to decrease the effect of volume expansion during the process of charge/discharge and endows abundant pathways to promote ion transportation as well as enhances the conductivity of the anode material. Furthermore, Ni_3S_4 NPs also shorten the path of Na^+ ions transports.

2. Experimental

2.1 Materials

The κ -carrageenans were purchased from Bright Moon Seaweed Group (Qingdao, China). Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), poly (vinylidene fluoride) (PVDF), and N-methyl-2-pyrrolidone (NMP) were bought from Sinopharm Chemical (Shanghai, China). The ethanol was of analytical grade and purchased from Sigma-Aldrich. The chemicals which did not require further purification were used.

2.2 Preparation of $\text{Ni}_3\text{S}_4/\text{CAs}$

Firstly, we prepared the mass ratio of 2 wt% κ -carrageenan solution at 85 °C for 55 minutes. Then, the above solution was dripped into the 0.2 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ethanol solution stirring under a high speed at room temperature to form carrageenan- Ni^{2+} hydrogel. Secondly, the obtained carrageenan- Ni^{2+} hydrogel was washed in deionized water and frozen -40 °C, generating carrageenan- Ni^{2+} aerogel. Thirdly, the aerogel was pyrolyzed at 700 °C for 1 hour with the heating rate of 4 °C under N_2 atmosphere. Then, the pyrolyzed sample was kept at 600 °C for t h with a heating rate of 8 °C under CO_2 atmosphere to reduce the content of carbon. The $\text{Ni}_3\text{S}_4/\text{CAs}$ samples were obtained. In the preparation of the samples, the samples were named as $\text{Ni}_3\text{S}_4/\text{CAs}-t$,

where t presents the reaction time in CO₂ atmosphere. Samples, namely Ni₃S₄/CAs, Ni₃S₄/CAs-1 and Ni₃S₄/CAs-2 were prepared successively.

2.3 Characterization

The crystalline structures were examined with X-ray diffraction (XRD, DX2700, China) at the scan rate (2θ) of 2 min⁻¹ with an applied current of 30 mV, operating with Cu K α radiation at 40 kV. X-ray photoelectron spectroscopy (XPS) was carried out with ESCALab250 electron spectrometer (Thermo Scientific Corporation) to characterize the chemical composition of obtained material. Raman spectroscopy were investigated on a Renishaw 1000 Raman spectrometer with the 514.5 nm excitation line of an Ar ion laser. Thermogravimetric analysis (TGA) measurement was obtained on an EXSTAR TG/DTA 6300 instrument (Seiko Instruments, Japan) in air. The specific surface area was gained from the Brunauer-Emmett-Teller (BET) analysis instrument (3H-2000PS2 static volume method), and the relative pressure (P/P_0) ranged between 0.01 and 0.2. The pore size distribution was calculated from isotherms. The morphology and structure of the as-prepared Ni₃S₄/CAs were carried out by transmission electron microscopy (TEM), high-resolution TEM operated at an accelerating voltage of 200 kV (JEM-2100F). The field emission scanning electron microscopy (FESEM) images were obtained on electron microscope (JSM-7001F, JEOL, Tokyo, Japan). The elemental composition of the resulting material was analyzed by energy dispersive X-ray spectrometer (EDS) attached to the FESEM instrument.

2.4 Electrochemical Measurements.

The $\text{Ni}_3\text{S}_4/\text{CAs-}t$, poly (-vinylidene fluoride) (PVDF) and acetylene black were mixed with a weight ratio of 8:1:1 into a solvent of N-methyl-2-pyrrolidone (NMP) to generate the slurry. The obtained slurry was coated on a Cu foil uniformly. The obtained electrode sheet was pressed after drying at 100 °C for 10 h, in which the mass loading of the active material is approximately 1.95 mg cm^{-2} . CR2025-type coin cells were assembled in the argon-filled glovebox ($\text{H}_2\text{O} < 0.1 \text{ ppm}$ and $\text{O}_2 < 0.1 \text{ ppm}$). The composition of the electrolyte is a mixed solution of 1.0 M NaClO_4 in ethylene carbonate/dimethyl carbonate (1:1 vol%) containing 5 wt% of fluoroethylene carbonate. Sodium metal as the counter electrode was served. All the electrochemical performances were performed in a voltage window between 0.01 and 3.0 V vs Na^+/Na using a cell testing equipment (LAND CT2001A). Cyclic voltammetry (CV) (0.01 to 3.0 V at a scan rate of 0.1 mV s^{-1}) was performed by CHI 760E electrochemical workstation.

3. Results and discussion

As shown in **Scheme 1**, firstly, in the aqueous solution the ι -carrageenan coils distribute randomly. Then, the above solution was dripped into the Ni^{2+} ethanol solution. In this way, Ni^{2+} cations would impel the shift of ι -carrageenan to double-helix structure from random coils. Furthermore, Ni^{2+} cations interact with sulfate groups belonging to different double-helix and then the random double helix structures are interconnected to form a carrageenan- Ni^{2+} hydrogels. Secondly, the carrageenan- Ni^{2+} porous aerogel would emerge during solvent evaporation process through freeze drying. Thirdly, the $\text{Ni}_3\text{S}_4/\text{CAs}$ were obtained from carrageenan- Ni^{2+}

aerogels through the pyrolysis at 700 °C under N₂ atmosphere. During the pyrolysis of carrageenan-Ni²⁺ aerogels, the binding Ni²⁺ ions and sulfate groups transported into Ni₃S₄ (NPs) and carrageenan converted to porous carbon, constructing the Ni₃S₄/CAs. Lastly, Ni₃S₄/CAs-*t* samples were prepared through removing carbon at 600 °C under CO₂ for *t* (*t* = 0, 1 and 2 hours).

The X-ray diffraction (XRD) patterns suggest the successful synthesis of Ni₃S₄/CAs. As shown in **Fig. 1a**, the patterns of as-prepared Ni₃S₄/CAs, Ni₃S₄/CAs-1 and Ni₃S₄/CAs-2 all show a broad diffraction peak at approximately 22.0°, indicating the existence of amorphous carbon in the sample. In addition, other sharp diffraction peaks at 2θ values of 26.5, 31.2, 37.9, 49.9 and 54.6 are observed from all the three samples, corresponding to the diffractions of (220), (311), (400), (511) and (440) planes of compound Ni₃S₄ (JCPD no. 47-1739), respectively. The intensity ratio (*I_D*/*I_G*) of the D and G bands about the obtained Ni₃S₄/CAs, Ni₃S₄/CAs-1 and Ni₃S₄/CAs-2 were determined to be 0.826, 0.877 and 0.901, respectively (**Fig. 1b**). The small *I_D*/*I_G* ratio also indicate that a highly graphitic structure exists in the CA matrix, which can enhance the electronic conductivity [27]. Subsequently, the weight content of three samples was measured by TGA under air atmosphere. A remained weight of 43.8%, 58.5% and 62.4% can be observed at 800 °C, corresponding to Ni₃S₄/CAs, Ni₃S₄/CAs-1 and Ni₃S₄/CAs-2, respectively (**Fig. S1**). This weight loss mainly centered on two parts. The first weight loss appeared from 300 to 550 °C, which is probably due to two aspects: combustion of carbon to CO₂ and the oxidation of Ni₃S₄ to SO₂, NiSO₄ and NiO. The second weight loss from 650 to 780 °C can be attributed

to the decomposition of residual NiSO_4 to NiO , which can be proved by the XRD patterns in **Fig. S2** [28]. Based on the TGA results, the percentages of carbon in the $\text{Ni}_3\text{S}_4/\text{CAs}$, $\text{Ni}_3\text{S}_4/\text{CAs-1}$ and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ are calculated to approximately 40.4%, 20.5% and 15.3%, respectively.

The specific surface area and porous characteristics of the samples were investigated by N_2 adsorption-desorption measurement. As illustrated in **Fig. 1c**, N_2 sorption isotherms of $\text{Ni}_3\text{S}_4/\text{CAs}$, $\text{Ni}_3\text{S}_4/\text{CAs-1}$, and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ all exhibit type II curves with conspicuous hysteresis loop at relatively high pressure, indicating the coexistence of micro- and meso-porous structures. These micro and mesopores are attributed to the pyrolysis of carrageenan macromolecule in which the active groups ($-\text{OH}$, $-\text{COOH}$ and $-\text{SO}_4\text{H}$) were thermally decomposed into small molecules (H_2O , CO_2 and SO_2) at high temperatures and released. The specific surface areas of $\text{Ni}_3\text{S}_4/\text{CAs}$, $\text{Ni}_3\text{S}_4/\text{CAs-1}$, and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ were 508, 485 and $378 \text{ m}^2 \text{ g}^{-1}$, respectively. The average pore size distributions were shown in **Fig. 1d**. Apparently, typical mesopores exists in the sample and they are centered at 3-4 nm. The pore size distribution of micropores were shown in **Fig. S3**, where the micropore sizes centered at 0.6-0.7 nm for these samples.

To further specifically investigate elementary composition of as-prepared $\text{Ni}_3\text{S}_4/\text{CAs-1}$, the X-ray photoelectron spectroscopy (XPS) measurement was conducted. (**Fig. 2** and **S4**). As displayed in **Fig. 2a**, the signals of C, O, S and Ni elements can be detected according to the XPS survey spectrum. The Ni 2p peaks at 873.2 eV (Ni $2p_{1/2}$) and 855.6 eV (Ni $2p_{3/2}$) accompanied with satellite peaks indicate

the existence of Ni^{2+} and Ni^{3+} [29,30] (**Fig. 2b**). The presence of nickel ions with mixed valences could improve the conductivity of nickel sulfide [15,30]. For S 2p spectra, the peaks at 162.0 eV (S 2p_{3/2}) and 163.7 eV (S 2p_{1/2}) are attributed to metal-sulfur bonds in as-prepared Ni_3S_4 [29,31]. The appearance of peaks at 165.2 eV may be attributed to sulfur oxides [32] (**Fig. 2c**). In addition, the C 1s can be deconvoluted into four peaks (**Fig. 2d**). Peaks at 284.5 eV, 285.1 eV, 286.1 eV and 288.6 eV are corresponded to the C-C, C-O, C-S and C=C peaks [33-35]. The C=C peak confirms the existence of a graphitic structure in this composite. And the C-S bond indicates the strong combination of porous carbon and Ni_3S_4 NPs [15,31,36]. The O 1s peaks at 532.1 eV and 533.5 eV are related to the S-O bond and O-C bond, respectively [30,37] (**Fig. S4**).

The morphologies of the fabricated $\text{Ni}_3\text{S}_4/\text{CAs-}t$ were measured by field emission scanning electron microscopy (FESEM). Despite a large number of nanopores were proved by the nitrogen adsorption-desorption isotherm, a typical macro-porous structure can be easily observed on the surface of $\text{Ni}_3\text{S}_4/\text{CAs-}t$ (**Fig. 3a, 3c and S5**). The formation of macro-pores can be attributed to freeze drying process of the carrageenan-Ni hydrogels, in which the solvent was directly sublimated and produced macro-pores. According to the **Fig. 3b**, abundant mesopores can also be observed on the surface of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ due to the pyrolysis of carrageenan macromolecules. This result matches well with the result of N_2 adsorption-desorption measurement. These pores are necessary to restrain the expansion of Ni_3S_4 in charge/discharge and enlarge the electrode/electrolyte area, which can be beneficial

for the property of cycling and reversible specific capability. In addition, this structure can shorten the Na^+ diffusion path, promoting the ion/electron transport kinetics [35,38]. Besides, the number of pores in $\text{Ni}_3\text{S}_4/\text{CAs-2}$ is fewer than that in $\text{Ni}_3\text{S}_4/\text{CAs}$ and $\text{Ni}_3\text{S}_4/\text{CAs-1}$ due to the increase of carbon removal time. The elemental composition of the sample was confirmed by the SEM energy dispersive X-ray spectroscopy (EDS). The C, Ni and S elements were uniformly distributed in $\text{Ni}_3\text{S}_4/\text{CAs-1}$ (**Fig. 3d**).

The transmission electron microscopy (TEM) images (**Fig. 4a-c**) unambiguously reveal that Ni_3S_4 NPs uniformly distributed in the carbon matrix in the $\text{Ni}_3\text{S}_4/\text{CAs-}t$ samples. The diameters of Ni_3S_4 NPs become large with the extension of carbon removed time, which is ascribed to the clustering of Ni_3S_4 NPs when the carbon is removed [32] (**Fig. S6**). In high resolution TEM (HRTEM) image (**Fig. 4d**), lattice fringes having a layer spacing of 0.285 nm can be clearly observed, which is corresponded to (311) planes of Ni_3S_4 [26]. It confirms that the Ni_3S_4 NPs with the size of ~ 20 nm were incorporated into to the porous carbon frameworks in $\text{Ni}_3\text{S}_4/\text{CAs}$ composite.

We employed $\text{Ni}_3\text{S}_4/\text{CAs-1}$ material as an anode material to evaluate the electrochemical performance for SIBs. The electrochemical properties of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ were conducted in the half cell configuration. **Fig. 5a** records the initial three cyclic voltammetry (CV) profiles of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ at a scan rate of 0.1 mV s^{-1} in the voltage window between 0.01 V and 3.0 V (vs Na^+/Na). In the first CV cycle, the cathodic reductive peaks of 0.01 and 0.96 V are contributed to the stepwise sodiation of Ni_3S_4

to generate Na_2S and Ni and generation of the solid electrolyte interface (SEI) [39,40]. Cathodic peak at 0.84 V and anodic peak at 1.66 V in the two subsequent cathodic scans indicate the structure change at the first discharge and then convert reversible structure [40]. The following two cycles of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ sample exhibit no difference, implying the good stability and reversibility toward sodium adsorption/desorption. **Fig. 5b** displays galvanostatic charge/discharge voltage profiles of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ at 1 A g^{-1} . During the first cycle discharge process, there is a plateau that can be observed at ~ 1.0 V due to the conversion of Ni_3S_4 to Na_2S and Ni . The corresponding charging plateau is at ~ 1.6 V. For the following two cycles of $\text{Ni}_3\text{S}_4/\text{CAs-1}$, the charge and discharge profiles are almost overlapped, corresponding to remarkable reversibility. Moreover, $\text{Ni}_3\text{S}_4/\text{CAs-1}$ delivers an initial discharge capacity of 360.6 mAh g^{-1} and reversible capacity of 260.3 mAh g^{-1} , with an initial coulombic efficiency (ICE) of 72.1%. In the process, the irreversible capacity loss is ascribed to the generation of SEI.

The long cycling stability of $\text{Ni}_3\text{S}_4/\text{CAs}$, $\text{Ni}_3\text{S}_4/\text{CAs-1}$, and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ at 1 A g^{-1} are also exhibited in **Fig. 5c**. After 100 cycles, the $\text{Ni}_3\text{S}_4/\text{CAs-1}$ still presents an outstanding reversible capacity of 297 mAh g^{-1} , indicating an excellent cycling stability. The $\text{Ni}_3\text{S}_4/\text{CAs-1}$ presents much higher capacity than of $\text{Ni}_3\text{S}_4/\text{CAs}$ (213 mAh g^{-1}) and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ after 100 cycles because of the optimal carbon content in these composites. For the $\text{Ni}_3\text{S}_4/\text{CAs-2}$ sample, its reversible capacity declines rapidly due to the collapse of the porous resulting from a violent volume expansion. Additionally, the pure CAs electrode only exhibits a reversible capacity of 75 mAh g^{-1}

(**Fig. S7**). The rate performances of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ electrode at different current density were studied (**Fig. 5d**). As expected, when the current density periodically increases from 0.2 A g^{-1} to 0.5 A g^{-1} , 1 A g^{-1} , 2 A g^{-1} and 5 A g^{-1} , the charge capacities declines from 424 to 340, 275, 230 and 179 mAh g^{-1} , respectively. When the current density recovered back to 0.2 A g^{-1} , $\text{Ni}_3\text{S}_4/\text{CAs-1}$ still stably delivers a high charge capacity up to 383 mAh g^{-1} , reaching 90.3% of that at the first 0.2 A g^{-1} . It indicates an excellent rate performance of $\text{Ni}_3\text{S}_4/\text{CAs-1}$, which can be ascribed to uniformly distribution of Ni_3S_4 NPs in the conductive CAs network and the hierarchical pore structure. The Ni_3S_4 NPs and the pores can alleviate the volume change and facilitate reaction kinetics, while the CAs network promotes conductivity and restraints particle crushing during cycling. Compared with the previously reported Ni_xS_y SIB anode material (**Table S1**), the $\text{Ni}_3\text{S}_4/\text{CAs-1}$ electrode exhibits higher reversible capacity and more excellent sodium storage performance than most of them [41,42]. In addition, no additional toxic sulfur source is required during the synthesis of this electrode material, which facilitates large-scale preparation of the metal sulfide-based SIB anode material.

CV profiles at different scan rate were measured to explore the apparent diffusion coefficients of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ electrode (**Fig. 5e**). According to Randles-Sevcik equation (1), the apparent diffusion coefficient (D_{Na^+}) can be calculated from the relationship between the peak current (I_p) of the CV curve and the square root of the scan rate ($v^{1/2}$) [37,43]. Based on the information of **Fig. S8**, the apparent diffusion coefficients are estimated to be 9.15×10^{-12} and $4.06 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$

for the reduction and the oxidation peaks, respectively. The electrochemical performance of $\text{Ni}_3\text{S}_4/\text{CAs-}t$ electrodes can be further evaluated by electrochemical impedance spectra (EIS). As illustrated in **Fig. 5f**, The Nyquist plots of $\text{Ni}_3\text{S}_4/\text{CAs}$, $\text{Ni}_3\text{S}_4/\text{CAs-1}$, $\text{Ni}_3\text{S}_4/\text{CAs-2}$ samples all show typical semicircles in high frequencies and oblique line in the low frequency region before the initial charge/discharge process with the corresponding same equivalent circuit shown in **Fig. S9**. The $\text{Ni}_3\text{S}_4/\text{CAs-1}$ sample with the smaller diameter than those of $\text{Ni}_3\text{S}_4/\text{CAs}$ and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ indicates the smaller charge transfer resistance at the interface between electrolyte and electrodes (R_{ct}). The R_{ct} values of $\text{Ni}_3\text{S}_4/\text{CAs}$, $\text{Ni}_3\text{S}_4/\text{CAs-1}$ and $\text{Ni}_3\text{S}_4/\text{CAs-2}$ electrodes are tested to be 248.5, 180.3, and 364.1 Ω , respectively. It indicates that Ni_3S_4 with a small size and coated with appropriate carbon content can reduce the resistance of the electrodes and improve charge transfer and Na^+ diffusion.

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{\text{Na}^+}^{1/2} v^{1/2} C \quad (1)$$

where n , A , and C represent the number of electrons involved in the redox reaction, the surface area of the electrode and the molar concentration of sodium ions in the anode, respectively.

The $\text{Ni}_3\text{S}_4/\text{CAs-1}$ anode material reveals high reversible capacity, rate performance and stability for SIBs, which is attributed to Ni_3S_4 NPs and proper porous micro/macro structure [44]. As illustrated in **Fig. 6**, due to suitable pore structure and carbon content, the carbonaceous network can maintain the stable structure of Ni_3S_4 NPs during the process of Na^+ insertion and desertion in $\text{Ni}_3\text{S}_4/\text{CAs-1}$ electrode. In addition, according to the TEM analysis of the electrode

after cycling (**Fig. S10a**), the Ni_3S_4 particles can maintain the uniform dispersion characteristics after the insertion of Na^+ without aggregation. However, for $\text{Ni}_3\text{S}_4/\text{CAs-2}$ electrode, the lower carbon content and larger size of Ni_3S_4 NPs lead to severe volume changes and deteriorate active materials after Na^+ insertion [32] (**Fig. S10b**). And the agglomeration of Ni_3S_4 nanoparticles may leads to severe pulverization of the electrode structure, resulting in irreversible capacity loss. As a result, the unique structure of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ facilitates the contact of electrolyte and active material, inhibits the dissolution of the intermediate polysulfide, shortens the distance of Na^+ diffusion and prevents loss of the active material during charge/discharge process. In addition, the porous micro/macro structure can act as a channel for rapid electron transport, resulting in excellent electrochemical property and high rate capability.

4. Conclusions

In conclusion, the Ni_3S_4 NPs embedded in the carbon aerogel with hierarchical pore structure were successfully synthesized from carrageenan-Ni hydrogels. Sulfate groups located in the double-helix structure can uniformly limit Ni^{2+} , which ensures the uniform dispersion of Ni_3S_4 NPs in carbon matrix. The hierarchical micro/mesoporous structure shortens the electron/ion transport path and effectively improves the structural stability of $\text{Ni}_3\text{S}_4/\text{CAs-1}$ during charge/discharge process. The prepared $\text{Ni}_3\text{S}_4/\text{CAs-1}$ sample exhibits high reversible capacity as high as 297 mAh g^{-1} after 100 cycles at 1 A g^{-1} , excellent rate capability and good cycle stability when employed as SIBs anode materials. Because the operation is simple and fast and there

is no toxic sulfur source in the synthesis process, this work provides a simple renewable and green method for preparing advanced metal sulfide-based SIBs anode materials with an excellent performance.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (grant no. 21501105, 51473081 and 51672143), Taishan Scholars Program and Outstanding Youth of Natural Science in Shandong Province (JQ201713).

References

- [1] Z. Yang, J. Zhang, M. C. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, Electrochemical energy storage for green grid, *Chem. Rev.* 111 (2011) 3577-3613.
- [2] C. Yang, X. Yu, S. Heissler, A. Nefedov, S. Colussi, J. Llorca, A. Trovarelli, Y. Wang, C. Woll, Surface faceting and reconstruction of ceria nanoparticles, *Angew. Chem. Int. Ed.* 56 (2017) 375-379.
- [3] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, *Chem. Rev.* 114 (2014) 11636-11682.
- [4] Y. M. Chiang, Building a better battery, *Science* 330 (2010) 1485-1486.
- [5] X. Rui, H. Tan, Q. Yan, Nanostructured metal sulfides for energy storage, *Nanoscale* 6 (2014) 9889-9924.
- [6] X. Wei, W. Li, J. A. Shi, L. Gu, Y. Yu, FeS@C on carbon cloth as flexible electrode for both lithium and sodium storage, *ACS Appl. Mater. Inter.* 7 (2015) 27804-27809

- [7] Y. Xu, W. Li, F. Zhang, X. Zhang, W. Zhang, C.-S. Lee, Y. Tang, In situ incorporation of FeS nanoparticles/carbon nanosheets composite with an interconnected porous structure as a high-performance anode for lithium ion batteries, *J. Mater. Chem. A* 4 (2016) 3697-3703.
- [8] H. Wang, J. Ma, S. Liu, L. Nie, Y. Chai, X. Yang, R. Yuan, CoS/CNTs hybrid structure for improved performance lithium ion battery, *J. Alloy. Compd.* 676 (2016) 551-556.
- [9] X. Wang, X. Liu, G. Wang, Y. Zhou, H. Wang, General formation of three-dimensional (3D) interconnected $MxSy$ ($M = Ni, Zn, \text{ and } Fe$)-graphene nanosheets-carbon nanotubes aerogels for lithium-ion batteries with excellent rate capability and cycling stability, *J. Power. Sources* 342 (2017) 105-115.
- [10] X. Li, Y. Chen, J. Zou, X. Zeng, L. Zhou, H. Huang, Stable freestanding Li-ion battery cathodes by in situ conformal coating of conducting polypyrrole on NiS-carbon nanofiber films, *J. Power. Sources* 331 (2016) 360-365.
- [11] C. H. Lai, M. Y. Lu, L. J. Chen, Metal sulfide nanostructures: synthesis, properties and applications in energy conversion and storage, *J. Mater. Chem.* 22 (2012) 19-30.
- [12] D. Zhang, W. Sun, Y. Zhang, Y. Dou, Y. Jiang, S. X. Dou, Engineering hierarchical hollow nickel sulfide spheres for high-performance sodium storage, *Adv. Funct Mater.* 26 (2016) 7479-7485.
- [13] T. Wang, P. Hu, C. Zhang, H. Du, Z. Zhang, X. Wang, S. Chen, J. Xiong, G. Cui, Nickel disulfide-graphene nanosheets composites with improved electrochemical

- performance for sodium ion battery, *ACS Appl. Mater. Inter.* 8 (2016) 7811-7817.
- [14] N. Mahmood, C. Zhang, Y. Hou, Nickel sulfide/nitrogen-doped graphene composites: phase-controlled synthesis and high performance anode materials for lithium ion batteries, *Small* 9 (2013) 1321-1328.
- [15] A. A. AbdelHamid, X. Yang, J. Yang, X. Chen, J. Y. Ying, Graphene-wrapped nickel sulfide nanoprisms with improved performance for Li-ion battery anodes and supercapacitors, *Nano Energy* 26 (2016) 425-437.
- [16] J. Li, S. Xiong, Y. Liu, Z. Ju, Y. Qian, High electrochemical performance of monodisperse NiCo_2O_4 mesoporous microspheres as an anode material for Li-ion batteries, *ACS Appl. Mater. Inter.* 5 (2013) 981-988.
- [17] Y. Tang, Y. Zhang, J. Deng, D. Qi, W. R. Leow, J. Wei, S. Yin, Z. Dong, R. Yazami, Z. Chen, X. Chen, Unravelling the correlation between the aspect ratio of nanotubular structures and their electrochemical performance to achieve high-rate and long-life lithium-ion batteries, *Angew. Chem. Int. Ed.* 53 (2014) 13488-13492.
- [18] L.-Z. Fan, S.-S. Chi, L.-N. Wang, W.-L. Song, M. He, L. Gu, Synthesis of TiO_x nanotubular arrays with oxygen defects as high-performance anodes for lithium-ion batteries, *ChemElectroChem.* 2 (2015) 421-426.
- [19] L. Wang, H. Gong, C. Wang, D. Wang, K. Tang, Y. Qian, Facile synthesis of novel tunable highly porous CuO nanorods for high rate lithium battery anodes with realized long cycle life and high reversible capacity, *Nanoscale* 4 (2012) 6850-6855.

- [20] F. Zhang, C. Yang, X. Gao, S. Chen, Y. Hu, H. Guan, Y. Ma, J. Zhang, H. Zhou, L. Qi, SnO₂@PANI core-shell nanorod arrays on 3d graphite foam: a high-performance integrated electrode for lithium-ion batteries, ACS Appl. Mater. Inter. 9 (2017) 9620-9629.
- [21] D. Li, C. Lv, L. Liu, Y. Xia, X. She, S. Guo, D. Yang, Egg-box structure in cobalt alginate: a new approach to multifunctional hierarchical mesoporous N-doped carbon nanofibers for efficient catalysis and energy storage, ACS Cent Sci. 1 (2015) 261-269.
- [22] Y. Pan, X. Cheng, L. Gong, L. Shi, T. Zhou, Y. Deng, H. Zhang, Double-morphology CoS₂ anchored on N-doped multichannel carbon nanofibers as high-performance anode materials for Na-ion batteries, ACS Appl. Mater. Inter. 10 (2018) 31441-31451.
- [23] R. Jin, Q. Zhai, Q. Wang, Amorphous transition metal sulfides anchored on amorphous carbon-coated multiwalled carbon nanotubes for enhanced lithium-ion storage, Chemistry 23 (2017) 14056-14063.
- [24] S. Janaswamy, R. Chandrasekaran, Effect of calcium ions on the organization of iota-carrageenan helices: an X-ray investigation, Carbohydr. Res. 337 (2002) 523-535.
- [25] V. L. Campo, D. F. Kawano, D. B. d. Silva, I. Carvalho, Carrageenans: biological properties, chemical modifications and structural analysis – a review, Carbohydr. Polym. 77 (2009) 167-180.
- [26] D. H. Li, D. J. Yang, X. F. Yang, Y. Wang, Z. Q. Guo, Y. Z. Xia, S. L. Sun, S. J.

- Guo, Double-helix structure in carrageenan-metal hydrogels: a general approach to porous metal sulfides/carbon aerogels with excellent sodium-ion storage, *Angew. Chem. Int. Ed.* 55 (2016) 15925-15928.
- [27] G. Xu, J. Han, B. Ding, P. Nie, J. Pan, H. Dou, H. Li, X. Zhang, Biomass-derived porous carbon materials with sulfur and nitrogen dual-doping for energy storage, *Green. Chem.* 17 (2015) 1668-1674.
- [28] G. Zhao, Y. Zhang, L. Yang, Y. Jiang, Y. Zhang, W. Hong, Y. Tian, H. Zhao, J. Hu, L. Zhou, H. Hou, X. Ji, L. Mai, Nickel chelate derived NiS_2 decorated with bifunctional carbon: an efficient strategy to promote sodium storage performance, *Adv. Funct. Mater.* 28 (2018) 1803690.
- [29] D. L. Legrand, H. W. Nesbitt, G. M. Bancroft, X-ray photoelectron spectroscopic study of a pristine millerite (NiS) surface and the effect of air and water oxidation, *Am Mineral.* 83 (1998) 1256-1265.
- [30] Y. Zou, X. Yang, C. Lv, T. Liu, Y. Xia, L. Shang, G. I. Waterhouse, D. Yang, T. Zhang, Multishelled Ni-rich $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers with low cation mixing as high-performance cathode materials for Li-ion batteries, *Adv. Sci.* 4 (2017), 1600262.
- [31] S. Qin, T. Yao, X. Guo, Q. Chen, D. Liu, Q. Liu, Y. Li, J. Li, D. He, $\text{MoS}_2/\text{Ni}_3\text{S}_4$ composite nanosheets on interconnected carbon shells as an excellent supercapacitor electrode architecture for long term cycling at high current densities, *Appl. Surf. Sci.* 440 (2018) 741-747.
- [32] D. Li, Y. Sun, S. Chen, J. Yao, Y. Zhang, Y. Xia, D. Yang, Highly porous

- FeS/carbon fibers derived from fe-carrageenan biomass: high-capacity and durable anodes for sodium-ion batteries, *ACS Appl. Mater. Inter.* 10 (2018) 17175-17182.
- [33] S. Zhang, D. Li, S. Chen, X. Yang, X. Zhao, Q. Zhao, S. Komarneni, D. Yang, Highly stable supercapacitors with MOF-derived Co_9S_8 /carbon electrodes for high rate electrochemical energy storage, *J. Mater. Chem. A* 5 (2017) 12453-12461.
- [34] D. Yuan, G. Huang, D. Yin, X. Wang, C. Wang, L. Wang, Metal-organic framework template synthesis of NiCo_2S_4 @C encapsulated in hollow nitrogen-doped carbon cubes with enhanced electrochemical performance for lithium storage, *ACS Appl. Mater. Inter.* 9 (2017) 18178-18186.
- [35] N. Li, S. Liao, Y. Sun, H. W. Song, C. X. Wang, Uniformly dispersed self-assembled growth of $\text{Sb}_2\text{O}_3/\text{Sb}$ @graphene nanocomposites on a 3D carbon sheet network for high Na-storage capacity and excellent stability, *J. Mater. Chem. A* 3 (2015) 5820-5828.
- [36] H. Wang, M. Liang, D. Duan, W. Shi, Y. Song, Z. Sun, Rose-like Ni_3S_4 as battery-type electrode for hybrid supercapacitor with excellent charge storage performance, *Chem. Eng. J.* 350 (2018) 523-533.
- [37] C. Lv, X. Yang, A. Umar, Y. Xia, Y. Jia, L. Shang, T. Zhang, D. Yang, Architecture-controlled synthesis of M_xO_y ($\text{M} = \text{Ni}, \text{Fe}, \text{Cu}$) microfibrils from seaweed biomass for high-performance lithium ion battery anodes, *J. Mater. Chem. A* 3 (2015) 22708-22715.

- [38] C. Wu, J. Maier, Y. Yu, Generalizable Synthesis of metal-sulfides/carbon hybrids with multiscale, hierarchically ordered structures as advanced electrodes for lithium storage, *Adv. Mater.* 28 (2016) 174-180.
- [39] Q. Chen, S. Sun, T. Zhai, M. Yang, X. Zhao, H. Xia, Yolk-shell NiS_2 nanoparticle-embedded carbon fibers for flexible fiber-shaped sodium battery, *Adv. Energy Mater.* 8 (2018), 1800054.
- [40] J. Deng, Q. Gong, H. Ye, K. Feng, J. Zhou, C. Zha, J. Wu, J. Chen, J. Zhong, Y. Li, Rational synthesis and assembly of Ni_3S_4 nanorods for enhanced electrochemical sodium-ion storage, *ACS Nano*. 12 (2018), 1829-1836.
- [41] R. Sun, S. Liu, Q. Wei, J. Sheng, S. Zhu, Q. An, L. Mai, Mesoporous NiS_2 nanospheres anode with pseudocapacitance for high-rate and long-life sodium-ion battery, *Small*. 13 (2017), 1701744.
- [42] M. Lu, W. Yu, J. Shi, W. Liu, S. Chen, X. Wang, H. Wang, Self-doped carbon architectures with heteroatoms containing nitrogen, oxygen and sulfur as high-performance anodes for lithium and sodium-ion batteries, *Electrochim. Acta* 251 (2017), 396-406.
- [43] P. Lu, Y. Sun, H. Xiang, X. Liang, Y. Yu, 3D amorphous carbon with controlled porous and disordered structures as a high-rate anode material for sodium-ion batteries, *Adv. Energy Mater.* 8 (2018), 1702434.
- [44] G. Dong, H. Wang, W. Liu, J. Shi, S. Sun, D. Li, H. Zhang, Y. Yang, Y. Cui, Nitrate salt assisted fabrication of highly N-doped carbons for high-performance sodium ion capacitors, *ACS Appl. Energy Mater.* 1 (2018), 5636-5645.

Scheme and Figure captions

Scheme 1. The synthesis process of $\text{Ni}_3\text{S}_4/\text{CAs}$.

Figure 1. (a) XRD patterns of $\text{Ni}_3\text{S}_4/\text{CAs-}t$. (b) Raman spectroscopy of $\text{Ni}_3\text{S}_4/\text{CAs-}t$. (c) Nitrogen adsorption-desorption isotherms of $\text{Ni}_3\text{S}_4/\text{CAs-}t$. (d) The corresponding pore size distribution curves of $\text{Ni}_3\text{S}_4/\text{CAs-}t$.

Figure 2. The XPS spectra of $\text{Ni}_3\text{S}_4/\text{CAs-1}$, (a) full survey scan, (b) Ni 2p, (c) S 2p, and (d) C 1s.

Figure 3. FESEM images of (a, b) $\text{Ni}_3\text{S}_4/\text{CAs-1}$, (c) $\text{Ni}_3\text{S}_4/\text{CAs-2}$. (d) The EDS mappings of Ni, C and S elements.

Figure 4. TEM images of (a) $\text{Ni}_3\text{S}_4/\text{CAs}$, (b) $\text{Ni}_3\text{S}_4/\text{CAs-1}$, and (c) $\text{Ni}_3\text{S}_4/\text{CAs-2}$. (d) HRTEM image of $\text{Ni}_3\text{S}_4/\text{CAs-1}$.

Figure 5. (a) CV curves of $\text{Ni}_3\text{S}_4/\text{CAs-1}$. (b) The $\text{Ni}_3\text{S}_4/\text{CAs-1}$ cycled at the 1st, 2nd and 3rd from 0.01 V to 3.0 V (vs. Na^+/Na) at a current density of 1 A g⁻¹. (c) Comparison of the long cycling performances of $\text{Ni}_3\text{S}_4/\text{CAs-}t$. (d) The reversible capacity of the $\text{Ni}_3\text{S}_4/\text{CAs-1}$ at different rates. (e) CV curves of the $\text{Ni}_3\text{S}_4/\text{CAs-1}$ under various scan rates (from 0.1 to 1.2 mV s⁻¹). (f) Nyquist plots of $\text{Ni}_3\text{S}_4/\text{CAs-}t$ electrodes.

Figure 6. Schematic of reaction process of Na^+ de/insertion for $\text{Ni}_3\text{S}_4/\text{CAs-1}$ and $\text{Ni}_3\text{S}_4/\text{CAs-2}$.

Scheme 1. The synthesis process of $\text{Ni}_3\text{S}_4/\text{CAs}$.

Figure 1. (a) XRD patterns of $\text{Ni}_3\text{S}_4/\text{CAs}-t$. (b) Raman spectroscopy of $\text{Ni}_3\text{S}_4/\text{CAs}-t$. (c) Nitrogen adsorption-desorption isotherms of $\text{Ni}_3\text{S}_4/\text{CAs}-t$. (d) The corresponding pore size distribution curves of $\text{Ni}_3\text{S}_4/\text{CAs}-t$.

Figure 2. The XPS spectra of $\text{Ni}_3\text{S}_4/\text{CAs-1}$, (a) full survey scan, (b) Ni 2p, (c) S 2p, and (d) C 1s.

Figure 3. FESEM images of (a, b) Ni₃S₄/CAs-1, (c) Ni₃S₄/CAs-2. (d) The EDS mappings of Ni, C and S elements.

Figure 4. TEM images of (a) $\text{Ni}_3\text{S}_4/\text{CAs}$, (b) $\text{Ni}_3\text{S}_4/\text{CAs-1}$, and (c) $\text{Ni}_3\text{S}_4/\text{CAs-2}$. (d) HRTEM image of $\text{Ni}_3\text{S}_4/\text{CAs-1}$.

Figure 5. (a) CV curves of $\text{Ni}_3\text{S}_4/\text{CAS}-1$. (b) The $\text{Ni}_3\text{S}_4/\text{CAS}-1$ cycled at the 1st, 2nd and 3rd from 0.01 V to 3.0 V (vs. Na^+/Na) at a current density of 1 A g^{-1} . (c) Comparison of the long cycling performances of $\text{Ni}_3\text{S}_4/\text{CAS}-t$. (d) The reversible capacity of the $\text{Ni}_3\text{S}_4/\text{CAS}-1$ at different rates. (e) CV curves of the $\text{Ni}_3\text{S}_4/\text{CAS}-1$ under various scan rates (from 0.1 to 1.2 mV s^{-1}). (f) Nyquist plots of $\text{Ni}_3\text{S}_4/\text{CAS}-t$ electrodes.

Figure 6. Schematic of reaction process of Na^+ de/insertion for $\text{Ni}_3\text{S}_4/\text{CAs-1}$ and $\text{Ni}_3\text{S}_4/\text{CAs-2}$.