This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Fan, Qi; Zhang, Yuanjian; Xu, Qingyu; Wang, Jun; Lei, Lixu; Sun, Yueming; Lund, Peter D.

Coral-shaped porous LiFePO₄/graphene hybrids for high rate and all-climate battery applications

Published in:
Energy Storage Materials

DOI:
[10.1016/j.ensm.2019.06.020](https://doi.org/10.1016/j.ensm.2019.06.020)

Published: 01/01/2019

Document Version
Peer reviewed version

Published under the following license:
CC BY-NC-ND

Please cite the original version:
Fan, Q., Zhang, Y., Xu, Q., Wang, J., Lei, L., Sun, Y., & Lund, P. D. (2019). Coral-shaped porous LiFePO₄/graphene hybrids for high rate and all-climate battery applications. *Energy Storage Materials*. <https://doi.org/10.1016/j.ensm.2019.06.020>

Coral-shaped porous LiFePO₄/graphene hybrids for high rate and all- climate battery application

Qi Fan^{1,2}, Yuanjian Zhang¹, Qingyu Xu³, Jun Wang⁴, Lixu Lei¹,

Yueming Sun^{*1}, Peter D. Lund^{*2,4}

¹ School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P.R. of China

² School of Science, Aalto University, P.O. Box 15100, FI-00076 Aalto, Espoo, Finland

³ Department of Physics, Southeast University, Nanjing 211189, P.R. of China

⁴ Key Laboratory in Solar Energy Science & Technology, Southeast University, Jiangsu Province, Nanjing 210096, P.R. of China

* Corresponding authors: sun@seu.edu.cn, peter.lund@aalto.fi

Abstract

Tailor-designed cathode materials are essential for Li-ion batteries with both high energy density and outstanding capacity retention. Here we have designed and fabricated coral-shaped hierarchical porous LiFePO₄/graphene hybrids for lithium-ion batteries. These novel hybrid materials exhibit excellent electrochemical performance over a wide temperature range from -40 °C to +60 °C. Even at -40 °C, the hybrid cathode can deliver a high initial capacity of 120 mAhg⁻¹ and still maintain a discharge capacity of 80 mAhg⁻¹ after 500 cycles with a very low capacity loss of 0.066 % per cycle. The excellent wide-temperature performance can be ascribed to the porous structure and fast ion/electronic transport kinetics of the high conductive framework.

Keywords: Li-ion battery, LiFePO₄, graphene, hierarchical porous structures, all-climate.

1. Introduction

The interest in Li-ion batteries (LIB) as a storage medium for electric transportation and for energy storage of variable electricity sources is increasing [1-3] due to the high energy density and long cycle life of LIBs. However, there still are several challenges for their practical applications. For example, severe power losses at low temperatures and fast capacity decay at high temperature need to better be addressed when LIBs are used with electric vehicles. Also, severe voltage drops at low temperature could cause safety hazards in electric applications. Therefore, the development of a low-cost, wide-temperature, and high-power LIB system is of high relevance [4-6].

LiFePO₄ is a promising positive electrode material due to its intrinsic thermal safety and reasonable electrochemical performance [7-11]. However, the slow Li-ion diffusion and poor electronic conductivity of LiFePO₄ seriously inhibit the capacity and rate performance [9-14]. Moreover, previous results have demonstrated that the performance of such cathodes deteriorate at low temperatures (< -20 °C) due to lower electrical conductivity and poorer Li⁺ diffusion [15-18]. Various strategies have been used to overcome these limitations [10-19]. For example, porous structures and graphene-based (G) framework have been found to boost the electrochemical performance of LiFePO₄ [20-37]. However, the effect of graphene additives to the electrochemical properties of simple designed LiFePO₄-graphene hybrids is limited as it can only partially improve the electronic conductivity of the cathode. On the other side, there is rarely any work addressing the low temperature performance of the LiFePO₄-graphene cathode as so far [38-42]. Thus, the feasibility of using more complex LiFePO₄-graphene structure to improve Li⁺ and e⁻ transport at low temperature still needs elaboration.

In this work, for the first time, we analyze the use of porous structures and graphene-based framework to optimize the performance of LIB over a wide temperature range (-40°C...+60°C). A tailor-designed coral-shaped porous hierarchical LiFePO₄-graphene material (PHLG) was developed for this purpose by adopting a pH-mediated self-assembled strategy in the sol-gel process to ensure that graphene oxide (GO) can form a hierarchical porous backbone of the composites. Due to the high electronic conductivity of graphene backbones and the novel hierarchical porous structure which address lithium-ion diffusion, structure stability, and electrolyte diffusion, the PHLG structure exhibits balanced high performance in respect to rate capability, cyclability, in particular at low and high temperatures clearly demonstrating scientific progress compared to the state-of-the-art [23-25,

31, 34, 35]. A specific capacity of 80 mAhg^{-1} at -40°C for 250 recharging cycles was measured with an unprecedented capacity decay rate as low as 0.1% per cycle, showing the effectiveness of the tailor-designed PHLG structure in achieving the desired properties. This is the best performance result for a LiFePO_4 cathode at -40°C reported so far in literature.

2. Experimental section

2.1. Preparation of materials

In the synthesis process, graphene oxide (GO) sheets, which were derived from graphite, were dispersed into an aqueous ethanol solution using a powerful ultrasonicator. The dispersion can be stable for more than a month. A solution of $\text{Fe}(\text{NO}_3)_3$ and LiH_2PO_4 in a molar ratio of 4:4.1 with an appropriate amount of citric acid was added into the GO dispersion. Then a proper amount of ammonia was added drop by drop until a pH of 6-8 was reached. The dispersion was heated at 60°C under vigorous stirring until a homogeneous gel was formed. This gel was dried at 80°C in a vacuum. Finally, the dried gel was first decomposed at 350°C for 2 h and then sintered for 10 h at 700°C in a tube furnace under purified N_2 gas flow to produce a PHLG composite.

In order to demonstrate the superiority of PHLG composites, we prepared $\text{LiFePO}_4\text{-C}$ and mechanically mixed LiFePO_4 -graphene (MLG) samples as control groups. The precursors of both samples were synthesized utilizing the same procedure as in the PHLG synthesis process, but without adding GO. The $\text{LiFePO}_4\text{-C}$ sample was acquired following a sintering process at 350°C for 2 h and 700°C for 10 h under N_2 gas flow. The precursors of the MLG sample were first mixed with an appropriate amount of GO sheets with the ball-milling method. The weight of mixed GO sheets in the precursors of the MLG sample is nearly 5.5%. Then the mixture was calcinated at 350°C for 2 h and 700°C for 10 h under N_2 gas flow. The morphologies of $\text{LiFePO}_4\text{-C}$ and MLG samples are shown in Figures S1 and S2 (Supplementary Information).

2.2. Materials characterization

X-ray diffraction (XRD) analyses were performed with a D/Max-RA X-ray diffractometer with $\text{Cu K}\alpha$ irradiation. The morphology was characterized by Transmission Electron Microscope (TEM) and high-resolution TEM (HRTEM) (FEI Tecnai F20 S-Twins), and a Scanning Electron Microscope (Hitachi S-4800) equipped with a field emission gun. The

carbon content of the samples was measured using a Heraeus CHN–O–Rapid elemental analyser (see Supporting Information).

Nitrogen sorption isotherms of the PHLG composites were collected at 77 K with a Thermo Scientific Surfer. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) were used for the specific surface area and porosity evaluations, respectively. Raman spectra (Renishaw) were recorded via a spectrometer with excitation at 514.5 nm provided by an Ar⁺ laser at 20 mW.

2.3. Electrochemical measurements

For the electrochemical measurements, a composite cathode (8-10 milligram weight ; $\Phi=10$ mm) was prepared by mixing the active materials with carbon black (super P) and PTFE in a weight ratio of 90:5:5. The cells were assembled in an Ar-filled glove box with the as-prepared cathode, a Li anode, and a separator (Celgard polymer) saturated with a 1 mol L⁻¹ LiPF₆ solution in EC+DMC+DEC+EMC (1:1:1:3, v /v) electrolyte [11, 15]. The freezing temperature of the electrolyte is below -40 °C. All of the charge–discharge tests were performed in battery cyclers (Arbin BT-2000 Battery Test System) with a voltage range of 2.0–4.2 V in a low and high temperature test chamber (RGD-250, Beijing) (see Supporting Information). All the capacities were calculated based on pure LiFePO₄ mass.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with a CHI660C potentiostat/galvanostat (Shanghai Chenhua Technology Inc., China). The electrodes typically had an active material content of 8-10 mg. A Li foil served as a counter and as reference electrodes. The impedance spectra were recorded with the help of ZPlot/ZView software.

The electronic conductivity of PHLG, MLG, and LiFePO₄-C was measured using a 4-probe method at controllable temperatures. The composites were dried at 120 °C overnight and pressed into pellets under 200 kPa at room temperature. Electrical measurements were performed with a Keithley 2400 Digital SourceMeter in a temperature-controlled system from -50 °C to +100 °C.

3. Results

3.1 Structure and morphology of PHLG composites

Figure 1. Schematic synthetic route for the PHLG hybrids (the scale bar is 0.5 μm).

The coral-shaped PHLG material was prepared by a sequential synthesis as illustrated in Figure 1. GO sheets (Figure S3 in Supplementary Information) were uniformly dispersed into an aqueous ethanol solution by a vigorous and extensive ultrasonic treatment at a pH 1-2 (Figure 1a). The eventual formation of a colloid indicates the protonation of carboxylic groups on the GO sheets. When ammonia was added into the solution, some of the carboxylic groups on the GO sheets were deprotonated, enabling them to form hydrogen bonds with protonated carboxylic groups on adjacent GO sheets to form a hierarchically assembled structure. Meanwhile, Fe^{3+} and Li^+ were adsorbed on the surface of the GO sheets and combined with PO_4^{3-} to form the nucleus of LiFePO_4 at a higher pH. As the reaction progressed, the LiFePO_4 crystal nuclei grew into the nanoparticles and were subsequently wrapped by the interlaced GO sheets, forming the building blocks of the PHLG composites. Finally, the building blocks agglomerated together to form a hierarchical structure (Figure 1b). This is the assumed path for formation of the coral-shaped graphene-based composites.

The synthesized composites were preserved during a controlled heating process (700 $^{\circ}\text{C}$, GO sheets to graphene sheets). Because the hybrids consist of many aggregated graphene sheets, the coral-shaped PHLG appears rough with many holes inside (Figure 1c). Such structures can act as mini-electrochemical reaction chambers for electrolyte transport and Li^+

intercalation [21, 25], while electrons can quickly conduct to the current collector through the highly-conductive graphene-based 3D-networks [31, 34, 35].

The XRD image of the PHLG is shown in Figure 2a. All the Bragg peaks can well be indexed to the orthorhombic LiFePO_4 with a space group of Pnma , indicating high crystallinity of the PHLG composites [43]. No other phase was observed in the XRD pattern. The Raman spectroscopy (Figure 2b) provides more information about the PHLG hybrids: two broad peaks at $1,350$ and $1,600\text{ cm}^{-1}$ are attributed to the D and G bands, respectively. The relative intensities ($I_{\text{D}}/I_{\text{G}}$) can be utilized to analyze the amount of carbon defects in the samples [44]. Compared to the control group ($\text{LiFePO}_4\text{-C}$), the $I_{\text{D}}/I_{\text{G}}$ of the PHLG is lower and the band attributed to the symmetric PO_4^{3-} (948 cm^{-1}) is weak, indicating that LiFePO_4 particles are well covered by the graphene sheets and carbon coating layers [39, 45]. The low value of $I_{\text{D}}/I_{\text{G}}$ (0.872) of the PHLG hybrids indicate a highly ordered graphene structure and suggests that GO was successfully converted to thermally reduced graphene-sheets, which can lead to the increased electronic conductivity of the composites. The typical FT-IR spectrum of PHLG composites is shown in Figure S4 (see Supplementary Information). There is not any obvious shift which can correspond to $-\text{OH}$ and $-\text{COOH}$ response, indicating the introduced GO is successfully converted to thermally reduced graphene-sheets in the PHLG sample.

Figure 2. Typical morphology of PHLG hybrids. (a) XRD pattern is well indexed to the orthorhombic LiFePO_4 phase; (b) Raman spectrum of PHLG hybrids. (c-d) SEM images of PHLG hybrids; (e) TEM images of PHLG hybrids.

Analysis of the morphology of PHLG composite demonstrates precise control of the hierarchical shape. As shown in Figure 2c, the coral-shaped frameworks are assembled by many lamellar-shape nanocomposites. The magnified SEM image (Figure 2d) displays more details about the nanocomposites. It shows a porous structure with more space for electrolyte permeation and Li^+ transport between the cathode/electrolyte interfaces [32]. Such hierarchical structures are very helpful for facilitating charge and mass transport during the Li^+ intercalation process and lead to improved electrochemical properties, which will be discussed later.

The TEM image (Figure 2e) shows the texture of the lamellar-shaped composites: LiFePO_4 nanoparticles were well-dispersed and wrapped by the mutually interlaced large graphene-sheets. These superimposed graphene-sheets can greatly improve the electron transport in the cathode/collector system [30-32]. The contact between the nanoparticles and graphene-sheets is shown in the inset. The HRTEM image exhibits clear lattice fringes indicating single crystallinity of the nanoparticles. The width (0.52 nm) of neighboring lattice fringes corresponds to the (200) plane of LiFePO_4 . The highly crystalline LiFePO_4 nanoparticles are in close contact with the highly conductive graphene-sheets. This guarantees efficient electronic transport between them. Figure S5 (see Supplementary Information) depicts HRTEM images of the LiFePO_4 nanoparticles in PHLG composites, which exhibits clear lattice fringes indicating single crystallinity of the LiFePO_4 nanoparticles. The SAED image (inset in Figure S5b) displays well-defined diffraction spots suggesting a highly ordered single crystalline state of the particles. The perfect lattice fringes of the as-synthesized composite in the HRTEM image further verify the good crystalline state of the samples. X-ray photoelectron spectroscopy (XPS) analysis was carried out to analyze the possible interaction between LiFePO_4 and graphene. Figure S6 (Supplementary Information) shows the C1s of as-synthesized PHLG hybrids, the binding energy of C–C appears at a value of 284.0 eV, which is smaller than the standard value as 284.6 eV. This may be ascribed to the charge transfer between LiFePO_4 and graphene [43]. Figure S7 (Supplementary Information) shows the Fe2p of as-synthesized PHLG hybrids. From the picture, the ratio of Fe^{2+} : Fe^{3+} appears to be 0.10, indicating that almost all of the Fe^{3+} species are reduced to Fe^{2+} , also keeping the state when exposed to the air.

3.2. Porous structure and outstanding conductivity of PHLG

Brunauer–Emmett–Teller (BET) measurements were performed to investigate the pore-size distribution in the composites (Figure 3a). The BET surface area of the hierarchical porous composite is $91 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution was calculated from the N_2 -desorption measurements using the Barrett–Joyner–Halenda (BJH) method (Figure 3b). Two regions of pore size distribution can be identified: (1) a sharp peak at around 60 nm which may be attributed to the macropores on the porous lamellar-shaped composites; (2) many mesopores with sizes between 3–30 nm. Also, we can observe several large pores ($>200\text{nm}$) in Figure 2c and 2d indicating that the composite has a hierarchical porous structure. Such a complex framework creates larger interface areas along with more sufficient interspaces for the electrochemical reactions between the electrode and electrolyte when used as a cathode for LIBs.

Figure 3. (a-b) BET results with pore-size distribution; (c) Electronic conductivity of the PHLG hybrids, MLG and $\text{LiFePO}_4\text{-C}$ in all-climate conditions. (d) Impedance spectra of the PHLG hybrids compared with pristine $\text{LiFePO}_4\text{-C}$ and mechanically mixed $\text{LiFePO}_4\text{-G}$ (MLG).

Efficient electron transfer in the cathode material is very important for boosting the electrochemical performance of the PHLG composites. Figure 3c shows the electronic

conductivity of PHLG, MLG, and LiFePO₄-C from -50 °C to +100 °C. PHLG has the most stable electronic conductivity ($> 6 \text{ S cm}^{-1}$) demonstrating the importance of hierarchically assembled structures in improving the electronic conductivity of PHLG composites, especially at low temperatures, also indicating that PHLG's electronic property is between a semiconductor and a metal. Undoubtedly, the relatively high electrical conductivity of the PHLG composite can be attributed to its well-connected 3D conductive paths.

Electrochemical impedance spectroscopy (EIS) was conducted to measure the impedance spectra of PHLG. Figure 3d shows the Nyquist plots for the PHLG, MLG, and LiFePO₄-C composites, which all show a high-to-medium frequency depressed semicircle followed by a linear tail in the low-frequency region. Whereas the former is related to the charge-transfer process at the electrode/electrolyte interfaces (R_{ct}), the latter represents the Warburg impedance associated with Li diffusion in the LiFePO₄ crystal lattice (Z_w). The diameter of the semicircle for PHLG and the MLG electrodes in the high-to-medium frequency region are significantly smaller than that of the LiFePO₄-C composite, suggesting that the kinetics of charge transfer between electrolyte and PHLG or MLG is faster than LiFePO₄-C composites.

In addition, compared to both graphene decorated LiFePO₄ materials, the R_{ct} value of PHLG is noticeably lower than that of the MLG. This indicates that PHLG possesses the lowest contact and charge-transfer impedance of the three materials measured, allowing for rapid electron transport during the electrochemical Li⁺ insertion/extraction reaction.

In addition to R_{ct} , the Li diffusion coefficient D_{Li} also shows a noticeable improvement linked to the hierarchically assembled architecture. The values of D_{Li} were calculated according to the inclined lines in the Warburg region using the following equation [28]:

$$D_{Li} = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma^2) \quad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the concentration of Li⁺, and σ represents the Warburg factor which is associated to Z' ($Z' \propto \sigma \omega^{-1/2}$). After linear fitting between Z' and $\omega^{-1/2}$ to estimate σ , D_{Li} could be obtained from the above equation. The D_{Li} value of PHLG was $4.69 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ which is much higher than that of MLG ($6.18 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$) and LiFePO₄-C composites ($4.52 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$). The relatively high D_{Li} value of PHLG may satisfy the reaction requirement under large charge/discharge currents or under low-temperature conditions.

3.3. Balanced high battery performance of PHLG over a wide temperature range

Figure 4. Electrochemical performance of PHLG hybrids at 20 °C. (a) Typical charge-discharge plots of PHLG hybrids. (b) Charge/discharge profiles of PHLG hybrids shows outstanding rate capacity. (c) Rate performance of PHLG compared with the MLG and LiFePO₄-C. (d) PHLG capacity and coulombic efficiency during 250 cycles at high rates (1.0, 2.0, and 5.0 A g⁻¹).

The battery performance of PHLG composites at room temperature (20 °C) was investigated to test its potential application in LIBs. The electrochemical properties of PHLG were compared to those of MLG and LiFePO₄-C composites. Figure 4a shows their typical charge/discharge profiles at a low current density of 40 mA g⁻¹ (completing the charge or discharge process in about 4 hours). The discharge capacity of PHLG is 162 mAh g⁻¹, which is significantly higher than that of the other samples. Moreover, as illustrated in the enlarged Figure S7 (Supplementary Information) the polarization of the charge/discharge plateau of the PHLG is lower (46 mV) than that of the MLG and LiFePO₄-C composites, suggesting that the kinetics of PHLG is significantly improved by the hierarchical structure framework. The rate

capability of PHLG was first evaluated at different rates (Figure 4b). The reversible capacities at different current densities (i.e. 40, 80, 160, 500 mA g⁻¹) were 162, 159, 156, and 149 mAh g⁻¹, respectively. Even at a high current rate of 1.0 Ag⁻¹ (6 C) and 2.0 Ag⁻¹ (12 C), capacities of 143 mAhg⁻¹ and 139 mAhg⁻¹ were still obtained (Figure 4b). As seen in Figure 4c, the charge/discharge capacity of PHLG is clearly higher and more stable than that of the MLG and LiFePO₄-C composites, especially at higher current rates. To further demonstrate the potential of PHLG in high-power applications, Figure 4d shows the sustained cycling performance when the current density is increased from 1.0 Ag⁻¹ (6 C, 100 cycles) to 5.0 Ag⁻¹ (30 C, 100 cycles). PHLG exhibits a coulombic efficiency of almost 100% during the entire process. The initial discharge capacity at 2.0 Ag⁻¹ is 137 mAh g⁻¹ and remains at 134 mAhg⁻¹ after 100 cycles. Even at a current density of 5.0 Ag⁻¹, the composites still delivered 94% capacity retention at 108 mAhg⁻¹ after 50 cycles with an initial capacity of 115 mAhg⁻¹. The superior cyclability demonstrates the stability of the hierarchical structure and fast e⁻/Li⁺ transport during the cycling process. Thus, PHLG could be a potential candidate cathode in high-power and high-safety LIBs.

To demonstrate the suitability of the PHLG for all-climate lithium battery storage, the electrochemical performance of the hybrid cathode was monitored under varying temperature conditions. Figure S9 (Supplementary Information) shows the charge-discharge profiles of the PHLG cathode with 80 mA g⁻¹ and 0.5 A g⁻¹ at -40°C. The cell with the PHLG cathode delivers a high reversible capacity of 123 mAh g⁻¹ at 80 mA g⁻¹ (0.5 C), indicating that the PHLG electrode can endure such a low temperature. Figure 5a compared the discharge plots for PHLG, MLG and LiFePO₄-C at -40°C. PHLG demonstrates excellent rate capacities of 101 mAhg⁻¹ at 0.5 Ag⁻¹ (3 C), greatly exceeding any previously reported results of Li-ion batteries [15-19]. The MLG shows a lower capacity of 100 mAhg⁻¹ at 80 mA g⁻¹ and 48 mAhg⁻¹ at 0.5 Ag⁻¹, but the LiFePO₄-C shows a poor capacity of only 77 mAhg⁻¹ at 80 mA g⁻¹ and 32 mAhg⁻¹ at 0.5 Ag⁻¹. The battery performance of a commercial sample at -40°C is shown in Figure S10 (Supplementary Information) indicating a poor rate capacity (36 mAhg⁻¹, 3C) quite similar to a LiFePO₄-C cathode. Figures 5b and 5c show the cycle performance of PHLG and LiFePO₄-C at -40°C and 60°C. At -40°C, PHLG demonstrates impressive cyclability with only 3.4% capacity loss after the first 20 cycles at 80 mA g⁻¹ and 9% capacity loss after 20 cycles at 0.5 Ag⁻¹. In comparison, the MLG exhibits a 24.6% and LiFePO₄-C a 30 % capacity loss after 20 cycles at 80 mA g⁻¹, respectively. A similar cycling test was performed at 60 °C: The rate capacity of all three samples was higher at 60°C since a higher temperature improves the Li⁺ transport and electronic conductivity of the cathode. However,

the cyclability of $\text{LiFePO}_4\text{-C}$ was deteriorated, possibly due to accelerated side reactions between the cathode and electrolyte. Unlike $\text{LiFePO}_4\text{-C}$, the PHLG and MLG samples show relatively stable battery performance during the cycling tests. The PHLG sample demonstrates the most stable cycling performance, because the closely wrapped graphene sheets can hinder side reactions and thus maintain a steady and excellent rate capacity of 161 mAhg^{-1} at 80 mA g^{-1} and 158 mAhg^{-1} at 0.5 A g^{-1} [46, 47].

Figure 5. Battery performance of PHLG at all-climate conditions: (a) Discharge profiles of the PHLG hybrids, MLG sample and $\text{LiFePO}_4\text{-C}$ at -40°C ; (b) Rate performance of the PHLG hybrids, MLG sample and $\text{LiFePO}_4\text{-C}$ at -40°C ; (c) Rate performance of the PHLG hybrids, MLG sample and $\text{LiFePO}_4\text{-C}$ at $+60^\circ\text{C}$; (d) Cycle performance of PHLG hybrids with 80 mA g^{-1} at varying temperature from -40°C to $+60^\circ\text{C}$; (e) Long cycle performance of PHLG hybrids with 80 mA g^{-1} at -40°C .

To evaluate the impact of the temperature change on the cyclability of the PHLG cathode, the battery was cycled at 80 mA g^{-1} while the working temperature was changed from -40°C to $+20^\circ\text{C}$ and then to $+60^\circ\text{C}$. At each temperature change, the reversible capacity of the battery increased noticeably. It is worth mentioning that the battery could still deliver a large capacity at $+60^\circ\text{C}$ (160 mA h g^{-1}) after cycling at -40°C and $+20^\circ\text{C}$, indicating that the electrochemical properties of a PHLG cathode are not significantly affected by the low-temperature conditions. Long-term cycling performance of the PHLG electrode at -40°C was further demonstrated in Figure 5e. The battery shows a remarkable stability with a retention of 72.6 % at 80 mA g^{-1} for over 500 cycles, corresponding to a capacity decay of as low as 0.066 % per cycle with excellent Coulombic efficiency of nearly 99 %. To our best knowledge, this result represents the highest cycling stability that has ever been achieved by Li-ion batteries under comparable measurement conditions [15-19, 48-53]. Even after this extended cycling test, the morphology of PHLG composites was preserved as demonstrated by Figure S11 (Supplementary Information). The composite maintained the coral-shaped structure assembled from many lamellar-shape nanocomposites (similar to Figure 2c and 2d), indicating that the hierarchical porous structure may improve the stability of the PHLG composites. To further demonstrate the enhanced performance of our PHLG cathode, the temperature-dependent battery performance of PHLG with other cathode materials for rechargeable batteries (not only Li-ion batteries) are compared and summarized in Tables S1 and S2 [15-19, 48-58] (Supplementary Information). The PHLG cathode represents a balanced and highly competitive capacity retention rate and cycling performance over a wide temperature range from $+60^\circ\text{C}$ down to -40°C .

The superior electrochemical performance of the PHLG hybrids at all-climate conditions, with respect to high specific capacity, good rate capability, and unprecedented cycling stability at low and high temperatures, is a direct result of the unique material structure. There are three key elements for its superior electrochemical performance: 1) graphene-based 3D-networks, which provide stable electronic conductivity ($>1 \text{ S cm}^{-1}$) over a wide temperature range; 2) A novel designed coral-shaped porous hierarchical structure, which greatly facilitates electrolyte diffusion and Li^+ transport at the cathode/electrolyte interface; 3) Intimate contact between LiFePO_4 and porous G sheets that stabilizes the structure of the composite. Figure S12 (Supplementary Information) illustrates the mechanism behind the improvement. Although the electron and Li^+ transport of LiFePO_4 at low temperature was greatly hindered by kinetic limitations, graphene-based 3D-networks can efficiently increase

the electronic conductivity. The porous hierarchical framework facilitates electrolyte diffusion in and out of the PHLG, thus drastically improving the low-temperature performance of the battery. The design of the PHLG framework can also enhance the rate performance and cyclability of the battery, thereby providing a new approach to achieving better cathode materials for LIBs.

4. Conclusions

We have developed a coral-shaped LiFePO_4 -graphene composite to improve the Li-ion battery performance at all-climate conditions (-40°C to $+60^\circ\text{C}$). This hybrid material simultaneously addresses the electron conduction, lithium ion diffusion, structure stability and electrolyte diffusion problems to boost the performance of the LiFePO_4 cathode. All of these contribute to the excellent rate capability, stable cycling, and superior performance at low and high temperatures. The porous hierarchical LiFePO_4 -graphene material was able to deliver a reversible capacity of 161 mAhg^{-1} and 123 mAh g^{-1} at $+60^\circ\text{C}$ and -40°C , respectively. This meets the requirements of all-climate usage. Considering the easiness of fabricating these or similar structures, the strategy presented here may provide an interesting path for achieving better electrode materials for Li-ion batteries.

Acknowledgements

The authors acknowledge financial supports from the National Natural Science Foundation of China (51736006, 51471085 and 51407029), and the International Postdoctoral Exchange Fellowship Program under Grant No. 20140056 by China Postdoctoral Council. We thank the SEU-FEI Nano-Pico Center for helpful discussions and technical assistance. This work is partially supported by the Aalto University.

References

- [1] K. Green, J. C. Wilson, *Electron. & Comm. Eng. J.* 13 (2001) 43-47.
- [2] R. J. Zou, Q. Liu, G. J. He, M.F. Yuen, K. B. Xu, J. Q. Hu, et al., *Adv. Ener. Mater.* 7 (2017) 1601363.
- [3] D. Zhou, R.L. Liu, J. Zhang, X. G. Qi, Y. B. He, B. H. Li, et al., *Nano Ener.* 33 (2017) 45-54.

- [4] J. T. Hu, W. Li, Y. D. Duan, S. H. Cui, X. H. Song, Y. D. Liu, et al., *Adv. Ener. Mater.* 7 (2017) 1601894.
- [5] Q. Fan, L. X. Lei, Y. M. Sun, *Nanoscale* 6 (2014) 7188-7192
- [6] Q. Fan, L. X. Lei, G. Yin, Y. M. Sun, *Chem. Commun.* 50 (2014) 2370-2373.
- [7] Q. Fan, L. X. Lei, Y. F. Chen, Y. M. Sun, *J. Power Sources* 244 (2013) 702-706.
- [8] C. Y. Wang, G. S. Zhang, S. H. Ge, T. Xu, Y. Ji, X. G. Yang, et al., *Nature* 529(2016) 515-518.
- [9] C. Delacourt, P. Poizot, J. M. Tarascon, C. Masquelier, *Nat. Mater.* 4 (2005) 254-260.
- [10] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, F. Weill, *Nat. Mater.* 7 (2008) 665.
- [11] B. Kang, G. Ceder, *Nature* 458 (2009) 190-193.
- [12] Y. H. Zou, S. Chen, X. F. Yang, N. Ma, Y. Z. Xia, D. J. Yang, et al., *Adv. Ener. Mater.* 6 (2016) 1601549.
- [13] G. M. Song, Y. Wu, Q. Xu, G. Liu, *J. Power Sources* 195 (2010) 3913-3917.
- [14] Y. G. Wang, Y. R. Wang, E. J. Hosono, K. X. Wang, H. S. Zhou, *Angew. Chem. Int. Edit.* 47 (2008) 7461-7465.
- [15] X. Liao, Z. F. Ma, Q. Gong, Y. He, L. Pei, L. Zeng, *Electrochem. Commun.* 10 (2008) 691 -694.
- [16] X. Wu, Y. Guo, J. Su, J. Xiong, Y. Zhang, L. Wan, *Adv. Energy Materials*, 3.9 (2013) 1155.
- [17] B. K. Zou, H. Y. Wang, Z. Y. Qiang, Y. Shao, X. Sun, Z. Y. Wen, et al., *Electrochim. Acta* 196 (2016) 377-385.
- [18] D. Xie, G. L. Cai, Z. C. Liu, R. S. Guo, D. D. Sun, C. Zhang, et al., *Electrochim. Acta* 217 (2016) 62-72.
- [19] R. J. Chen, W. J. Qu, J. Qian, N. Chen, Y. J. Dai, C. Guo, et al., *J. Mater. Chem. A* 5 (2017) 24677-24685.
- [20] C. M. Doherty, R. A. Caruso, C. J. Drummond, *Ener. Envir.Sci.* 3 (2010) 813-823.
- [21] R. Dominko, M. Bele, J. M. Goupil, M. Gaberscek, D. Hanzel, I. Arcon , et al., *Chem. Mater.* 19 (2007) 2960-2969.

- [22] W. Liu, Z. Chen, G. M. Zhou, Y. M. Sun, H. R. Lee, C. Liu, et al., *Adv. Mater.* 28 (2016) 3578-3583.
- [23] Y. M. Wu, Z. H. Wen, J. H. Li, *Adv. Mater.* 23 (2011) 1126-1129.
- [24] B. Wang, T. F. Liu, A. M. Liu, G. J. Liu, L. Wang, T. T. Gao, et al., *Adv. Ener. Mater.* (2016) 1600426.
- [25] Y. K. Zhou, J. Wang, Y. Y. Hu, R. O'Hayre, Z. P. Shao, *Chem. Commun.* 46 (2010) 7151-7153.
- [26] X. Y. Zhang, L. L. Hou, C. Artur, S. Paolo, *Adv. Ener. Mater.* 6 (2016) 1600671.
- [27] Y. K. Zhou, J. M. Lu, C. Deng, H. X. Zhu, Z. Chen, S. W. Zhang, et al., *J. Mater. Chem. A*, 4 (2016) 12065 -12072.
- [28] S. S. Li, Y. H. Luo, W. Y. Lv, W. J. Yu, H. S. Wu, P. X. Hou, et al., *Adv. Ener. Mater.* 1 (2011) 486.
- [29] X. Liu, D. Chao, D. Su, S. Liu, L. Chen, C. Chi, et al., *Nano Ener.* 37 (2017) 108-117.
- [30] H. L. Wang, Y. Yang, Y. Y. Liang, L. F. Cui, H. S. Casalongue, Y. G. Li, et al., *Angew. Chem.* 50 (2011) 7364-7368.
- [31] B. Chen, E. Liu, T. Cao, F. He, C. Shi, C. He, et al., *Nano Ener.* 33 (2017) 247-256.
- [32] X. Zhao, C. M. Hayner, M. C. Kung, H. H. Kung, *Adv. Ener. Mater.* 1 (2011) 1079.
- [33] J. X. Zhu, K. Sun, D. H. Sim, C. Xu, H. Zhang, H. H. Hng, et al., *Chem. Commun.* 47 (2011) 10383-10385.
- [34] Y. Zou, Y. Wang, *Acs Nano* 5 (2011) 8108-8114.
- [35] X. F. Zhou, F. Wang, Y. M. Zhu, Z. P. Liu, *J. Mater. Chem.* 21 (2011) 3353-3358.
- [36] G. Xu, Q. B. Yan, A. Kushima, X. Zhang, J. Pan, J. Li, *Nano Ener.* 31(2017) 568-574.
- [37] Q. Fan, L. X. Lei, G. Yin, Y. Chen, Y. Sun, *Electrochem. Commun.* 38 (2014) 120-123.
- [38] G. Longoni, J. K. Panda, L. Gagliani, R. Brescia, L. Manna, F. Bonaccorso, et al., *Nano Ener.* 51 (2018) 656-667.
- [39] H. Wang, L. Liu, R. Wang, X. Yan, Z. Wang, J. Hu, et al., *Chemsuschem* 11 (2018) 2255-2261.
- [40] C. C. Yang, Y. H. Hsu, J. Y. Shih, Y. S. Wu, C. Karupiah, T. H. Liou, et al., *Electro. Acta* 258 (2017) 773-785.

- [41] L. He, W. Zha, D. Chen, J. Alloy. Comp. 727 (2017) 948-955.
- [42] H. Wang, N. Zhao, C. Shi, L. Ma, F. He, C. He, et al., Electro. Acta 247 (2017) 1030-1037.
- [43] Q. Fan, L. X. Lei, X. Xu, G. Yin, Y. Chen, Y. Sun, J. Power Sources 257 (2014) 65-69.
- [44] H. Huang, Y. Xia, X. Tao, J. Du, J. Fang, Y. Gan, et al., J. Mater. Chem. 22 (2012) 10452-10456.
- [45] A. Murugan, T. Muraliganth, A. Manthiram, J. Phys. Chem. C 112 (2008) 14665-14671.
- [46] X. Fang, M. Ge, J. Rong, C. Zhou, J. Mater. Chem. A 1.12 (2013): 4083-4088.
- [47] W. B. Luo, S. L. Chou, Y. C. Zhai, H. K. Liu, J. Mater. Chem. A 2.14 (2014): 4927-4931.
- [48] J. Wang, P. Nie, G. Y. Xu, J. M. Jiang, Y. T. Wu, R. R. Fu, et al., Adv. Funct. Mater. 28 (2018) 1704808.
- [49] Y. Liu, B. C. Yang, X. L. Dong, Y. G. Wang, Y. Y. Xia, Angew. Chem. 56 (2017) 16606-16610.
- [50] H. G. Jung, M. W. Jang, J. Hassoun, Y. K. Sun, B. Scrosati, Nat. Commun. 2 (2011) 516.
- [51] S. Tan, L. Wang, L. Bian, J. Xu, W. Ren, P. Hu, et al., J. Power Sources 277 (2015) 139-146.
- [52] D. Luo, G. S. Li, C. Yu, L. S. Yang, J. Zheng, X. F. Guan, et al., J. Mater. Chem. 22 (2012) 22233–22241.
- [53] S. Zhu, Y. Wang, J. Jiang, X. Yan, D. Sun, Y. Jin, et al., ACS Appl. Mater. Inter. 8 (2016) 17253-17259.
- [54] Z. Zhang, H. Xu, Z. Cui, P. Hu, J. Chai, H. Du, et al., J. Mater. Chem. A 4 (2016) 2277–2285.
- [55] Y. You, H. R. Yao, S. Xin, Y. X. Yin, T. T. Zuo, C. P. Yang, et al., Adv. Mater. 33 (2016) 7243-7248.
- [56] T. F. Liu, B. Wang, X. X. Gu, L. Wang, M. Ling, G. Liu, et al., Nano Ener. 30 (2016) 756-761.
- [57] H. Chen, H. Xu, S. Wang, T. Huang, J. Xi, S. Cai, et al., Sci. Adv. 3(12), 7233.
- [58] J.-Y. Hwang, S.-M. Oh, S.-T. Myung, K. Y. Chung, I. Belharouak, Y.-K. Sun, Nat.

Commun. 6 (2015) 6865.