### Carbon 173 (2021) 809-816

Contents lists available at ScienceDirect

### Carbon

journal homepage: www.elsevier.com/locate/carbon



# Super heating/cooling rate enabled by microwave shock on polymeric graphene foam for high performance Lithium–Sulfur batteries



Carbon

Yiyang Liu<sup>a</sup>, Yan Zhang<sup>b, c, d</sup>, Yang Liu<sup>b, c, d</sup>, Jie Zhu<sup>b, c, d</sup>, Zhen Ge<sup>b, c, d</sup>, Zhongjun Li<sup>a, \*\*</sup>, Yongsheng Chen<sup>b, c, d, \*</sup>

<sup>a</sup> College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China

<sup>b</sup> The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China

<sup>c</sup> State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, China

<sup>d</sup> Renewable Energy Conversion and Storage Center (RECAST), Nankai University, Tianjin, 300071, China

### ARTICLE INFO

Article history: Received 11 October 2020 Received in revised form 15 November 2020 Accepted 20 November 2020 Available online 30 November 2020

Keywords: Polymeric graphene foam Super heating/cooling rate Microwave shock synthesis Lithium—sulfur electrocatalyst

### ABSTRACT

3D polymeric graphene foam (PGF) deposited with  $Mn_3O_4$  nanocrystals are synthesized via a structuralenhanced microwave plasma technique as highly efficient electrocatalyst for lithium–sulfur battery. The uniform pore-structure of PGF enables high-temperature Ar plasma around 1536 K under microwave irradiation, which leads to super heating/cooling rate of >13700 K s<sup>-1</sup> forming  $Mn_3O_4$  nanocrystals in 1.2 s. Interconnected PGF layers deposited with the  $Mn_3O_4$  crystals around 8 nm in diameters can effectively promote the electron transport and anchoring/catalyzing the polysulfides conversion. The cathode exhibits a good capacity fading of 0.092% per cycle over 300 discharge/charge cycles at 0.2 C, indicating good reversibility. The high  $Mn_3O_4$ /graphene ratio and small particle size of the nanocomposite are hard to achieve by other methods within this short period. The instant and low-cost synthesis method is readily scalable and may provide a promising direction for the practical manufacturing of high-performance Li–S batteries.

© 2020 Elsevier Ltd. All rights reserved.

### 1. Introduction

Lithium sulfur (Li–S) battery excels other cathode candidates as the next-generation energy storage system due to its high theoretical energy density (2600 Wh kg<sup>-1</sup>) and high theoretical capacity (1675 mA h g<sup>-1</sup>), which is 5–7 times higher than existing commercial lithium ion batteries (theoretical capacity <272 mA h g<sup>-1</sup>). In principle, Li–S battery accommodates several complex reactions, in which intermediate polysulfides Li<sub>2</sub>S<sub>x</sub> (1 $\le x \le 8$ ) are generated. Severe problems such as the fast capacity decay, selfdischarge, and low columbic efficiency may be attributed to a series of issues such as the shuttle effect, low conductivity, and volume change of short-chain polysulfides Li<sub>2</sub>S<sub>x</sub> (2  $\le x \le 4$ ). Among them, shuttle effect is a critical problem which is caused by the polysulfides  $\text{Li}_2S_x$  ( $2 \le x \le 8$ ) dissolving and shuttling to the anode. Therefore, a crucial step is needed to simultaneously solve the shuttle effect and enhance the anchoring&redox kinetics of the lithium polysufides (LiPSs) [1,2].

Carbon nanomaterials such as carbon nanotubes (CNTs) [3], carbon nanofibers (CNFs) [4], graphene oxide (GO) [5], reduced graphene oxide (rGO) [6,7], highly porous carbon [8], etc. can provide large specific surface area for increased conductivity and structural stability. However, the poor adsorption of carbon-based materials limits the encapsulation effect of LiPSs due to their low binding energy. In order to better relieve the shuttle effect of the easily dissolved LiPSs, electrocatalysts such as sulfides [9], nitrides [10], phosphides [11], metal oxides [12], metal-organic [13], etc. have been utilized to anchor the LiPSs. These polar hosts possess high binding energy with LiPSs as well as poor pore structure and low conductivity, which compromise the capacity and rate capability. Generally, dual-encapsulation strategies were used to balance the overall performance of Li–S batteries, in which the carbon materials were incorporated with electrocatalysts as the cathode of



<sup>\*</sup> Corresponding author. The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China. \*\* Corresponding author.

*E-mail addresses:* lizhongjun@zzu.edu.cn (Z. Li), yschen99@nankai.edu.cn (Y. Chen).

Li–S battery [14]. Graphene is an outstanding carbon nanomaterials for its high conductivity, stability, and rich anchoring sites for catalytic materials as well as LiPSs [15]. Therefore, graphene structures were coupled with numerous of electrocatalysts including MoS<sub>2</sub> [16], CoS<sub>2</sub> [17], V<sub>2</sub>O<sub>5</sub> [18], VN [10], MnO<sub>2</sub> [19], etc.

The battery industry requires huge resources and energy input during ore mining, synthesizing, and recycling. Though sulfur possesses a series of environmentally friendly properties e.g. relatively large reserve (sustainable), easy separation (low mining cost), and low toxicity (easy handling and recycling). The synthesis of highly efficient catalytic composites of Li–S batteries employs complex processes (template synthesis, hydrothermal synthesis, high-temperature calcination, etc.) that are time- and energyconsuming. Among these, in-situ hydrothermal (HT) is a facial route to synthesis nanoparticle-graphene composites with good cycling performance in Li–S batteries. Yet the mass loading of the active materials is limited since vastly precursor may severely undermine the 3D structure of the graphene foam [20,21]. A two-step HT strategy is usually utilized to achieve both optimal mass loading and 3D structure. However, it suffers from the long process time and large particle sizes range from tens to hundreds of nanometers, which leads to lowered electrocatalytic&anchoring performance of the LiPSs conversion [22,23]. For example, Li et al. report an in-situ HT synthesis of Fe<sub>3</sub>O<sub>4</sub>@graphene to encapsulate LiPSs in a Li-S battery. However, a collapsed structure with a large particle size of ~31 nm suggests a lowed electrocatalytic efficiency. HT with Mn ions as precursors were also reported, Shaik et al. [24] and Huang et al. [25] proposed an in-situ HT synthesis of Mn<sub>3</sub>O<sub>4</sub>@rGO which exhibits an enhanced energy storage performance. Yet, the large crystal size around 65 nm/40 nm and long reaction time of about 12 h limit their further applications.

As an emerging technology in nanocomposites synthesizing, microwave heating synthesis [26-30] excels traditional highpower synthesis technologies such as arc-electric and pulsedlaser ablation due to its fast synthesis, evenly distributed nanoparticles, low energy consumption, and high feasibility in mass producing [31]. Xu et al. [32] reported a microwave heating of ovendried rGO deposited with Ru, Pd, and Ir. The high temperature at ~1600 K leads to a small size of the metals of ~10 nm. The microwave heating shows a promising future in fast and size-controlling preparation of nanocomposites, yet the Li-S battery requires a high nanoparticle-graphene ratio which is hard to achieve by normal microwave heating. Polymeric graphene foam (PGF) possesses unique energy band structure, high electric conductivities, and tremendous amount of defects for high electromagnetic wave shielding properties. Furthermore, its unique 3D structure provides vast pores and interfaces that can efficiently absorb/reflect inside the bulk for a structural-enhanced microwave plasma (MP) synthesis [31]. Thus, we took advantage of the structural-enhanced MP of PGF for a facial and instant synthesis of Li-S cathode with high catalytic efficiency and good cyclic performance.

In this work, we report a fast MP synthesis of  $Mn_3O_4$  on polymeric graphene foam (Mn@PGF) as a highly efficient electrocatalytic nanocomposite in electrochemical conversion and anchoring the LiPSs. The powerful MP can complete the reaction within 1.2 s at a high temperature of 1549 K and super heating/ cooling rate of >13700 K s<sup>-1</sup> owing to the high electron/heat conductivity and the structural enhanced microwave absorption of the 3D PGF. The super-heating/cooling enables an efficient breakdown of the micro-sized precursor into nanocrystals of ~8 nm in diameter, which can effectively enhance the redox reactivity of LiPSs due to their high chemical affinity. Moreover, the 3D PGF can realize a high  $Mn_3O_4$ /graphene ratio that efficiently anchors the LiPSs, which is unachievable by most of the other methods. The electrochemical performance of the microwave plasma synthesized Mn@PGF (MP-

Mn@PGF) composite further explains the promoted LiPSs redox kinetics, in which an excellent cyclic performance was realized. The sulfur-loaded MP-Mn@PGF (MP-Mn@PGF-S) promises 14% and 31% increment in discharge capacity after 100 cycles and 300 cycles compare to the sulfur-loaded HT-Mn@PGF (HT-Mn@PGF-S). Besides, a good cycling performance of 790 mA h g<sup>-1</sup> after 300 cycles at 0.2 C was achieved (capacity fade rate of 0.092% per cycle).

### 2. Results and discussions

### 2.1. Microwave plasma (MP) synthesized Mn@PGF composite

HT and MP synthesized Mn@PGF (HT-Mn@PGF and MP-Mn@PGF) processes are demonstrated in Fig. 1a and b, respectively. Pure PGF is the starting material of both methods with a 3D interconnected structure (Fig. S1). A two-step HT treatment was applied to the pre-synthesized PGF (details in supporting info.). On the other hand, the MP was triggered by a kitchen microwave machine that was purchased in a supermarket. Specifically, the precursor-loaded PGF (~1.2 cm<sup>3</sup> with a density of ~1.50 mg cm<sup>-3</sup>) was put in a glass bottle filled with Ar, then microwaved to induce the Ar plasma for nanocomposite synthesis. The as-prepared MP-Mn@PGF was characterized by transmission electron microscope (TEM) and X-ray diffraction (XRD) to compare the size of the nanocrystals on PGF. Fig. 1c and d are the TEM images with insets show the size distribution of the HT and MP synthesized Mn<sub>3</sub>O<sub>4</sub> nanocrystals. HT is one of the most used techniques in synthesizing nanoparticles-graphene composites. It is reported that the mass loading of the product is highly dependent on the precursor concentration in an HT synthesis. A severely small precursor concentration (e.g. 0.001 mol  $L^{-1}$ ) may lead to a lowed product size of <10 nm [33]. However, to achieve a decent electrocatalytic and anchoring performance toward the LiPSs, a high concentration of precursor was utilized in this approach (0.1 mol  $L^{-1}$ ). The sizes of the HT-synthesized Mn<sub>3</sub>O<sub>4</sub> range from 50 to 140 nm, and with an average value of 91 nm. As a comparison, the instant MP heating transfers the manganese acetate crystals into Mn<sub>3</sub>O<sub>4</sub> nanocrystals of sizes range from 4.9 to 13.7 nm (8.2 nm on average, the size distributions of the nanocrystals are indexed in Fig. S2) with a high metal oxide/graphene ratio of about 4:1. The XRD of HT-Mn@PGF and MP-Mn@PGF were indexed with the database of powder diffraction file (PDF). The HT process leads to a single-phase Mn<sub>3</sub>O<sub>4</sub> (PDF#024-0734) grown on PGF, while the MP synthesized nanocomposite shows major Mn<sub>3</sub>O<sub>4</sub> signals with distinguished minor peaks of MnO (PDF#007-0230). This may be attributed to the fundamental of HT processes, in which the Mn<sup>2+</sup> was thoroughly oxidized on the oxygen-rich defects of the GO (-OH, -COOH, etc.) after a long time HT. As to the MP-Mn@PGF, the high temperature of MP instantly reduced the GO, which leaves almost no oxygen-rich defects in Ar environment. The thermogravimetric analysis in Fig. S3 indicates there are a partially reduced PGF with oxygen residues during the HT treatment, while the MP synthesis results in a well reduced PGF with less oxygen content. Therefore, a tiny ratio of Mn ions forms MnO instead of Mn<sub>3</sub>O<sub>4</sub> as heterostructures. The TEM lattice fringe image along with SAED analysis are shown in Fig. S4. Selected areas are indexed with typical diffraction planes e.g. the interplanar lattice distances of 4.92 Å and 1.69 Å in ① are assigned to (100) and (312) crystal plane of the  $Mn_3O_4$ . The 2.57 Å, 1.69 Å, and 2.76 Å interplanar lattice distances in ④ can be assigned to (101), (312), and (103) of the Mn<sub>3</sub>O<sub>4</sub>, while the 2.57 Å is from the (211) of the MnO, which highly supports that the formation of heterostructures. Furthermore, the (211) peaks of Mn<sub>3</sub>O<sub>4</sub> of both samples were calculated by the Scherrer equation (Eq. S1). The crystal sizes of HT-Mn@PGF and MP-Mn@PGF of 122 nm and 19 nm accord well with the TEM results.



**Fig. 1.** (a) Schematic of the HT and (b) MP setup. (c) and (d) are the TEM images of the  $Mn_3O_4$  nanocrystals synthesized by two methods (insets are the size distributions of the particles). (e) and (f) are the corresponding XRD characterizations indexed with the standard crystal database. (A colour version of this figure can be viewed online.)

### 2.2. MP heating of the Mn@PGF

Our previous work [34] shows PGF can effectively absorb electromagnetic (EM) wave as heat in a wide range of frequency (2–18 GHz), especially around the home microwave frequency (2.45 GHz). The PGF with suitable pore sizes around tens of micrometers can confine the microwave in the structure. The microwave can either penetrate or reflect in the 3D network, which causes a high-temperature plasmonic breakdown of the Ar in the pores (Fig. 2a). As a consequence, the high-frequency plasma (50 Hz) can lead to a high heating/cooling rate that efficiently shocks the large precursor particles into nanocrystals around 8 nm (Fig. 2b and c). A short slow-motion video was shoot to visually show the MP synthesis (Fig. 2d is a screenshot from Video S1). Previous joule/microwave heating studies usually utilize a professional spectrometer or a high-speed camera to acquire the light information then convert them into temperature parameters by a color ratio pyrometry. Generally, the spectrometer offers much



**Fig. 2.** Illustrations of the mechanism of MP synthesis: (a) The MP induced by the uniform and suitable pore sizes of PGF. (b)  $Mn(Ac)_2$  precursor particles were shocked and decomposed along the surface of the PGF walls. (c) Fine  $Mn_3O_4$  crystals with sizes around 8 nm were formed after the continuous shock. (d) Actual image of the MP during the synthesis. (e) The spectrum is acquired by a high-end spectrometer. (f) The computer-processed light-intensity plot of the acquired information from [260,290] to [260,300] of the pixel region of the slow-motion video. (A colour version of this figure can be viewed online.)

more precise light information, while the high-speed camera excels in high frame numbers. To better analyze the temperature and ramping rate of the structural enhanced MP, we took advantage of both techniques. Fig. 2e is a spectrum acquired from the high-end spectrometer with the highest intensity during the MP synthesis. The temperature of the MP-Mn@PGF can be ramped to as high as 1549 K based on the calculations of the broad peak of the spectrum. The sharp peaks at 589 nm, 346 nm, and 777 nm can be assigned to the emission of sodium (from the glass), Mn<sup>4+</sup>(from the MP-Mn@PGF), and Ar, respectively [35,36]. The color change of the MP-Mn@PGF was captured by a domestic high-speed camera, and all the images were computer-processed to analyze the heating/ cooling rate. Based on the light intensity plot, it is known that the MP was lasting for about 1220 ms until the MP was ceased with a frequency of 50 Hz. Previous works usually show a ramping-up temperature along with the reaction, yet we've observed heating/ cooling cycles without significant ramping-up (Fig. 2f) which indicates a high cooling rate. After combining the calculations of both techniques, a heating/cooling rate of >13700 K s<sup>-1</sup> was achieved (Fig. S5). This unique phenomenon may be ascribed to the combination of high-permittivity precursors (with Mn-, O-rich bonds) and the PGF's pore/interface-induced polarization under EM irradiation [37]. Moreover, Fig. S6 shows the precursor with sizes around 3 µm before the MP synthesis. The dramatic decline of the particle size from thousands of nanometers to less than 10 nm can be attributed to the powerful shock of the structural enhanced MP. The expose of the Mn<sub>3</sub>O<sub>4</sub> surface can largely enhance the electrocatalytic&anchoring effects, decrease the contact resistance, and provide increased electron transfer pathway, which may lead to an enhanced Li–S cycling performance.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2020.11.061

### 2.3. Structural&elemental characterizations

To study the structural morphologies of the MP-Mn@PGF-S, scanning electron microscopy (SEM) images along with energydispersive spectroscopy (EDS) mapping was captured. Fig. 3a shows the 3D network after the sulfur loading of the MP-Mn@PGF, while Fig. 3b—e are the correlated EDS mapping of Mn, C, S, and O,

812

respectively. It can be seen that the 3D structure of the PGF was maintained after the MP treatment and the sulfur filtration. X-ray photoelectron spectroscopy (XPS) of the electrode before and after cycling is also acquired (Mn spectrum is shown in Fig. S7). The reactions of MP-Mn@PGF and LiPSs were studied via the S 2p peaks of the fresh cell and the cycled cell (Fig. 3f and g). The equal full width at half maximum (FWHM) with 2:1 area ratio was used to fit the S 2p doublet  $2p_{3/2}$  and  $2p_{1/2}$  peaks. Only the lower binding energy  $S2p_{3/2}/2p_{1/2}$  spin-orbit components are discussed. There are 4 sets of doublet peaks with binding energy at 162.9, 164.1, 168.4, 169.3 eV, and 1 single peak with binding energy at 166.5 eV in the highly resolved XPS spectrum of the electrode after the initial discharge. The corresponding doublet peaks of the cycled electrode shift to 162.5, 163.6, 168.8, and 169.7 eV. Based on the previous works [38,39], the I peaks can be assigned to the short-chain LiPSs and the II peaks are mainly from S<sub>8</sub>. The initial response of I and II peaks are more predominant due to the disproportion of the intermediate LiPSs since the polarization of electrons from the sulfur to the interface of the catalyst can be induced by the electrocatalytic MP-Mn@PGF [40]. While the cycled electrode shows good interaction plus a small ratio of unreacted sulfur&short-chain LiPSs. The IV peak around 167.2 eV represents the thiosulfate ions, while the IIII peaks around 170.2 eV can be assigned to the sulfur ions from the sulfate salts. The largely increased IV and IIII peaks suggest an increased density of electron clouds of the  $[SO_3^{2-}]$  and  $[SO_4^{-2}]$  ions, which is consistent with the previous discussions that the nanocomposites show a prominent conversion effects of the LiPSs after cycling.

## 2.4. Electrochemical&catalytic properties of the sulfur loaded Mn@PGF composites

To further demonstrate a good electrocatalytic effect of MP-Mn@PGF towards LiPSs, studies of the electrochemical performance of the Mn@PGF was evaluated. Coin-cell batteries were assembled with a high sulfur content of 91.5 wt% and MP-Mn@PGF content of 8.5% (Fig. S8) plus conductive additive and binder (overall sulfur content 77.8%). Fig. 4a shows the cyclic voltammetry (CV) of Mn@PGF synthesized by HT and MP, respectively. The two cathodic peaks are located at 2.36 V and 2.04 V. The former peak



**Fig. 3.** (a) SEM image of the 3D PGF network after the sulfur loading. (b–e) The correlated EDS mapping of Mn, C, S, and O of the SEM image, respectively. (f) Highly resolved XPS spectrums of the cathode after the initial discharge and (g) cycled for. (A colour version of this figure can be viewed online.)



**Fig. 4.** (a) CV of the HT- and MP-Mn@PGF-S cathode at a scan rate of 0.1 mV s<sup>-1</sup> within 1.7–2.7 V versus Li/Li<sup>+</sup>. (b) Nyquist plots of the MP-Mn@PGF-S electrodes from the 1st to 10th cycles from 100 kHz to 0.01 Hz. (c–d) Galvanostatic charge-discharge profiles at 0.1 C for up to 105 cycles and 0.2 C for 300 cycles. (A colour version of this figure can be viewed online.)

corresponds to the formation of long-chain LiPSs (Li<sub>2</sub>S<sub>x</sub>, x = 4-8) and the latter one is for the conversion of long-chain to short-chain LiPSs (Li<sub>2</sub>S<sub>2</sub>, Li<sub>2</sub>S) [41]. The anodic peak around 2.38 V corresponds to the reverse conversion from Li<sub>2</sub>S to Li<sub>2</sub>S<sub>8</sub> [42,43]. The MP-Mn@PGF-S enables voltage polarizations of around 49 mV and 31 mV for the cathodic peaks. Similar to the previous discussion

[44], the output voltage of the Li–S cell (E) can be represented as equation (1):

$$\mathbf{E} = E_0 - iR_i \tag{1}$$

where  $E_0$  is the standard potential and  $R_i$  is the internal resistance,



Fig. 5. Computational calculation of binding energies of Li<sub>2</sub>S<sub>8</sub>, Li<sub>2</sub>S<sub>6</sub>, Li<sub>2</sub>S<sub>6</sub>, Li<sub>2</sub>S<sub>6</sub>, Li<sub>2</sub>S<sub>2</sub>, and Li<sub>2</sub>S onto the surface of Mn<sub>3</sub>O<sub>4</sub>. (A colour version of this figure can be viewed online.)

which including the electrolyte resistance, contact resistance, activation polarizations, and concentration polarization. As seen in Fig. 4a and the inset, the output voltages of the HT-Mn@PGF-S are larger than those of the MP-Mn@PGF-S ( $2.36 \rightarrow 2.31$  V,  $2.03 \rightarrow 2.00$  V), indicating that the vast nanocrystal surfaces have decreased the internal resistance and activation polarizations while anchoring the LiPSs for enhanced electrocatalytic kinetics. The charge-discharge plateaus in the inset of Fig. 4a indicate an initial discharge capacity of around 1330 mA h g<sup>-1</sup> and 1490 mA h g<sup>-1</sup> of the HT-Mn@PGF-S and MP-Mn@PGF-S, respectively. The voltage polarization of the charge-discharge plateaus is also consistent with the CV. The discharge peaks of MP-Mn@PGF-S are more prominent than the HT-Mn@PGF-S, which indicates favorable Li bonds are formed and prompt the reaction kinetics [45].

The stable 3D structure of MP-Mn@PGF-S realizes fast electrontransfer kinetics by providing a conductive network. This is further supported by the electrochemical impedance spectroscopy (EIS) Nyquist plot. Fig. 4b (inset is the magnified curves) shows the EIS plot after 10 activation cycles with different charge-discharge cycles. The fresh cell has a starting point in the higher frequency of over 10 kHz, which represents the resistance of electrolyte of 2  $\Omega$ . In the high-frequency region, there is an obvious semicircle related to the interphase resistance, which simulates the process of electron transfer from the current collector to the MP-Mn@PGF-S (Rint// CPE<sub>int</sub>). The R<sub>int</sub>//CPE<sub>int</sub> increased from 3.8  $\Omega$  to 8.2  $\Omega$  when the cell was operated at the 20th cycle. That is probably due to the undermined surface contact of the cathode caused by the volume expansion of the short-chain LiPSs when they dissolved into the electrolyte. As to the middle frequency, a flat semicircle shows in the fresh cell correlates to the charge-transfer resistance, which reflects the electrochemical processes between the MP-Mn@PGF/ sulfur and the LiPSs/electrolyte ( $R_{ct}$ //CPE<sub>dl</sub>). The increased  $R_{ct}$ // CPE<sub>dl</sub> may be ascribed to the semi-solidification of the electrolyte over the charge-discharge cycles. In specific, there is excessive electrolyte loaded on the electrodes to prevent depletion in the beginning. Yet the electrolyte may slowly vaporize and transfers to the spare space in the coin-cell, thus the solutes are concentrated to form a homogeneous semi-liquid state. The plots end with inclined

lines in the low frequency, which agrees with the previous report [6].

In the cycling test of HT-Mn@PGF-S and MP-Mn@PGF-S (Fig. 3c and d) at 0.1 C rate, a fluctuating columbic efficiency of 97 %–104% along with the discharge capacity of 1486 mA h g<sup>-1</sup> and 1536 mA h g<sup>-1</sup> was delivered in the beginning, respectively. After several activation cycles, the columbic efficiency of almost 100% was achieved to promise a good cycling performance with a sulfur mass loading of around 3.1 mg cm<sup>-2</sup>. The MP-Mn@PGF-S still maintains a discharge capacity of 917 mA h g<sup>-1</sup> after 100 cycles while the HT-Mn@PGF-S can only remain around 794 mA h g<sup>-1</sup>. A cycling test under 0.2 C rate was also done to show the long cycling performance of the MP-Mn@PGF-S electrode (Fig. 4d). Excels the 49.2% capacity retention of the HT-Mn@PGF-S after 300 cycles, a high initial specific capacity of 1248 mA h g<sup>-1</sup> with increased 64.8% capacity retention was achieved, which indicates good cycling stability with 0.092% capacity loss per cycle.

The rate capability of the HT-Mn@PGF-S and MP-Mn@PGF-S cathode was tested at different charge/discharge current rates from 0.1 to 1 C and then back to 0.5 C every five cycles (Fig. S9). The discharge capacities of HT-Mn@PGF-S at 0.1, 0.2, 0.5, and 1 C  $(1 \text{ C} = 1675 \text{ mA g}^{-1})$  are 1419, 1082, 811, and 605 mA h g<sup>-1</sup>, respectively. On the other hand, the MP-Mn@PGF-S cathode is with discharge capacities of 1504, 1237, 949, and 823 mA h  $g^{-1}$  at 0.1, 0.2, 0.5, and 1 C, which indicates an overall good rate performance. In comparison, the HT-Mn@PGF-S can deliver good specific capacity and columbic efficiency in the beginning. However, the agglomeration of the crystals undermines the electrocatalytic effect of the Mn@PGF thus a prominent shuttle effect exists. The slightly rough curve was shown during the charge-discharge which is probably due to the strong binding between the Mn<sub>3</sub>O<sub>4</sub>/MnO and the LiPSs [46,47]. Overall, the size-dependent catalyzing efficiency was promised by the decreased voltage polarization. The good longcycling performance suggests the volume expansion was accommodated by the 3D PGF, and the expose of the Mn<sub>3</sub>O<sub>4</sub>/MnO surface with crystal sizes around 8 nm indicates promoted anchoring effects towards the shuttling of LiPSs.

### 2.5. Computational analysis of graphene&Mn<sub>3</sub>O<sub>4</sub> composite

It is believed that transition metal oxides can act as electrocatalysts in the conversion from  $Li_2S_8$  to  $Li_2S$  and facilitates the encapsulation of LiPSs [48]. Therefore, density functional theory (DFT) calculations such as TiO/TiO<sub>2</sub> [49,50],  $V_2O_5/MO_2O_3$  [51], MnO/ MnO<sub>2</sub> [52] et al. were done to explain the high binding energy between the transition metal oxides and the LiPSs. However, the theoretical calculations of Mn<sub>3</sub>O<sub>4</sub>–Li<sub>2</sub>S<sub>x</sub> (x = 1, 2, 4, 6, 8) haven't been reported yet [53]. Therefore, the binding energies (E<sub>bind</sub>) of LiPSs with Mn<sub>3</sub>O<sub>4</sub> (001) surface were calculated as equation (2).

$$E_{\text{bind}}(Li_2S_x) = E(Li_2S_x / M) - E(Li_2S_x) - E(M)$$
(2)

E<sub>bind</sub> is the binding energy related to a stable substrate-adsorbate system. M represents the Mn<sub>3</sub>O<sub>4</sub> which correlates to the Mn@PGF-LiPSs interactions, respectively. The absolute values of E<sub>bind</sub> were discussed instead of E<sub>bind</sub> since a large absolute value of E<sub>bind</sub> indicates strong bonds formation. The illustration in Fig. 5 shows the geometrical configurations of the most stable states of each substrate-adsorbate systems of Mn<sub>3</sub>O<sub>4</sub>-LiPSs, and the plot indicates their corresponding binding energies. The Li<sub>2</sub>S<sub>8</sub> and Li<sub>2</sub>S<sub>6</sub> are absorbed on the surface of Mn@PGF with -Ebind of 5.52 and 5.83 eV, respectively. They are much higher (7-11 times higher) than the -E<sub>bind</sub> of the carbon [54]/graphene [55]-Li<sub>2</sub>S<sub>x</sub> based on previous reports. The fully lithiated of S<sub>8</sub> to Li<sub>2</sub>S leads to higher binding energy at 7.19 eV than other Mn<sub>x</sub>O<sub>v</sub>-based cathodes [56]. It further supports a highly efficient electrocatalytic and anchoring effect of the 3D Mn@PGF by absorbing the short-chain LiPSs on the vast sites of the Mn@PGF. This computational analysis also agrees well with the electrochemical tests and XPS analysis in which the Mn@PGF can efficiently anchor the LiPSs to relieve the shuttle effect by forming strong bonds.

### 3. Conclusions

In summary, a facial and instant structural enhanced MP synthesis for Mn<sub>3</sub>O<sub>4</sub>/PGF nanocomposites has been demonstrated. The ultrafine Mn<sub>3</sub>O<sub>4</sub> nanocrystals were deposited on PGF with high catalytic efficiency and high cycling performance. Compared with conventional HT synthesis or microwave heating, this structural enhanced MP technique can achieve a super heating/cooling rate that larger than 13700 K s<sup>-1</sup> and a maximum temperature at 1549 K. This technique can effectively downsize the precursor particles (~3 µm) into Mn<sub>3</sub>O<sub>4</sub> nanocrystals (~8 nm) within 1.2 s. The as-prepared MP-Mn@PGF can both structurally accommodate the volume expansion and chemically relief the shuttle effect. Overall, the MP synthesized cathode delivers a good cycling stability of 795 mA h  $g^{-1}$  at 0.2 C after 300 cycles (0.092% capacity loss per cycle), which may pave an broad way for the design and preparation of highly efficient nanocatalysts for energy storage applications.

### **CRediT** authorship contribution statement

Yiyang Liu: Conceptualization, Resources, Investigation, Data curation, Writing - original draft, preparation, Writing - review & editing. Yan Zhang: Software, Formal analysis. Yang Liu: Methodology. Jie Zhu: Formal analysis. Zhen Ge: Conceptualization. Zhongjun Li: Supervision. Yongsheng Chen: Supervision, Funding acquisition, Writing - review & editing.

### **Declaration of competing interest**

The authors declare that they have no known competing

financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgements

The authors gratefully acknowledge the financial support from the Ministry of Science and Technology of China (MoST 2016YFA0200200) and the National Natural Science Foundation of China (NSFC 51633002 and 21671176), and 111 Project (B12015).

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2020.11.061.

### References

- [1] G. Zhou, L. Yin, D. Wang, L. Li, S. Pei, I.R. Gentle, F. Li, H. Cheng, ACS Nano 7 (6) (2013) 5367–5375.
- [2] Y. Fu, C. Zu, A. Manthiram, J. Am. Chem. Soc. 135 (48) (2013) 18044–18047.
  [3] R. Fang, K. Chen, L. Yin, Z. Sun, F. Li, H. Cheng, Adv. Mater. 31 (9) (2019) 1800863.
- [4] L. Li, L. Hou, J. Cheng, T.J. Simmons, N. Koratkar, Energy Storage Mater 15 (2018) 388–395.
- [5] J. Huang, T. Zhuang, Q. Zhang, H. Peng, C. Chen, F. Wei, ACS Nano 9 (3) (2015) 3002–3011.
- [6] X. Yang, L. Zhang, F. Zhang, Y. Huang, Y. Chen, ACS Nano 8 (5) (2014) 5208–5215.
- [7] D. Sui, M. Wu, Y. Liu, Y. Yang, H. Zhang, Y. Ma, L. Zhang, Y. Chen, Nanotechnology 32 (1) (2020), 015403.
- [8] C. Lai, X.P. Gao, B. Zhang, T.Y. Yan, Z. Zhou, J. Phys. Chem. C 113 (11) (2009) 4712–4716.
- [9] D. Guo, Z. Zhang, B. Xi, Z. Yu, Z. Zhou, X.a. Chen, J. Mater. Chem. 8 (7) (2020) 3834–3844.
- [10] Z. Sun, J. Zhang, L. Yin, G. Hu, R. Fang, H. Cheng, F. Li, Nat. Commun. 8 (1) (2017) 14627.
- [11] J. He, A. Manthiram, Energy Storage Mater 20 (2019) 55–70.
- [12] Z. Sun, L. Xu, C. Dong, H. Zhang, M. Zhang, Y. Ma, Y. Liu, Z. Li, Y. Zhou, Y. Han, Y. Chen, Nano Energy 63 (2019) 103887.
- [13] S. Tang, W. Guo, Y. Fu, Adv. Energy Mater. (2020) 2000802.
- [14] Y. Liu, Z. Ge, Z. Sun, Y. Zhang, C. Dong, M. Zhang, Z. Li, Y. Chen, Nano Energy 67 (2020) 104216.
- [15] R. Fang, S. Zhao, Z. Sun, D. Wang, H. Cheng, F. Li, Adv. Mater. 29 (48) (2017) 1606823.
- [16] L. Tan, X. Li, Z. Wang, H. Guo, J. Wang, ACS Appl. Mater. Interfaces 10 (4) (2018) 3707–3713.
- [17] Z. Yuan, H. Peng, T. Hou, J. Huang, C. Chen, D. Wang, X. Cheng, F. Wei, Q. Zhang, Nano Lett. 16 (1) (2016) 519–527.
- [18] X. Liu, Z. Li, X. Liao, X. Hong, Y. Li, C. Zhou, Y. Zhao, X. Xu, L. Mai, J. Mater. Chem. 8 (24) (2020) 12106–12113.
  [19] Y. Li, D. Ye, W. Liu, B. Shi, R. Guo, H. Zhao, H. Pei, J. Xu, J. Xie, ACS Appl. Mater.
- [19] T. Li, D. Te, W. Liu, D. Shi, K. Guo, H. Zhao, H. Pei, J. Xu, J. Xie, ACS Appl. Mater. Interfaces 8 (42) (2016) 28566–28573.
   [20] L. Dong, M. Li, L. Dong, M. Zhao, J. Feng, Y. Han, J. Deng, X. Li, D. Li, X. Sun, Int. J.
- Hydrogen Energy 39 (28) (2014) 16116–16122. [21] G. He, J. Li, H. Chen, J. Shi, X. Sun, S. Chen, X. Wang, Mater. Lett. 82 (2012)
- [21] G. He, J. Li, H. Chen, J. Shi, X. Sun, S. Chen, X. Wang, Mater. Lett. 82 (2012) 61–63.
   [22] F. Kang, M. D. Jian, H. Dalini, H. Girani, A. Dashel, M.C. Tarach, Nucl. Microsci. 41 (2012) 61–63.
- [22] E. Karaoğlu, H. Deligöz, H. Sözeri, A. Baykal, M.S. Toprak, Nano-Micro Lett. 3 (1) (2011) 25–33.
- [23] M. Bentabol, M. Cruz, F. Huertas, J. Linares, Clay Clay Miner. 54 (2006) 667–677.
- [24] D.P.M.D. Shaik, R. Pitcheri, Y. Qiu, O.M. Hussain, Ceram. Int. 45 (2, Part A) (2019) 2226–2233.
- [25] H. Huang, Z. Zhao, W. Hu, C. Liu, X. Wang, Z. Zhao, W. Ye, J. Taiwan Inst. Chem. E. 84 (2018) 101–109.
- [26] C. Liu, K. Chang, C. Hu, W. Wen, J. Power Sources 217 (2012) 184–192.
- [27] J. Tu, H. Li, T. Lan, S. Zeng, J. Zou, Q. Zhang, X. Zeng, J. Alloys Compd. 822 (2020) 153751.
- [28] G. Zhong, S. Xu, C. Chen, D.J. Kline, L. Hu, Adv. Funct. Mater. (2019) 1904282.
  [29] N. Bundaleska, D. Tsyganov, A. Dias, E. Felizardo, J. Henriques, F.M. Dias,
- M. Abrashev, Z. Kissovski, E. Tatarova, Phys. Chem. Chem. Phys. 10 (2018) 1039.
- [30] E. Tatarova, A. Dias, J. Henriques, d.R. A.M. Botelho, A.M. Ferraria, M.V. Abrashev, C.C. Luhrs, J. Phillips, F.M. Dias, C.M. Ferreira, J. Phys. D Appl. Phys. 47 (38) (2014) 385501.
- [31] S. Xu, G. Zhong, C. Chen, M. Zhou, D.J. Kline, R.J. Jacob, H. Xie, S. He, Z. Huang, J. Dai, Matter 1 (3) (2019) 759–769.
- [32] Y. Liu, Z. Ge, Z. Li, Y. Chen, Nano Energy 80 (2021) 105500.
- [33] K. Sue, K. Kimura, K. Arai, Mater. Lett. 58 (25) (2004) 3229-3231.
- [34] Y. Zhang, Y. Huang, T. Zhang, H. Chang, P. Xiao, H. Chen, Z. Huang, Y. Chen, Adv. Mater. 27 (12) (2015) 2049–2053.

### Y. Liu, Y. Zhang, Y. Liu et al.

- [35] S. Wang, Q. Sun, J. Liang, L. Sun, B. Devakumar, X. Huang, Inorg. Chem. Commun. 116 (2020) 107903.
- [36] M.T. Jamil, J. Ahmad, S.H. Bukhari, M.E. Mazhar, G. Murtaza, Dig. J. Nanomater. Bios. 12 (2) (2017) 595-604.
- [37] H. Lv, Y. Guo, Z. Yang, Y. Cheng, L.P. Wang, B. Zhang, Y. Zhao, Z.J. Xu, G. Ji, J. Mater. Chem. C. 5 (3) (2016) 491–512.
- [38] X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, L.F. Nazar, Nat. Commun. 6 (2015) 5682.
- [39] X. Wang, G. Li, J. Li, Y. Zhang, A. Wook, A. Yu, Z. Chen, Energy Environ. Sci. 9 (8) (2016) 2533-2538.
- [40] M. Cuisinier, P. Cabelguen, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bolin, M. Balasubramanian, L.F. Nazar, J. Phys. Chem. Lett. 4 (19) (2013) 3227–3232.
- [41] Y. Jung, S. Kim, Electrochem. Commun. 9 (2) (2007) 249-254. [42] Y.X. Yin, S. Xin, Y.G. Guo, L.J. Wan, Angew. Chem. Int. Ed. 52 (50) (2013) 13186-13200.
- [43] Y. Su, A. Manthiram, Nat. Commun. 3 (2012) 1166.
- [44] J. Yan, X. Liu, B. Li, Adv. Sci. (2016) 1600101.
  [45] T.Z. Hou, W.T. Xu, X. Chen, H.J. Peng, J.Q. Huang, Q. Zhang, Angew. Chem. Int. Ed. 56 (28) (2017) 8178–8182.

- [46] J. Yan, X. Liu, B. Li, Adv. Sci. 3 (12) (2016) 1600101.
- [47] G. Xu, A. Kushima, J. Yua, H. Dou, W. Xue, X. Zhang, X. Yan, J. Li, Energy Environ. Sci. 10 (12) (2017) 2544–2551.
- [48] B. Wang, S.M. Alhassan, S.T. Pantelides, Phys. Rev. Appl. 2 (3) (2014), 034004.
- [49] W. Yao, C. Chu, W. Zheng, Z. Liang, Y.L. Wang, J. Mater. Chem. 10 (2018) 1039. [50] Z. Li, J. Zhang, B. Guan, D. Wang, L.M. Liu, X.W. Lou, Nat. Commun. 7 (2016)
- 13065.
- [51] Q. Zhang, Y. Wang, Z.W. Seh, Z. Fu, R. Zhang, Y. Cui, Nano Lett. 15 (6) (2015) 3780
- [52] X. Wang, G. Li, J. Li, Y. Zhang, A. Wook, A. Yu, Z. Chen, Energy Environ. Sci. 9 (8) (2016) 2533–2538.
- [53] J. Wu, Q. Ma, C. Lian, Y. Yuan, D. Long, Chem. Eng. J. 370 (2019) 556-564.
- [54] J. Wang, H. Yang, Z. Chen, L. Zhang, J. Liu, P. Liang, H. Yang, X. Shen, Z.X. Shen, Adv. Sci. 5 (11) (2018) 1800621.
- [55] K.C. Wasalathilake, M. Roknuzzaman, K. Ostrikov, G.A. Ayoko, C. Yan, RSC Adv. 8 (5) (2018) 2271–2279.
- [56] Y. Zhong, K.R. Yang, W. Liu, P. He, V. Batist, H. Wan, J. Phys. Chem. C. 121 (2017) 14222–14227.