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Seaweed-derived Synthesis of $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2/\text{r-GO}$ Aerogels as Air Stable Cathode Materials for Sodium-Ion Batteries

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Abstract

Due to the high theoretical capacity and open frameworks, the low-cost sodium iron pyrophosphate $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2$ has become a promising candidate for cathode materials of the sodium ion batteries (SIBs). However, NFPO is very sensitive to moisture and CO_2 , which causes serious surface oxidation reaction and results in degraded high-rate charge/discharge performance and cyclic stability. Herein, we developed a seaweed-derived synthesis strategy to prepare air stable NFPO/r-GO aerogels by using sodium alginate (SA) and reduced graphene oxide (r-GO) as precursors. X-ray photoelectron spectroscopy (XPS) proved that there were no residual Na species on the surface of prepared NFPO/r-GO aerogels and no any oxidized impurities after exposing in air for 100 days. When evaluating the NFPO/r-GO aerogels as cathode materials for SIBs, the sample exhibits excellent reversible capacity of 116.1 mAh g^{-1} at 0.1 C, 88.82 % capacity retention after 5000 cycles and superior rate capacity of 72.3 mAh g^{-1} at 20 C. The superior electrochemical performances are mainly attributed the delicate structure, which can not only increase the electronic conductivity, but also improve air stability of NFPO by suppressing surface side reactions with moisture and CO_2 .

Keywords: NFPO/r-GO aerogels, Air stable, Seaweed-directed synthesis, Porous structure, Sodium ion batteries.

1. Introduction

Nowadays, the secondary batteries are considered to be the most promising electrochemical energy storage systems for application in portable electronic devices and electric vehicles. Due to the high energy density, high voltage platform and lasting service life, lithium-ion batteries (LIBs) are currently premier energy storage system for electronic products and electric vehicles [1-4]. However, the high cost and scarce resource of lithium will be problems influencing its application in large-scale energy storage seriously [5, 6]. Most recently, sodium-ion batteries (SIBs), which operate on a similar electrochemical reaction principle to LIBs, have become the most attractive alternatives for large scale energy storage because of its abundant resource and low cost [7-11].

Recently, $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2$ (NFPO) has caught more and more attention as promising SIB cathode, because the $\text{Fe}_2\text{P}_4\text{O}_{22}$ and $\text{Fe}_2\text{P}_4\text{O}_{20}$ consisted of symmetrically arranged FeO_6 octahedral and P_2O_7 units can result in reversible Na^+ intercalation ability in NFPO. The theoretical capacity of NFPO can achieve 117.4 mAh g^{-1} based on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. However, the electronic conductivity of this polyanion cathode material is unsatisfactory due to a separation of FeO_6 octahedra by the P_2O_7 polyanions [12, 13]. Therefore, tremendous efforts have been devoted to resolve this problem. For instance, coral-like NFPO/C [14], NFPO/multi-walled carbon nanotube [15] and hollow NFPO microspheres [16] have been synthesized and reported with an improved rate performance. However, the high-rate charge/discharge performance and the cyclic stability are still unsatisfactory, which results from another serious problem of its high surface sensitive to moisture and CO_2 . Ha et al. first reported this phenomenon and Lin et al. further explained the dynamic oxidation mechanism [14, 17]. The severe

surface oxidation can form insulating Na_2CO_3 and NaOH during synthesis process and its discharge/charge process, leading to undesirable side reactions with the electrolyte and sluggish diffusion of Na^+ , thus deteriorating the reversible capacity and cyclic stability [14, 17, 18]. Therefore, it is imperative to seek a convenient and efficient method to synthesize air stable NFPO for good high-rate charge/discharge performance and the cyclic stability.

Herein, NFPO NPs were embedded into a reduced graphene oxide aerogel (NFPO/r-GO) with the assistance of alginate (an extract of sustainable seaweed). The delicate structure can not only increase the electronic conductivity, but also improve air stability of NFPO by suppressing surface side reactions with moisture and CO_2 . The air stable feature of NFPO/r-GO stems from the electrostatic absorption with Na^+ via the negatively charged carboxyl groups in β -D-mannuronate (M) blocks of alginate [19, 20] and uniform encapsulation for NFPO NPs by 3D porous r-GO aerogel in the subsequent pyrolysis process [21, 22]. Furthermore, the addition of r-GO can avoid particles aggregation during carbonization process and increase special surface area, which enlarges electrode-electrolyte contact area to improve the electronic conductivity [23]. As expected, the NFPO/r-GO aerogels exhibit excellent reversible capacity of 116.1 mAh g^{-1} at 0.1 C , 88.82 % capacity retention after 5000 cycles and superior rate capacity of 72.3 mAh g^{-1} at 20 C .

2. Experimental

2.1 Materials

Sodium Alginate (SA) ($(\text{C}_6\text{H}_7\text{O}_6\text{Na})_n$) was purchased from Aladdin. Sodium nitrate (NaNO_3), Sodium carbonate (Na_2CO_3), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were purchased from Sinopharm Chemical Reagent

(Shanghai, China) and used without further purification. Iron(II) Acetate ($\text{Fe}(\text{CH}_3\text{COO})_2$) and Sodium foil were purchased from Aladdin. Acetylene black and Al foil were purchased from Hefei Kejing Materials Technology Company (Anhui, China). Poly(vinylidene fluoride) (PVDF) was purchased from Sinopharm Chemical Reagent (Shanghai, China) and used without further purification. Electrolyte was purchased from Suzhou Qianmin Chemical Reagent Company (Jiangsu, China).

2.2 Synthesis of NFPO/r-GO aerogels

Firstly, 2.00 g sodium alginate and 0.20 g r-GO (10 wt %) were dispersed in 100 mL distilled water with magnetic stirring to form black collosol at room temperature. Secondly, 7.8 mmol NaNO_3 , 6.1 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 10 mmol $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in 100 mL distilled water to obtain a mixed aqueous solution. Then, the collosol was dropped into the mixed solution using a syringe needle at room temperature, and stirred for 1 h to form Na-Fe-P-SA/r-GO hydrogels. The obtained hydrogels were separated from the solution and washed with distilled water for several times, then frozen the as-prepared hydrogels at $-55\text{ }^\circ\text{C}$ for 12 h. Via a freeze-drying process, the hydrogels were dehydrated and lyophilized into aerogels. Finally, under 5 % H_2/Ar atmosphere, the aerogels were heated in a tube furnace at $600\text{ }^\circ\text{C}$ for 10 h to obtain aerogels denoted as NFPO/r-GO.

For comparison, three reference samples were prepared. Different from above process, two samples were only used sodium alginate to form hydrogels without r-GO, and one of them used oven instead of freeze-drying to remove moistures. The other sample was synthesized by a solid state reaction. 3.9 mmol Na_2CO_3 , 6.1 mmol $\text{Fe}(\text{CH}_3\text{COO})_2$, 10 mmol $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.26 g r-GO (10 wt %) were wet ball-milled with ethanol as solvent. The powders were heated at $300\text{ }^\circ\text{C}$ for 6 h and then $600\text{ }^\circ\text{C}$ for

12 h under Ar atmosphere. The reference sample only without r-GO was named as NFPO/C, and the sample without both r-GO and freeze-drying was denoted as d-NFPO/C, and the sample without SA but with r-GO was named as s-NFPO/r-GO, respectively.

2.3 Characterization

The phase structures of the products were characterized by powder X-ray diffraction (XRD, DX2700, China) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), ranging from 5-60° at a scan rate (2θ) of 2° min⁻¹. The experiment was operated at an accelerating voltage of 40 kV and an applied current of 30 mA. Field emission scanning electron microscopy (FESEM; JSM-7001F, JEOL, Tokyo, Japan) was used to investigate the morphology and structure of the NFPOs. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a FEI Tecnai 20 TEM with an accelerating voltage of 200 kV and energy dispersive X-ray spectroscopy (EDS). Near surface region chemical compositions were investigated by X-ray photoelectron spectroscopy (XPS) using an ESCALab250 electron spectrometer (Thermo Scientific Corporation) with monochromatic Al K α radiation (1486.7 eV, 150 W). The carbon contents of the samples were measured by the thermo gravimetric analysis (TGA; Seiko Instruments, Japan) from room temperature to 800 °C with a heating rate of 5 °C min⁻¹ in air. Nitrogen adsorption-desorption isotherms were measured to determine the specific surface area and pore size. The Brunauer-Emmett-Teller (BET) method calculated the specific surface area from the data in a relative pressure (P/P_0) range between 0.05 and 0.20. Based on the Barret-Joyner-Halenda (BJH) model, the pore size distribution plots were calculated from the adsorption branch of the isotherms, respectively.

2.4 Electrochemical measurements

The electrochemical characteristics of the samples were evaluated using CR2025 coin cells assembled in an Ar-filled glove box. To prepare the composite electrode, the NFPOs aerogels were mixed with acetylene black and poly (vinylidene fluoride) (PVDF) in a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) to form a slurry. Then the mixture was uniformly pasted on an Al foil substrate. The loading density of the active material in the electrode sheet was $\sim 0.85 \text{ mg cm}^{-2}$. The prepared electrode was dried in a vacuum oven at 120°C for 12 h to remove remained solvent. A solution of $1 \text{ mol L}^{-1} \text{ NaClO}_4$ dissolved in ethylene carbonate (EC) and propylene carbonate (PC) (1:1 v/v) was used as the liquid electrolyte. The cells were assembled using the prepared electrode as the working electrode, a glass microfiber separator film (diameter 47 mm, Whatman), and Na foil as the counter and reference electrode. The galvanostatic charge and discharge cycling was measured on a battery testing instrument (LAND CT2001A, Wuhan, China) in the voltage range of 1.6 to 4.0 V vs. Na^+/Na . Electrochemical impedance spectroscopy (EIS) and cycling voltammetry (CV) measurements were conducted using CHI760E electrochemical workstation at a scanning rate of 0.1 mV s^{-1} between 1.6 to 4.0 V. The EIS measurement was tested over a frequency range of 0.01 Hz-100 kHz.

3. Results and discussion

The synthesis procedure of NFPO/r-GO aerogels is shown in Scheme 1. Firstly, the mixed SA and r-GO were stirred to form the SA/r-GO collosol. Secondly, we used injector to add the SA/r-GO collosol into the aqueous solution containing Fe^{3+} , H_2PO_4^- , and Na^+ to form the Na-Fe-P-SA/r-GO hydrogels (Scheme 1a). This process confined

the Fe^{3+} cations into an “egg-box” through coordination by the four G-block of alginate [19, 23-25]. The Na^+ was immobilized electrostatically by the negatively charged carboxyl groups in M-block, which can protect the Na^+ from side reaction at the initial low-temperature annealing stage and convert to carbon/ Na^+ core/shell structure to suppress the formation of undesirable Na_2CO_3 and NaOH in subsequent calcination step [19, 20]. Thirdly, the prepared Na-Fe-P-SA/r-GO hydrogels were dehydrated by freeze-drying to obtain the Na-Fe-P-SA/r-GO aerogels (Scheme 1b). Scheme 1c has shown the carbonization process of Na-Fe-P-SA/r-GO aerogels. The cross-linked alginate macromolecules can form a porous carbonaceous matrix through thermal decomposition. Finally, the carbonaceous matrix and r-GO form a 3D aerogel with the novel open carbonaceous porous structured NFPO/r-GO aerogels. In addition, the samples prepared from Na-Fe-P-SA without freeze-drying (d-NFPO/C) and without addition of r-GO (NFPO/C) were also prepared for comparison.

The crystalline phases of all the samples were identified by XRD patterns displayed in Fig. 1a and Fig. S1a. In the patterns, all the diffraction peaks can be completely indexed to a triclinic structure (space group: $P\bar{1}$), indicating the high purity of these samples. The absence of impurity peaks indicates that the addition of r-GO has no effect on the crystal structure of NFPO [14, 17, 26].

XPS was carried out to further examine the composition and chemical state of the atoms in the samples. The wide XPS spectrum of NFPO/r-GO (Fig. S2a) shows that the binding energies of Na 1s, Fe 2p, O 1s, C 1s and P 2p are 1071.7, 710.1, 531.3, 284.7, and 133.6 eV, respectively [14, 19]. Fig. 1b presents the high-resolution XPS spectrum of Fe 2p of NFPO/r-GO. The binding energies positioned at 710.7 eV and 724.2 eV are attributed to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ with 13.5 eV energy separation, matching well with

previously reported spectra of Fe^{2+} oxidation state [27]. Fig. S2b presents the C 1s high resolution XPS spectrum of NFPO/r-GO. The higher binding energy featured at 284.6 eV corresponds to C-C, and higher binding energy observed at 286.3 eV is related to oxygen containing functional groups, such as C-O-C, C-OH arising from epoxide, hydroxyl, and carboxyl functionalities [19, 26]. The high resolution XPS spectra of O 1s and P 2p are shown at Fig. S2c and S2d. In Fig. S2c, the three different peaks are corresponded to oxygen ion (531.2 eV), H-O-C (532.6 eV) and O-C-O (535.6 eV), respectively [14, 28]. As shown in Fig. S2d, the peak at binding energy of 133.6 eV is ascribed to P-O bond [29]. The Na 1s XPS spectra of the NFPOs are shown at Fig. 1c, Fig. S1b and Fig. S3. In all the samples, there is only one peak at 1071.7 eV, which is associated with NFPO [14, 17]. It indicates that there is no residual Na species (Na_2CO_3 and NaOH) on the surface of all samples. The reason is that the immobilized Na^+ ions by M-blocks of alginate and encapsulation of NFPO NPs by carbonaceous matrix in the subsequent pyrolysis process can effectively suppress the formation of undesirable Na_2CO_3 and NaOH on the surface of NFPO.

Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model were conducted to acquire the specific surface area and pore size distributions of the NFPOs (Fig. 1d and 1e). As shown in Fig. 1d, all the adsorption curves are identified as type III. This kind of adsorption isotherm usually indicates the existence of mesopores. The calculated values of the BET specific surface area, average BJH pore diameters calculated from the desorption branch of the isotherm, and total pore volumes are listed in Table S1. The NFPO/r-GO displays a BET specific surface area of $86.03 \text{ m}^2 \text{ g}^{-1}$, which is higher than that of NFPO/C ($52.35 \text{ m}^2 \text{ g}^{-1}$) and d-NFPO/C ($62.86 \text{ m}^2 \text{ g}^{-1}$). The increased surface area may be attributed to the 3D porous r-GO aerogel structure, which

forms after the release of H_2O and CO_2 during the thermal decomposition of alginate. The average pore size is mainly centered at 9.2-10.6 nm for the three samples (Fig. 1e). The high surface area of NFPO/r-GO combined with its unique mesoporous feature is favorable for electrolyte accessibility and rapid Na^+ ion transport during electrochemical reaction. TGA (Fig. S4) is used to characterize the carbon content in the NFPOs. The specific carbon contents of NFPO/r-GO, NFPO/C, d-NFPO/C and s-NFPO/r-GO are 10.42%, 4.52%, 5.67% and 15.05%, respectively.

FESEM was used to investigate the morphology and microstructure of the NFPOs (see in Fig. 2 and Fig. S5). As shown in Fig. 2a-d, NFPO/r-GO and NFPO/C exhibit a more prosperous porous structure and a typical 3D framework structure, compared with d-NFPO/C and s-NFPO/rGO (Fig. 2e and 2f, Fig. S5a and S5b). The macropores and large mesopores are formed during the freeze-drying of the alginate/r-GO hydrogels. Furthermore, NFPO/r-GO exhibits a hierarchical porous structure and invisible exposed NFPO NPs. The exposed NFPO NPs are observed in the other samples especially the d-NFPO/C sample. It may be the reason that the r-GO sheet acts as a skeleton for the monodispersed Na-Fe-P-SA, leading to smaller particle size and better uniform dispersion which make NFPO NPs easily embed into 3D porous r-GO aerogel [30, 31]. This unique structure can effectively protect NFPO NPs from surface side reactions and significantly enhance the Na^+ ions transmission and conductivity during the electrochemical reactions, thus improves the electrochemical performance [32, 33].

TEM and HRTEM were used to further examine the architecture of NFPO/r-GO. As shown in Fig. 3a and Fig S5c, the NFPO NPs of NFPO/r-GO is homogeneously distributed in r-GO aerogel without aggregation, compared with NFPO/C and d-NFPO/C (Fig.S6a and S6c). Fig. 3b shows the enlarged

encapsulated NFPO NPs with a size of approximately 10-20 nm, much smaller than that of NFPO/C and d-NFPO/C sample (Fig. S6b and S6d). Similarly, the NPs size of s-NFPO/r-GO sample were about 10-50 nm (Fig. S5d), smaller than the other two references. These phenomena may be due to the r-GO acting as a dispersion skeleton, which can evenly disperse NFPO NPs and reduce particle size. The delicate structure can obstruct the air and offer a stable environment protecting NFPO from severe surface oxidation and forming insulating Na_2CO_3 and NaOH. The HRTEM image of NFPO/r-GO is shown in Fig. 3c and the corresponding Fast Fourier-Transform (FFT) pattern is shown in the inset of Fig. 3c. The NFPO/r-GO has well-textured with good crystallinity and the NFPO NPs are wrapped in carbon layer with a thickness of ~ 3 nm. The IFFT image of NFPO/r-GO is shown in Fig. S7a, and the d -spacing value of 0.397 nm is observed, which is corresponding to (022) plane of the NFPO phase (JCPDS Card No.12-4802) [26]. The elemental mapping by TEM energy dispersive X-ray spectroscopy (TEM-EDS) was further used to analyze the composition of NFPO/r-GO (Fig. 3d and Fig. S7b), indicating the uniformly presence of Fe, P, O and C elements in NFPO/r-GO sample.

The NFPOs were used as the cathode materials of SIBs to evaluate their electrochemical performance by CV and galvanostatic charge/discharge cycling techniques using coin-type half-cells. The tap density values of NFPO/r-GO, NFPO/C and d-NFPO/C are 0.50, 0.80 and 0.59 g cm^{-3} , respectively. Fig. 4a shows the galvanostatic charge/discharge curves of the NFPOs at a rate of 0.1 C (1 C=117.4 mA g^{-1}). The NFPO/r-GO exhibits a higher discharge capacity of 116.9 mAh g^{-1} than that of NFPO/C (96.1 mAh g^{-1}) and d-NFPO/C (68.4 mAh g^{-1}).

¹). In addition, CV technique is also effective to study the phase transition and ion diffusion process during the electrode reactions. The comparison about the CVs of the NFPOs is measured at a scan rate of 0.1 mV s⁻¹ in the potential voltage window of 1.6-4.0 V (*versus* Na⁺/Na). As shown in Fig. 4b and Fig. S8a, all the CVs exhibit three pairs of defined redox peaks. The initial anodic and cathodic peaks at approximately 2.5 V, 3.0 V and 3.3 V of the NFPOs can be attributed to series of sodium intercalation steps based on the Fe²⁺/Fe³⁺ redox reaction [15]. The corresponding redox reactions in the process of sodium extraction can be described by the following three equations [eqn. (1)-(3)]:

However, the position and intensity of the peaks are different from each other. Firstly, NFPO/r-GO shows the lowest overpotential of 61 mV and 104 mV between the anodic-cathodic peaks at the two major redox peaks of 2.5 V and 3.0 V, indicating the excellent electrode dynamics. This is consistent well with the charge/discharge examination results. Secondly, NFPO/r-GO has little change in the first three laps of the CVs compared with other samples (Fig. S9), indicating the high reversibility of Na intercalation/deintercalation in NFPO/r-GO. Thirdly, the order of peak current (*I_p*) is of NFPO/r-GO > NFPO/C > d-NFPO/C,

illustrating the largest Na^+ ion diffusion coefficient in NFPO/r-GO according to the following formula based on the classical Randles-Sevcik equation [33]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{\text{Na}^+}^{1/2} C_{\text{Na}^+} \nu^{1/2} (25^\circ \text{C}) \quad (4)$$

where I_p is the redox peak current (A), n is the electron transfer number involved in electrochemical reaction, A is the electrode surface area (cm^2), D_{Na^+} is the diffusion coefficient of Na^+ ($\text{cm}^2 \text{s}^{-1}$), C_{Na^+} is the concentration of Na^+ and ν is the potential scan rate (V s^{-1}).

Based on the above equation, we further tested the CV curves of the NFPOs at different scan rates to evaluate the sodium ion diffusion coefficient. As shown in Fig. S10, the redox peak current (I_p) is linear with the square root of the scan rate ($\nu^{1/2}$). According to the above Randles-Sevcik equation, the D_{Na^+} values are calculated to be 1.03×10^{-11} and $8.87 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$ for the cathodic and anodic peaks of NFPO/r-GO at 3.0 V, higher than that of NFPO/C (7.10×10^{-12} and $5.06 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$) and d-NFPO/C (4.61×10^{-12} and $3.40 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$), respectively.

In addition, the relation of $i = a\nu^b$ can be used to investigate the reaction kinetics of electrode redox reactions, where i is the redox peak current (mA), ν is the scan rate (mV s^{-1}), a and b are adjustable parameters [34]. Taking the logarithm on both sides of the above relation, we can get $\log i = b \log \nu + \log a$ [35]. If b value approaches 0.5, a Faradaic intercalation dominates the process; when b value approaches 1.0, a capacitive response is indicated [27]. As shown in Fig. S11a-c, $\log i$ is linear with $\log \nu$. The calculated b values of the cathodic and anodic peaks at the redox peaks of 2.5 and 3.0 V are shown in Table S2, indicating

that the electrochemical reactions of the NFPOs are composed of both Faradaic intercalation and capacitive response as the b value is between 0.5 and 1 for each redox peak. Based on the area integral method for the CV curves at different scan rates, the capacitance contribution of the NFPOs electrodes is shown in Fig. S11d-f. From the above data, we can see that the NFPO/r-GO electrode has higher b value and capacitance contribution percentage than reference electrodes. It can be suggested that Faradaic intercalation enables the NFPO cathode to operate at a fixed high-voltage potential, and capacitive response accelerates the high-rate Na^+ intercalation/deintercalation process with excellent cycling stability [36, 37].

EIS was also used to further quantitatively calculate the D_{Na^+} . The EIS profiles of the NFPOs measured at room temperature are shown in Fig. 4c, and the same simplified equivalent circuit is shown as the inset. All the plots are composed of the high-frequency flattened semicircle due to the sodium ion diffusion resistance in the surface layer of the electrode (R_{sf}), the high-middle frequency semicircle related to the charge-transfer resistance (R_{ct}) between the electrode and electrolyte interface, the low-frequency sloped line corresponding to the Warburg impedance (Z_{w}) [38]. The parameters of the equivalent circuit for the NFPOs are listed in Table S3. The R_{sf} values of NFPO/r-GO, NFPO/C and d-NFPO/C are 312.5, 404.7 and 498.2 Ω , respectively. The R_{ct} values of NFPO/r-GO, NFPO/C and d-NFPO/C are 461.0, 977.5 and 1143.0 Ω , respectively. The Z_{w} values of NFPO/r-GO, NFPO/C and d-NFPO/C are 0.004030, 0.005240 and 0.005380 Ω , respectively. From Table S3 we can see that NFPO/r-GO has the best sodium ion

diffusivity in the surface layer of the electrode and the lowest charge-transfer resistance between the electrode and electrolyte interface.

The resistance value of the sample can be obtained by fitting with a semicircular formula. The two intersections of the semicircle and the X axis are the two resistance values of the material at the high frequency and the low frequency. The conductivity of the sample can be obtained by the formula: $\sigma = 1/R$, so the electronic conductivities of NFPO/r-GO, NFPO/C and d-NFPO/C are 0.13 S m^{-1} , 0.07 S m^{-1} and 0.06 S m^{-1} , respectively. Compared with the other two samples, the NFPO/r-GO displays the reduced R_{ct} and increasing electronic conductivity (σ), which is related to the better rate capability. These mean that the novel 3D porous r-GO aerogel can significantly increase the electron transfer dynamics of the NFPO during Na^+ intercalation/deintercalation process.

Furthermore, the apparent Na^+ ion diffusion coefficient (D_{Na^+}) can illustrate the effective improvement of electrochemical kinetics. The value of D_{Na^+} is calculated using the following equation [39]:

$$D_{\text{Na}^+} = R^2 T^2 / 2 A^2 n^4 F^4 C^2 \sigma^2 \quad (5)$$

where R , T , A , n , F and C are the gas constant, the thermodynamic temperature, the electrode surface area, the electron number per molecule during electrode reaction, the Faraday's constant and the Na^+ concentration, respectively. The σ is the Warburg factor associated with Z_{re} ($Z_{re} \propto \sigma \omega^{-1/2}$). The relation plot between Z_{re} and $\omega^{-1/2}$ after the linear fitting are shown in Fig. 4d, which can estimate the Warburg factor σ and the apparent Na^+ ion diffusion coefficient. After substituting the corresponding counts, the D_{Na^+} values of NFPO/r-GO, NFPO/C

and d-NFPO/C are calculated to be 1.16×10^{-15} , 3.44×10^{-16} and $1.74 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, respectively. The improved D_{Na^+} of NFPO/r-GO compared with NFPO/C and d-NFPO/C in the whole electrode should stem from the novel 3D porous r-GO aerogel structure composed of carbonaceous matrix and r-GO skeleton, which can increase the electronic conductivity and suppress the formation of Na_2CO_3 and NaOH during alginate assist synthesis process.

As shown in Fig. 5a, the NFPO/r-GO displays superior rate capabilities of 116.1, 106.7, 98.3, 92.8, 86.9, 81.5 and 77.2 mAh g⁻¹ at the current densities of 0.1, 0.2, 0.5, 1, 2, 5, and 10 C, respectively. The rate performance of NFPO/r-GO and NFPO/C has been much improved compared with d-NFPO/C and s-NFPO/C (Fig. S8c). These results illustrate that the freeze-drying process can well maintain the 3D porous aerogel structure, thus providing more stable path for Na⁺ and electron transmission. Fig. 5b shows the typical charge/discharge plots of NFPO/r-GO with a stable charge/discharge potential-plateau at different current densities, indicating the expedite Na⁺ diffusion path and great energy density in NFPO/r-GO.

The cycle properties of the NFPOs measured at 1 C are shown in Fig. 5c and Fig. S8d. The NFPO/r-GO cathode exhibits an initial capacity of 94.3 mAh g⁻¹ and a reversible capacity of 85.0 mAh g⁻¹ after 300 charge/discharge cycles, indicating the excellent capacity retention of 90.14 %. We further investigated the cycling performance of all samples at both low (1 C) and high (10 C) rates in Fig. 5d. The NFPO/r-GO attains a capacity retentions of 95.97 % at 1 C and 97.09 % at 10 C, better than that of NFPO/C (93.23 % at 1 C and 94.22 % at 10 C) and d-NFPO/C (92.73 % at 1 C and 88.73 % at 10 C). This strongly confirms an

outstanding stable capacity of the NFPO/r-GO at large rate. The long-term cycling performance of the NFPOs at 20 C is also shown in Fig. 5e. The NFPO/r-GO electrode can still retain 88.82 % of the initial capacity after 5000 cycles, quite higher than NFPO (77.27 %) and d-NFPO/C (65.98% %) electrode. The FESEM images of the NFPOs electrodes after 5000 cycles are shown in Fig. S12, indicating that the morphology of NFPO/r-GO electrode remained well and other samples appeared agglomeration phenomenon, especially the d-NFPO/C electrode appeared pulverization phenomenon. Meanwhile, the stability of NFPO/r-GO is superior to most of the reported NFPO electrodes (Table S4) [14, 16, 17, 26, 36, 39-45]. That may be assigned to may be assigned to the 3D porous structure, which can not only buffer the volume expansion during Na^+ intercalation/deintercalation process, but also protect the NFPO NPs from surface side reactions.

We further explored the effect of the loading density of active material in the electrode and the r-GO adding weight percentage on electrochemical performance. We prepared several electrodes with different loading densities of 1.5, 2.0 and 2.5 mg cm^{-2} , respectively. As shown in Fig. S13a, after 200 charge/discharge cycles, the NFPO/r-GO electrodes display initial capacities of 81.3, 74.8 and 68.3 mAh g^{-1} and reversible capacities of 75.9, 68.6 and 62.1 mAh g^{-1} with loading density of 1.5, 2.0 and 2.5 mg cm^{-2} , respectively. With the increasing loading density, the rate capabilities of NFPO/r-GO decrease slightly (Fig. S13d). As shown in Fig. S13b,e,c,f, NFPO/C and d-NFPO/C show the same trend in cycle and rate performance as the loading density increasing.

In addition, we prepared the samples with different r-GO adding weight percentage of 5 wt%, 8 wt%, 10 wt%, 12 wt% and 15 wt%, respectively, corresponding to the different amounts of $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2$. As shown in Fig. S14, we obtained the best electrochemical performance with adding 10 wt % r-GO, and the electrochemical performance decreased when adding r-GO less or more than 10 wt %.

In order to confirm our envisage, XPS measurements of the NFPOs after exposure in air for 100 days were performed to investigate the influence on the surface oxidation by the 3D porous r-GO aerogel. As displayed in Fig. 6b and 6c, in addition to the peak at 1071.7 eV, there is the other peak at 1074.8 eV in Na 1s of NFPO/C and d-NFPO/C. This peak originates from the product of Na_2CO_3 from the surface oxidation. The side reaction equation is shown as follows [14]:

However, the peak at 1074.8 eV in Na 1s is not observed in NFPO/r-GO (Fig. 6a). The Fe 2p XPS spectras of the NFPOs after 100 days are shown in Fig. S15a-c. The binding energies positioned around 712.0 eV and 732.0 eV are attributed to Fe^{3+} . According to peak area integral, the percentages of Fe^{3+} in total iron of NFPO/r-GO, NFPO/C and d-NFPO/C are calculated as 12.0 %, 59.9 % and 60.7 %, respectively, indicating that the oxidation of NFPO/r-GO is the weakest. The XPS results strongly suggest that the 3D porous r-GO aerogel can effectively inhibit surface oxidation.

To further determine the influential mechanism of the 3D porous r-GO aerogel on the inhibition of surface oxidation, we used EIS to characterize the impedance

properties of all the samples exposed to air for different times. Fig. 6d shows the charge-transfer resistance of three samples exposed in air for different times. All samples show the same variation trend in initial, slowly increasing and finally stable. However, the NFPO/r-GO has the lowest values of R_{ct} , indicating the better conductivity and ions transmission. Moreover, we calculated the apparent oxidation rate based on the formula [14]:

$$\nu = \Delta R_{ct} / \Delta t \quad (7)$$

where ν is the apparent oxidation rate, R_{ct} is the charge-transfer resistance, and t is the air-exposure time.

The calculated values are shown in dotted lines of Fig. 6e. Same as the resistance results, the apparent oxidation rate of all samples has the same tendency of initially declining. Apparently, the NFPO/r-GO displays an excellent performance of far lower oxidation rate than the other two samples. We further compared the electrochemical performance of the NFPOs after exposure in air for 100 days. As shown in Fig. S15d and S15e, the NFPO/r-GO exhibits an initial capacity of 82.1 mAh g⁻¹ and a reversible capacity of 76.9 mAh g⁻¹ after 100 charge/discharge cycles, indicating the excellent capacity retention of 93.67 %, which is higher than that of NFPO/C (90.79 % capacity retention) and d-NFPO/C (83.19 % capacity retention). It means that the NFPO/r-GO is more air stable after exposure in air for 100 days. Based on the above results, we can determine the 3D porous r-GO aerogel together with the carbon layer coated outside the NFPO NPs can effectively reduce the contact between particles and CO₂ (H₂O) in the air, since they can suppress the occurrence of surface oxidation reaction and decreasing the apparent oxidation rate (Fig. 6f). The electrostatically immobilization

between negatively charged carboxylic acid groups in alginate and positively charged Na^+ can convert into a carbon/ Na^+ core-shell structure during the calcination process, which can effectively avoid the contact between Na^+ and CO_2 (H_2O) thus avoiding the formation of Na_2CO_3 (NaOH). At the same time, the cross-linked alginate macromolecule has a thermal decomposition and release CO_2 and H_2O to form a porous carbonaceous matrix. Finally the r-GO and porous carbon matrix formed by pyrolysis alginate are interlaced to form an open 3D carbonaceous porous aerogel, and the calcined NFPO NPs are evenly wrapped in the aerogel to inhibit the side reaction between NFPO and CO_2 (H_2O).

4. Conclusions

In summary, we successfully synthesized an air stable NFPO/r-GO aerogel cathode for SIBs using a seaweed-derived synthesis. The NFPO/r-GO aerogel cathode displays high specific capacity (reversible capacity of 116.1 mAh g^{-1} at 0.1 C) and good cycling stability (88.82 % capacity retention after 5000 cycles at 20 C). It is mainly attributed to the excellent electronic conductivity and much improved air stability, which stems from the electrostatic absorbed Na^+ through the negatively charged carboxyl groups in M-blocks of alginate and uniform encapsulation for NFPO NPs by 3D porous r-GO aerogel structure in the subsequent pyrolysis process. This study highlights the potential of NFPO/r-GO aerogels as cathode materials for future SIB systems and represents a successful application of seaweed derivative to synthesis of air stable cathode material for SIBs.

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Scheme and Figure captions

Scheme 1 The synthesis process of NFPO/r-GO aerogels. (a) Na-Fe-P-SA/r-GO hydrogels. (b) Na-Fe-P-SA/r-GO aerogels. (c) NFPO/r-GO aerogels.

Fig. 1 (a) XRD pattern of the NFPOs. (b) Fe 2p and (c) Na 1s level XPS spectra of NFPO/r-GO. (d) Nitrogen adsorption-desorption isotherms and (e) pore diameter distributions of the NFPOs.

Fig. 2 FESEM images of (a, b) NFPO/r-GO, (c, d) NFPO/C and (e, f) d-NFPO/C.

Fig. 3 (a, b) TEM images, (c) HRTEM image and (d) TEM-EDS mapping of NFPO/r-GO. The inset (c) shows the corresponding FFT pattern.

Fig. 4 (a) Charge/discharge curves of the NFPOs at 0.1 C. (b) CV curves of the NFPOs at a scan rate of 0.1 mV s^{-1} . (c) Nyquist plots of the NFPOs. (d) The relationship between Z_{re} and the reciprocal square root of the angular frequency in the low-frequency region.

Fig. 5 (a) Rate capability from 0.1 to 10 C of the NFPOs. (b) Charge/discharge curves of NFPO/r-GO from 0.1 C to 10 C. (c) Cycling properties of the NFPOs at 1 C. (d) Cycling properties of the NFPOs between 1 C and 10 C. (e) Long-term cycle properties of the NFPOs at 20 C.

Fig. 6 Na 1s XPS spectra of (a) NFPO/r-GO, (b) NFPO/C and (c) d-NFPO/C after exposure in air for 100 days. (d) R_{ct} of the NFPOs. (e) apparent oxidation rate (v) of the NFPOs. (f) Scheme of inhibiting surface oxidation for NFPO/r-GO.

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Highlights

- $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2/\text{r-GO}$ aerogels have superior electronic conductivity.
- $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2/\text{r-GO}$ aerogels have excellent air stability.
- Electrostatically immobilized Na^+ in alginate can be protected from side reaction.
- 3D porous r-GO aerogel can prevent NFPO NPs from side reaction with CO_2 (H_2O).
- The addition of r-GO can improve electronic conductivity.