Alginate/r-GO assisted synthesis of ultrathin LiFePO_4 nanosheets with oriented (010) facet and ultralow antisite defect

Yihui Zou^a, Guojing Chang^a, Shuai Chen^b, Tongchao Liu^c, Yanzhi Xia^a, Chengmeng Chen^b, Dongjiang Yang^{a,d,*}

^aCollaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, School of Environmental Science and Engineering, Qingdao University, Qingdao 266071, P. R. China.

^bState Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Science, Taiyuan 030001, P. R. China.

^cSchool of Advanced Materials, Peking University Shenzhen Graduate School, Peking University, Shenzhen 518055, P. R. China.

^dQueensland Micro- and Nanotechnology Centre and School of Natural Sciences, Griffith University, Nathan, Brisbane, QLD 4111, Australia.

*To whom correspondence should be addressed. E-mail: d.yang@qdu.edu.cn

KEYWORDS: LiFePO_4 ultrathin nanosheet, r-GO aerogel, Li-ion full-cell battery, Fe-Li antisite defect

ABSTRACT : $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$ (LTO/LFP) is a promising lithium ion batteries (LIBs) configuration due to its high safety and circularity. However, three factors result in the low capacity at high current density and low energy density in LTO/LFP: (i) low intrinsic electronic and ionic conductivities; (ii) long one-dimensional (1D) pathway along the [010] channel; (iii) Fe-Li antisite defect in LFP. It is still a great challenge to address the three problems simultaneously in LTO/LFP cell. Herein, we synthesized LFP ultrathin nanosheets (~ 5- 10 nm) with oriented (010) facet and ultralow Fe-Li antisite defects with the assistance of alginate and 2D reduced graphene oxide (LFP NS/r-GO). The novel “egg-box” structure in alginate is the key to restrain the Fe-Li antisites. The sandwich structure, which is formed by long range Van der

Waals forces and hydrogen bond between the Li-Fe-P-alginate molecules and 2D r-GO nanosheets, results in the formation of ultrathin LFP NSs with oriented (010) facet. The density functional theory (DFT) calculations reveal that the tacking of LFP ultrathin NS with oriented (010) facet on the r-GO has a strong ability of Li^+ ion deintercalation. When evaluating LFP NS/r-GO as cathode materials for LIBs, the sample displays outstanding rate capacity of 98.6 mA h g^{-1} at 100 C and its full cell with LTO anode achieves remarkable specific energy (265 W h kg^{-1}) and power density (6.81 kW kg^{-1}).

1. Introduction

Currently, research in rechargeable Lithium-ion batteries (LIBs) is focusing on employing LIB power packs in hybrid electric vehicles (HEV) and electric vehicle (EV) applications, which requires high energy density Li-ion power packs [1-4]. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$ (LTO/LFP) is a promising LIBs configuration due to its high safety and circularity [5,6]. However, the low energy density of this configuration is mainly ascribed to the low Li diffusion rate in LFP cathodes electrode [7-9]. The low Li diffusion rate in LFP cathodes stems from three factors: (i) low intrinsic electronic and ionic conductivities; (ii) the long one-dimensional (1D) pathway along the [010] channel between adjacent Li site; (iii) Fe-Li antisite defect in the LFP crystal [10-13]. Many efforts have been made to solve the three problems separately. To improve the electronic and ionic conductivities, conductive materials such as carbon nanotubes were introduced to modify the interface of LFP particles [14]. However, the full cell performance at the high discharge current density is still limited, because the addition of conductive carbon materials could only improve the inter-particle electric contact.

The essential problems to restrict Li^+ ion diffusion within the LFP crystal, the Fe-Li antisite defect and the long pathway of Li^+ migration along the 1D [010] channel [15], have not been addressed. Therefore recently, substantial efforts have been made to reduce the 1D diffusion path of Li^+ ions *via* controlling growth of LFP materials along their *b* axes. Zhao et al. have successfully synthesized (010) oriented LFP nanosheets with an average thickness of 50 nm [16]. However, the LFP nanosheets are not thin enough to combine with the conductive coating materials well to achieve the fast boundary diffusion of Li^+ ions [17,18]. Furthermore, studies with regard to suppressing Fe-Li antisite defects have been reported rarely. Paoletta et al. have reduced the Fe-Li antisite defects to 1 % with calcium ions by solvothermal method [19].

However, this method is too complex and the capacity at high current density is still not satisfying. Much recently, we developed a cost-effective method to suppress Fe-Li antisite defects to 0.23 % using the “egg-box” structure in alginate [20]. This makes it possible to develop a strategy to completely address the three problems and thus to achieve satisfying high electrochemical performance and energy density for a LTO/LFP cell.

In this work, LFP ultrathin nanosheets with oriented (010) facet and low Fe-Li antisite defects were synthesized with the assistance of “egg-box” in alginate and were attached onto reduced graphene oxide (r-GO) aerogel (LFP NS/r-GO). The novel “egg-box” structure in alginate is the key to restrain the Fe-Li antisites. The long range Van der Waals forces and hydrogen bond between the Li-Fe-P-alginate molecules and 2D r-GO nanosheets, results in the formation of ultrathin LFP NSs with oriented (010) facet. The novel strategy can address the three problems at the same time. Specifically, the ultrathin LFP NS with oriented (010) facet and low Fe-Li antisite defects could offer a short and unrestricted passageway for Li^+ diffusion in the LFP crystals. At the same time, the ultrathin structure of LFP NS made it possible to attach tightly with r-GO to achieve the fast boundary diffusion of Li^+ ions. The density functional theory (DFT) calculations reveal that the tacking of LFP ultrathin NS with oriented (010) facet on the r-GO has a strong ability of Li^+ ion deintercalation. When evaluated as cathode materials for LIBs, the sample displays outstanding rate capacity of 98.6 mA h g^{-1} at 100 C and its full cell with LTO anode achieves remarkable specific energy (265 W h kg^{-1}) and power density (6.81 kW kg^{-1}).

2. Results and discussion

The synthetic process of the LFP NS is represented in **Figure 1**. First, the sodium alginate (SA) was dissolved in r-GO/water to form SA/r-GO dispersion, followed by adding Fe^{3+} , H_2PO_4^- , and Li^+ with determined molar ratio (**Figure 1a**). In this case, the SA/r-GO dispersion was converted to hydrogel since the Fe^{3+} ions can coordinate with four G-blocks of SA, and the Li^+ ions were immobilized by the M blocks of SA. Then, the Fe-Li-P-alginate/r-GO hydrogel was dehydrated *via* a freeze-drying process to generate 3D Fe-Li-P-alginate/r-GO (**Figure 1b**). After calcination at 700°C in Ar/H_2 atmosphere, the 3D Li-Fe-P-alginate/r-GO was transferred into 3D LFP NS/r-GO-*x* (*x* = 2, 5, 8, 10, 12, mass ratio (%) of r-GO/SA). In addition, the samples prepared from Li-Fe-P-alginate without freeze-drying (C@LFP) and without addition of r-GO (C@LFP aerogel) were also prepared for comparison.

Figure 1. Procedure for the fabrication of LFP NS/r-GO based on a sol-gel process of alginate. (a) Formation of Li-Fe-P-alginate/r-GO hydrogel, (b) Formation of LFP NS/r-GO.

The formation mechanism of the ultrathin structure and crystal orientation of the LFP NS mainly stems from the synergistic effect of r-GO and SA molecules. When adding r-GO into the SA dispersion, the hydroxyl groups of SA can form hydrogen bonds with the surface hydroxyl groups of r-GO, and long range Van der Waals forces can be formed between hydrogen atoms of r-GO and SA molecules (see **Figure 1a**) [21]. That makes the gathered SA molecules distribute evenly between the layers of r-GO. Then after ion-exchange, the Fe-Li-P alginate molecules can also disperse well between the layers of r-GO [22]. The Fe-Li-P alginate interlayers converted to ultrathin LFP NS during the pyrolysis process, since the limited space of the layered r-GOs can supply the confined orderly microenvironment to prevent the aggregation of LFP NS further [23]. In addition, according to the surface energy calculation of LFP, it was found that the (010) facet of LFP is the most prominently oriented plane due to its lowest surface energy [24]. For nanosized crystals, such as NS, the morphology is especially expected to close to the equilibrium form with the most stable (010) face (see **Figure 1b**). So the LFP crystal grows along the facets perpendicular to (010) facet to form LFP NS with exposed (010) facet.

Figure 2. SEM images of (a) C@LFP, (b) C@LFP aerogel, (c) LFP NS/r-GO-10. (The inset is the corresponding overall appearance). (d) TEM image of LFP NS/r-GO-10. (e) TEM image of an individual LFP NS with the corresponding SAED pattern of the entire crystal. (f) HRTEM image of the area boxed in (e) with the corresponding FFT pattern.

The morphology and structure of the LFP NS/r-GO-x, C@LFP, and C@LFP aerogel were investigated by field-emission scanning electron microscopy (FESEM). As shown in **Figure 2a** and **2b**, the porous structure of LFP NS/r-GO-10 and C@LFP aerogel is more prosperous than C@LFP without freeze-drying (**Figure 2c**). Furthermore, LFP NS/r-GO-10, exhibit a hierarchical porous structure. The macropores and large mesopores are formed during the freeze-drying of the alginate/r-GO hydrogels. Other LFP NS/r-GOs with different r-GO additions also present the hierarchical porous structure (**Figure S1**). The specific surface area and pore size distributions of LFP NS/r-GO-10, C@LFP aerogel, and C@LFP were investigated by Brunauer-Emmett-Teller (BET) method and Barret-Joyner-Halenda (BJH) model. Their N_2 adsorption-desorption isotherms show typical type IV adsorption isotherm (**Figure S2a**). The BET specific surface area (S_{BET}) of LFP NS/r-GO-10 is $287.4 \text{ m}^2\text{g}^{-1}$, much higher than those of C@LFP aerogel ($170.9 \text{ m}^2\text{g}^{-1}$) and C@LFP ($87.4 \text{ m}^2\text{g}^{-1}$). The average BJH pore diameter calculated from the desorption branch of the isotherm is mainly centered at 2.1-3.4 nm for the three samples (**Figure S2b**). The high surface area of LFP NS/r-GO-10 combined with its unique 3D

hierarchical porous hybrid framework are favorable for electrolyte accessibility and rapid Li^+ ion transport during electrochemical reaction [25]. The transmission electron microscopy (TEM) images of LFP NS/r-GO-10 in **Figure 2d** and **2e**, show that the LFP NSs with the size of ~ 200 nm were attached on r-GO nanosheet tightly. Their high resolution TEM (HRTEM) image (**Figure 2f**) reveals that the d -spacing values of 0.47 and 1.03 nm are observed from the HRTEM image, which are corresponding to (001) and (100) lattice fringes of orthorhombic LFP (JCPDS card no 83-2092, space group Pnma, $a = 1.033$, $b = 0.601$, and $c = 0.469$ nm) [26], respectively. Selected-area electron diffraction (SAED) pattern (inset of **Figure 2e**) and the fast Fourier-transform (FFT) pattern of the selected area in the HRTEM image (inset of **Figure 2f**) all confirmed that these LFP NSs have the same crystalline phase and the zone axes can be indexed to [010]. The 1D channel oriented along [010] direction of LFP can efficiently facilitate the full insertion and extraction of Li^+ ions during the charging and discharging process.

Figure 3. (a) AFM image of LFP NS/r-GO-10. (b) The corresponding thickness analysis in (a). (c) TEM-EDS mapping of LFP NS/r-GO-10.

Atomic force microscopy (AFM) analyses of LFP NS/r-GO-10 (**Figure 3a,b**) display that the LFP NSs are as thin as ~ 5 -10 nm. The ultrathin LFP NS could attach tightly with r-GO nanosheets to facilitate the Li^+ ions intercalation through the phase-boundary. For comparison, the TEM images of C@LFP aerogel show that the LFP particles are gathered into bulk (see

Figure S3), which further certified the effect of r-GO on the forming of ultrathin structure. The elemental mapping by energy dispersive X-ray spectroscopy (EDS) was further used to analyze the composition of LFP NS/r-GO-10 (**Figure 3c**), revealing P, O and Fe elements are homogeneously distributed in the LFP NS.

Figure 4. (a) Rate capability from 0.5 C to 100 C of C@LFP, C@LFP aerogel, LFP NS/r-GO-10. (b) Charge-discharge curves of LFP NS/r-GO-10 from 0.5 to 100 C of LFP NS/r-GO-10. (c) The comparison of the rate capability of LFP NS/r-GO-10 with those of other LFP/C composite electrodes reported previously. (d) Cycling performance at 10 C (1 A g⁻¹) of C@LFP, C@LFP aerogel, LFP NS/r-GO-10 and the coulombic efficiency of LFP NS/r-GO-10.

The obtained LFP NS/r-GOs, C@LFP aerogel, and C@LFP were characterized by powder X-ray diffraction (PXRD). As shown in **Figure S4**, all diffraction peaks were perfectly indexed to olivine LFP (JCPDS Card no. 83-2092). In order to investigate the percentage of Fe-Li antisite defects in a material, all the PXRD data were analyzed by simultaneous Rietveld refinement with General Structure Analysis System (GSAS) software. The Rietveld refinement calculated from

Pnma phase group provides good fitting based on the Rp, Rwp and χ^2 fitting factors, as shown in **Figure S5**. According to the refinement results (see **Table S1, S2, S3**), the percentages of Fe-Li antisites were 0.27, 0.25, and 0.21 % for the C@LFP, C@LFP aerogel, and LFP NS/r-GO-10, respectively, indicating very low Li/Fe exchange defects in the final LFP crystallization [27]. Furthermore, a unit cell volume around 291.4-295.0 Å³ is believed to be well-crystallized for LFP, and the value of 291.4 Å³ is defect-free [20]. The values of the cell volume are 293.8-292.1 Å³ for the three samples (**Table S1-S3**), also suggesting that the concentration of Fe-Li antisite defects maintains at a very low level. The “egg-box” in alginate plays the key role in decreasing the Fe-Li antisite defects, as reported earlier by our group [20,28,29]. The Fe-Li antisite defects for the C@LFP, C@LFP aerogel, and LFP NS/r-GO-10 were further examined by Fourier transform infrared spectroscopy (FTIR). As shown in **Figure S6**, the infrared absorption bands at 948 cm⁻¹ corresponded to the symmetric stretching vibration of the P-O band, indicating defect-free LFP and a low Li-Fe antisite defect concentration [5].

The electrochemical properties of LFP NS/r-GOs as the cathode materials in Li half-cells were evaluated by galvanostatic charge/discharge techniques. As shown in **Figure 4a**, the LFP NS/r-GO-10 delivers stable capacities of 165.6, 159.5, 151.2, 143.0, 130.3, 117.6, 107.7, 98.6 mA h g⁻¹, respectively, as the current densities stepwise from 0.5 to 1, 2, 5, 10, 20, 50, and 100 C, which is superior to the other LFP NS/r-GOs (**Figure S7**), indicating the most appropriate addition of r-GO is 10 wt%. Meanwhile, the rate performance of LFP NS/r-GO-10 has been improved much compared with C@LFP and C@LFP aerogel. Typical charge/discharge profiles of LFP NS/r-GO-10 at different current rates in the first cycle are shown in **Figure 4b**. The stable and high discharge potential-plateau at each current rate indicates both the higher energy density and power density [12]. **Figure 4c** compares the rate capability of LFP NS/r-GO-10 with the previously reported LFP/C composites with different LFP morphology and carbon source. The performance of this work is superior to that of the reported LFP/C electrodes so far [7,8,10,11,17,18,26,30-34]. As shown in **Figure 4d**, the reversible capacity of LFP NS/r-GO-10 remains at 130.6 mA h g⁻¹ after 2000 cycles at 10 C with a capacity retention of 99.55 %, superior to C@LFP (93.42 %) and C@LFP aerogel (97.21 %). Meanwhile, the stability of LFP NS/r-GO-10 is much better than most reported work [9,34-36]. As shown in **Figure S8a**, there is no obvious morphology change of the LFP NS/r-GO-10 after cycling 2000 galvanostatic charge-discharge laps at 10 C, and the LFP NSs were still attached on the r-GO nanosheet

homogeneously (**Figure S8b**). The better recyclability of LFP NS/r-GOs may attribute to the well crystalline LFP NS with ultralow Fe-Li antisite defects and the fast capacity response of r-GOs component, which could efficiently buffer the impact to LFP under high-rate cycling condition [25]. Meanwhile, the 3D r-GO network is a stable skeleton for the monodispersed LFP NS, which enhances its holistic structure robustness and favors the cycling stability [37]. In addition, the corresponding average coulombic efficiency reaches to 99.42 %, suggesting the highly reversible Li^+ insertion/extraction kinetics.

Figure 5. (a) Charge/discharge profiles of C@LFP, C@LFP aerogel, LFP NS/r-GO-10 at 0.5 C. (b) CVs of C@LFP, C@LFP aerogel, LFP NS/r-GO-10 at the scan rate of 0.1 mV s^{-1} . (c) Nyquist plots of C@LFP, C@LFP aerogel, LFP NS/r-GO-10. (d) The relationship between $-Z_{im}$ and the reciprocal square root of the angular frequency in the low-frequency region.

Figure 5a shows the charge/discharge profiles of C@LFP, C@LFP aerogel and LFP NS/r-GO-10 at a low rate of 0.5 C. The charge/discharge potential-plateau of LFP NS/r-GO-10 was

more stable than that of other samples (the inset of **Figure 5a**), indicative of the more expedite Li^+ diffusion paths in LFP NSs [23]. The cyclic voltammetry (CV) of LFP NS/r-GO-10 was measured at a scan rate of 0.1 mV s^{-1} in the potential window range of 2.4 to 4.1 V vs. Li^+/Li . As displayed in **Figure 5b**, only one pair of well-defined anodic and cathodic peaks are observed from the CV pattern. However, the position and intensity of the peaks were different from C@LFP, C@LFP aerogel. Firstly, LFP NS/r-GO-10 displays the lowest overpotential of 143 mV between the anodic and cathodic peaks, indicating optimized electrode kinetics and reversibility. Secondly, the order of peak current (I_p) was $\text{LFP NS/r-GO-10} > \text{C@LFP aerogel} > \text{C@LFP}$. Therefore, LFP NS/r-GO-10 displays the largest Li^+ ion diffusion coefficient based on the following formula:

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

The D_{Li^+} value is proportional to $I_p^{-1/2}$ [38].

Electrochemical impedance spectroscopy (EIS) was further used to calculate the D_{Li^+} quantitatively. The impedance parameters are fitted by the same equivalent circuit shown as the inset in **Figure 5c**. The high-frequency intercept along the Z' axis is the combined resistance of the cell components and electrolyte (R_e). The high-middle frequency semicircle is the composed of two semicircles, which are related to the Warburg impedance (Z_w) and the charge-transfer resistance (R_{ct}) at the interface between the electrode and electrolyte. The low-frequency oblique line corresponds to the Warburg impedance (W), which is attributed to the Li^+ ion diffusion in the electrode materials. Obviously, the LFP NS/r-GO-10 shows the significantly reduced charge transfer resistance (R_{ct}) in comparison with the C@LFP aerogel, indicating that the conductive 3D r-GO aerogel is an ideal porous network for ion interfacial diffusion. Furthermore, the R_{ct} value of C@LFP aerogel (Ω) is smaller than that of C@LFP (Ω), demonstrating that 3D hierarchical porous structure of the aerogel is another effective factor in increasing the Li^+ interfacial diffusion.

In addition to R_{ct} , the apparent Li^+ ion diffusion coefficient (D_{Li^+}) also exhibits a noticeable synergistic effect. The values of D_{Li^+} were calculated from the inclined lines in the Warburg region using the following equation [6]:

$$D_{\text{Li}^+} = R^2 T^2 / 2 A^2 n^4 F^4 C^2 \sigma^2$$

Where σ is the Warburg factor associated with $-Z_{re}$ ($-Z_{re} \propto \sigma \omega^{-1/2}$). After the linear fitting, the relation plot between $-Z_{re}$ and the reciprocal square root of the angular frequency ω (**Figure 5d**)

was used to estimate the Warburg factor σ and the apparent Li^+ ion diffusion coefficient [38]. The D_{Li^+} values of LFP NS/r-GO-10, C@LFP aerogel, and C@LFP were calculated to be 4.74×10^{-12} , 8.01×10^{-13} , and $7.96 \times 10^{-13} \text{ cm}^2 \text{ S}^{-1}$, respectively. The much improved D_{Li^+} of LFP NS/r-GO-10 in the whole electrode must stem from the three aspects: (i) fast Li^+ diffusion in the crystals, (ii) fast Li^+ diffusion in the boundaries between the LFP NS and r-GO NS, (iii) efficient Li^+ diffusion at the interfaces between the LFP NS/r-GOs and electrolyte. This indicates that the special size and (010) facet oriented LFP with low Fe-Li antisites can offer a short and unrestricted path in the crystals. LFP ultrathin NS can combine tightly with the r-GO NS, which is favorable for the Li^+ boundary diffusion. Moreover, the conductive 3D hierarchical porous r-GO aerogel can offer improving Li^+ ion in the interfaces. Meanwhile, C-C, C-O-C, and C-OH arising from epoxide, hydroxyl and carboxyl functionalities were observed in the C 1s high resolution X-ray photoelectron spectroscopy (XPS) spectra of LFP NS/r-GO-10 (**Figure S9**) [34], which also ensure the hydrophilic of r-GO aerogel for ion interfacial diffusion.

Figure 6. Li deintercalation formation energy of the LFP NS/r-GO at the different facets of LFP NS/r-GO. (a) (010), (b) (100) and (c) (001), in which the white balls represent the Li vacancy, the yellow, purple, red, gray and brown balls represent Li, P, O, C and Fe atoms, respectively.

To further investigate the reason of fast Li^+ ions diffusion in LFP NS/r-GO-10, we calculated the Li deintercalation formation energy of the LFP NS with exposed facets of (001), (010), and (100) compositing in r-GO, respectively. The Li^+ ion diffusion is all along the [010] direction in the primitive cells for the three models. As shown in **Figure 6a**, the LFP NS with exposed facets of (010) exhibit the lowest Li deintercalation formation energy (-2.90 eV). The LFP NS with exposed facets of (001) has a Li^+ ion deintercalation formation energy of -3.48 eV, while the (100) facet shows -3.11 eV (**Figure 6b** and **6c**). The result indicates that LFP NS with exposed facets of (010) compositing in r-GO has a strong ability of Li^+ ion deintercalation, which was consistent with the improved electrochemical performance of LFP NS/r-GOs.

Figure 7. Electrochemical performance of LFP NS/r-GO-10/LTO full-cell. (a) Cell voltage profiles cycling at 0.5 C (0.05 A g⁻¹). (b) Rate capability as function of the applied current density (from 0.1 to 60 C). (c) Effect of the current density on the average discharge voltage. (d) Ragone-like plot displaying their specific energy and power (referred to the total active material amount, i.e., LFP NS/r-GO+LTO).

We utilized the as-synthesized LFP NS/r-GO-10 as cathode material and LTO as anode material to develop a LFP NS/r-GO-10/LTO lithium-ion full-cell. The average LFP/LTO active mass ratio is 0.82 with the specific capacity ratio of LTO anode to LFP cathode being 1.2 (calculated according to the practical capacities of $165.1 \text{ mA h g}^{-1}$ for LFP/Li half cell and $160.2 \text{ mA h g}^{-1}$ for LTO/Li half cell obtained at the 5th cycle at 0.5 C). **Figure 7a** displays the voltage profiles of the full-cells during the first charge/discharge cycles at a low current of 0.05 A g^{-1} . As expected, lithiation of the negative electrode has a clear influence on the discharge potential. In the case of LTO show the typical plateau at $1.5 \text{ V vs. Li/Li}^+$ (see **Figure S10**). The LFP NS/r-GO-10/LTO cell has a cell discharge potential up to 1.86 V , which is higher than most references [39-41]. **Figure 7b** shows the capacity of the full-cell under increasing current density, which shows a capacity of $142.0 \text{ mA h g}^{-1}$ at 0.5 C (0.05 A g^{-1}) and a very stable capacity values at any current density. The capacity retention is more than 52.44 % of the initial capacity at the highest current density of 60 C. In **Figure 7c**, the average discharge voltage of the full cells is plotted as a function of the applied current density. The discharge voltage of the LFP NS/r-GO-10 full-cell is remarkably retained upon increasing the current density. For instance, the discharge voltage is as high as 1.74 V when the applied current density is at 60 C. This means a fast kinetics in lithiation process, which is due to the short and expedite Li^+ diffusion path along the [010] channel, effective boundary Li^+ diffusion between the LFP NS and r-GO NS and interfacial Li^+ diffusion between the LFP NS/r-GOs and electrolyte. In addition, the channel structure of aerogels has created sufficient space between the particles, as a result, decreasing the concentration polarization when the electrode is subjected to high current loads [37]. As shown in **Figure 7d**, the Ragone-like plot displays a very high specific power of 6.81 kW kg^{-1} at 6 A g^{-1} , much higher than the reported values of 3.72 kW kg^{-1} for $\text{ZnFe}_2\text{O}_4\text{-C/LFP-CNT}$ and 4.50 kW kg^{-1} for graphene/LFP, respectively [40,41]. Furthermore, the specific energy shows a value of 265 W h kg^{-1} at a current density of 0.05 A g^{-1} . This value is much higher than the best specific energy (202 W h kg^{-1}) using an LFP-CNT cathode and $\text{ZnFe}_2\text{O}_4\text{-C}$ anode [41], indicating a remarkable achievement of such novel battery chemistry. It should be noted that the LTO/LFP NS/r-GO-10 full-cell contains a not negligible amount of carbon and binder. For instance, the carbon content in LFP NS/r-GO-10 is about 11.9 wt% by using thermogravimetric analysis (TGA, **Figure S11**). Given the total mass of the electrode (including active materials, carbon and

binder), the specific energy delivers a real value of 184 W h kg^{-1} . This has been improved $\sim 39\%$ compared with the best specific energy of 132 W h kg^{-1} reported by Varzi et al [41].

3. Conclusions

In summary, we demonstrated a sustainable biomass process for making LFP NS/r-GOs as high-performance cathode material in full cell assembled with LTO as anode material. The ultrathin LFP NSs displayed exposed (010) surface and ultralow Fe-Li antisite defects. The novel “egg-box” structure in alginate is the key to restrain the Fe-Li antisites. The long range Van der Waals forces and hydrogen bond between the Li-Fe-P-alginate molecules and 2D r-GO nanosheets have directionality to form LFP NS with oriented (010) facet. The oriented (010) facet, ultralow Fe-Li antisite defects, and the unique porous r-GO aerogel structure contributed to fast Li^+ diffusion in the crystals and its boundary and interface, which resulted in the excellent electrochemical performance of LFP NS/r-GOs. As expected, these LFP NS/r-GO cathode materials exhibited much better cycling performance and rate capability than those of the reported LFP/C cathodes. They also showed a remarkable specific energy and power density of 265 W h kg^{-1} and 6.81 kW kg^{-1} when used in full cell assembled with LTO anode material.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Nos. 51473081 and 51672143), Taishan Scholars Program, Outstanding Youth of Natural Science in Shandong Province (JQ201713), and ARC Discovery Project (No. 170103317).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi

References

- [1] Y. Liang, K. Wen, Y. Mao, Z. Liu, G. Zhu, F. Yang, W. He, *ChemElectroChem* 2 (2015) 1227-1237.
- [2] A. Manthiram, J. C. Knight, S.-T. Myung, S.-M. Oh, Y.-K. Sun, *Adv. Energy. Mater.* 6 (2016) 1501010-1501032.
- [3] H. J. Kim, S. Choi, S. J. Lee, M. W. Seo, J. G. Lee, E. Deniz, Y. J. Lee, E. K. Kim, J. W. Choi, *Nano Lett.* 16 (2016) 282-288.

- [4] W. Lv, Y. Niu, X. Jian, K. H. L. Zhang, W. Wang, J. Zhao, Z. Wang, W. Yang, W. He, *Appl. Phys. Lett.* 108 (2016) 083901-1-083901-4.
- [5] B. Wang, W. A. Abdulla, D. Wang, X. S, Zhao, *Energy Environ. Sci.* 8 (2015) 869-875.
- [6] W.-H. Cheng, L. Wang, Q.B. Zhang, Z. J. Wang, *J. Mater. Sci.* 52 (2017) 2366-2372.
- [7] X. Xie, Y. Yang, H. Zhou, M. Li, Z. Zhu, *Talanta.* 179 (2018) 822-827.
- [8] A. Paoletta, G. Berton, S. Marras, E. Dilella, M. Colombo, M. Prato, A. Riedinger, M. Povia, A. Ansaldo, K. Zaghib, L. Mana, C. George, *Nano Lett.* 14(2014) 6828-6835.
- [9] C. Zhu, Y. Yu, L. Gu, K. Weichert, J. Maier, *Angew. Chem. Int. Ed.* 123 (2011) 6402-6410.
- [10] M. Zhang, R. Liu, F. Feng, S. Liu, Q. Shen, *J. Phys. Chem. C* 119 (2015) 12149-12156.
- [11] J. Zhang, J. Lu, D. Bian, Z. Yang, Q. Wu, W. Zhang, *Ind. Eng. Chem. Res.* 53 (2014), 12209-12215.
- [12] B. L. Ellis, K. T. Lee, L. F. Nazar, *Chem. Mater.* 22 (2010) 691-714.
- [13] J. Chen, J. Graetz, *ACS Appl. Mater. Interfaces* 3 (2011) 1380-1384.
- [14] W. Zhang, *J. Power Sources* 196 (2011) 2962-2970.
- [15] X. Qin, J. Wang, J. Xie, F. Li, L. Wen, X. Wang, *Phys. Chem. Chem. Phys.* 14 (2012) 2669-2677.
- [16] Y. Zhao, L. Peng, B. Liu, G. Yu, *Nano Lett.* 14 (2014) 284-289.
- [17] C. A. Fisher, M. S. Islam, *J. Mater. Chem.* 18 (2008) 1209-1218.
- [18] Y. Liang, K. Wen, Y. Mao, Z. Liu, G. Zhu, F. Yang, W. He, *ChemElectroChem* 2 (2015) 1227-1237.
- [19] A. Paoletta, S. Turne, G. Bertoni, P. Hovington, R. Flacau, C. Boyer, *Nano Lett.* 16 (2016) 2692-2715.
- [20] Y. Zou, S. Chen, X. Yang, N. Ma, Y. Xia, D. Yang, S. Guo, *Adv. Energy Mater.* 6 (2016) 201601549-201601555.
- [21] J. Xu, L. Wang, Y. Zhu, *Langmuir* 28 (2012) 8418-8423.
- [22] F. Shahzad, M. Alhabed, C. B. Hatter, B. Anasori, S. M. Hong, C. M. Koo, Y. Gogotsi, *Science* 353 (2016) 1137-1140.
- [23] A. M. Puertas, A. Fernandez-Barbero, F. J. Nieves, L. F. J. Rull, *Langmuir* 20 (2004) 9861-9866.
- [24] M. S. Islam, D. J. Driscoll, C. A. J. Fisher, P. R. Slader, *Chem. Mater.* 17 (2005) 5085-5092.

- [25] X. Wu, Y. Guo, J. Su, J. Xiong, Y. Zhang, L. Wan, *Adv. Energy Mater.* 4 (2014) 1400054-1400061.
- [26] X. Yang, J. Yang, Y. Zhong, V. Garipey, M. Trudeau, K. Zaghib, J. Ying, *ChemSusChem*. 7 (2014) 1618-1622.
- [27] S. Lee, S. S. Park, *Chem. Mater.* 24 (2012) 3550-3556.
- [28] J. Sun, C. Lv, F. Lv, S. Chen, D. Li, Z. Guo, W. Han, D. Yang, S. Guo, *ACS Nano* 11 (2014) 6186-6193.
- [29] Y. Zou, X. Yang, C. Lv, T. Liu, Y. Xia, L. Shang, G. I. N. Waterhouse, D. Yang, T. Zhang, *Adv. Sci.* 4 (2017) 100262-100269.
- [30] J. Mun, H. Ha, W. Choi, *J. Power Sources* 251 (2014) 386-392.
- [31] K. Kang, J. Lee, P. Li, B. Kang, J. Kim, G. Yi, J. Park, *Nano Lett.* 15 (2015) 6756-6763.
- [32] W. Kim, W. Ryu, D. Han, S. Lim, J. Eom, H. Kwon, *ACS Appl. Mater. Interfaces* 6 (2014) 4731-4736.
- [33] X. K. Guo, Q. Fan, L. Yu, J. Liang, W. Ji, L. Peng, X. Guo, W. Ding, Y. Chen, *J. Mater. Chem. A* 1 (2013) 11534-11538.
- [34] J. Ha, S. Park, S. Yu, A. Jin, B. Jang, S. Bong, I. Kim, Y. Sung, Y. Piao, *Nanoscale* 5 (2013) 8647-8655.
- [35] D. Choi, D. H. Wang, V. V. Viswanathan, I. Bae, W. Wang, Z. Nie, J.-G. Zhang, G. L. Liu, Z. Yang, T. Duong, *Electrochem. Commun.* 12 (2010) 378-381.
- [36] H. Ni, J. Liu, L. Z. Fan, *Nanoscale* 5 (2013) 2164-2171.
- [37] Q. Li, F. Zheng, Y. Huang, X. Zhang, Q. Wu, D. Fu, J. Zhang, J. Yin, H. Wang, *J. Mater. Chem. A* 3 (2015) 2025-2040.
- [38] L. Peng, X. Zhang, Z. Fang, Y. Zhu, Y. Xie, J. Cha, G. Yu, *Chem. Mater.* 29 (2017) 10526-10533.
- [39] C.-C. Yang, H.-C. Hu, S. J. Lin, W.-C. Chien, *J. Power Sources* 258 (2014) 424-433.
- [40] D. Choi, D. Wang, V. V. Viswanathan, I. Bae, W. Wang, Z. Nie, J. Zhang, G. L. Graff, J. Liu, Z. Yang, T. Duong, *Electrochem. Commun.* 12 (2010) 378-381.
- [41] A. Varzi, D. Bresser, J. Zamory, F. Muller, S. Passerini, *Adv. Energy Mater.* 4 (2014) 1400054-1400062.

Highlights

1. A simple seaweed biomass conversion strategy was employed for preparation of LFP ultrathin nanosheets (LFP NS/r-GO).
2. LFP NS/r-GO is oriented (010) facet with ultralow Fe-Li antisite defects and unique porous r-GO aerogel structure.
3. The LFP NS/r-GO cathode materials exhibited excellent cycling performance and rate capability in Li half cells.
4. Its full cell with LTO anode material exhibited remarkable specific energy and power density.

Accepted Manuscript

Short communication

Alginate/r-GO assisted synthesis of ultrathin LiFePO_4 nanosheets with oriented (010) facet and ultralow antisite defect

Yihui Zou, Guojing Chang, Shuai Chen, Tongchao Liu, Yanzhi Xia, Chengmeng Chen, Dongjiang Yang

PII: S1385-8947(18)31142-2
DOI: <https://doi.org/10.1016/j.cej.2018.06.104>
Reference: CEJ 19315

To appear in: *Chemical Engineering Journal*

Received Date: 9 April 2018
Revised Date: 5 June 2018
Accepted Date: 15 June 2018

Please cite this article as: Y. Zou, G. Chang, S. Chen, T. Liu, Y. Xia, C. Chen, D. Yang, Alginate/r-GO assisted synthesis of ultrathin LiFePO_4 nanosheets with oriented (010) facet and ultralow antisite defect, *Chemical Engineering Journal* (2018), doi: <https://doi.org/10.1016/j.cej.2018.06.104>

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.