Enhanced Electrochemical Kinetics on Ni$_2$P Polar Mediators Integrated with Graphene for Lithium–Sulfur Batteries

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Lithium-sulfur batteries have evoked intensive attention caused by the urgent requirement of energy storage devices with higher energy density, long cycle life, and low cost. However, the insulating nature and the soluble reaction intermediate products still hinder its large-scale industry and acceptance by the market. Tremendous efforts focus on the composite of polar material and non-polar material to solve the weaknesses of material insulating nature and soluble reaction intermediate products. However, the linkage form between these two generic materials has been ignored. In this paper, by using typical Ni$_2$P as polar material and graphene as non-polar material, the reaction kinetics changes and its intrinsic theories on behavior enhancement have been proved, which construct different binding type between polar and non-polar materials. The Ni$_2$P/PrGO delivers an improved high specific capacity of 1254.6 mAh g$^{-1}$ than Ni$_2$P/rGO at 0.2 C. The relevant X-ray photoelectron spectroscopy result and the in situ electrochemical impedance spectroscopy tests prove that the linkage state between polar and non-polar material has strong influence on the sulfur cathode reaction kinetics. The enhanced reaction kinetics and polar adsorption behavior bring the soft pack battery testing unit over 150 stable cycles with decay ratio of 0.19% for each cycle.

1. Introduction

By ever-increasing demand for energy storage devices with high energy density, long cycle life and low manufacture cost, lithium–sulfur (Li–S) batteries have attached intensive consideration by its theoretical energy density (2500 Wh kg$^{-1}$) with the natural abundance and nontoxic behaviour. However, the sulfur cathodes have its own major technical barriers to the realization of high-performance energy storage device. 1) The insulating nature of sulfur limits the reaction depth of the active material and its rate performance.[2] 2) The soluble reaction intermediate products (lithium polysulfides) will easily shuttle into the electrolyte and diffuse between cathode and anode, which dramatically cause the consumption of lifespan.[3] 3) The high oxidation barrier from Li$_2$S$\_X$ to sulfur causes the fall of Coulombic efficiency.[4] Tremendous efforts have been proposed to synthesize composite in order to enhance the conductivity of sulfuric composites and suppress the shuttle effect. Carbonaceous materials have been considered as excellent host materials to reserve sulfur due to its high conductivity, irreplaceable porous structure, and natural abundance.[5] However, the nonpolar interface from uniform carbon atom arrays have less efficiency in entrapping polar polysulfides.[6] For another sight, independent polar materials are be thought to form a particular electrostatic field, which can grab the polar polysulfides in high efficiency.[7] Whereas, the lower conductivity and weak electrochemical activity hinder its further development.[7c,8] Moreover, these polar molecules cannot be independently used as a host to reserve sulfur species because there molecular...
structures cannot form effective 3D porous structure with internal conductive network.

To satisfy these respective advantages and solve the weakness of such materials simultaneously, the hybrid structure of polar materials and carbon materials have been widely concerned and have some positive results.[9] However, the electrochemical reaction of polysulfides on hybrid materials are a series of complex multistep reaction process.[7c] Due to the separation of the reaction active site (boundary of polar material and carbon material), the adsorption site (polar surface) and the electron transfer route (carbon material) for reaction, the gap between polar materials and carbon matrix will highly influence on the reaction barrier and the electrochemical behavior cause by the linkage state changes and synergistic effect.[4a,10] Unfortunately, such interaction rule has not been explained clearly on how to build up a satisfying linkage.

In this work, we find out a special linkage state of which shows good behavior by forming two different linkage state between Ni3P, as typical polar material, and graphene, as typical nonpolar carbon material, by different anneal process. The linkage states have been provided by XPS study and following in situ EIS tests prove that the linkage between two functional materials give an opportunity to level down the reaction barrier and reduce the reaction overpotential. By designing on a series of experiments, the enhancement of electrochemical behaviors is attributed to the formation of new linkage between two functional materials. That is of crucial importance in achieving high reversible capacity and prolonging reaction depth. This desirable cathode delivers a high specific capacity of 1254.6 mAh g\(^{-1}\) at 0.2C and large-scaled soft package Li–S batteries are assembled and stably cycled for over 150 cycles.

Figure 1. a) Schematic illustration of the preparation of the Ni3P/PrGO and Ni3P/rGO. b,c) The SEM images of the Ni-precursor/rGO and d,e) Ni3P/PrGO for high and low magnification. f) The EDX element mapping of S@Ni3P/PrGO and corresponding content.
2. Results and Discussion

The preparation of Ni$_2$P/PrGO and Ni$_2$P/rGO with simple hydrothermal reaction and following programmed anneal process is shown schematically in Figure 1a. For the synthesis of such composites, first the Ni-precursor/rGO was performed by the reduction of GO solution with Ni(NO$_3$)$_2$·6H$_2$O and HMT inside at 180 °C. After following freeze drying, and programmed anneal process under PH$_3$/Ar atmosphere, Ni$_2$P nanoparticles are dispersed uniformly on such functionalized graphene sheets to increase their active reaction zone. For comparison, the Ni$_2$P/rGO is synthesis under the same anneal program without PH$_3$ over 350 °C. For the precursor of Ni-precursor/rGO, Figure S1 in the Supporting Information demonstrates that there are no obvious nanoparticles on the rGO sheet before being annealed in PH$_3$ atmosphere. However, after the programmed anneal process, FE-SEM images clearly demonstrate that the homogeneous distribution of Ni$_2$P nanoparticles as given in Figure 1b,c by the field emission scanning electron microscopy. In the case of Ni$_2$P/rGO composite, a spatial distribution of nanoparticles over the layered graphene sheets was observed clearly. To further confirm the morphology and quantify the crystal structure of Ni$_2$P/PrGO, transmission electron microscopy (TEM) were carried out and illustrated in Figure 1d. TEM images also confirm that the homogeneous distribution of nanoparticle obviously, which consist with the SEM result (Figure 1c). The high-resolution TEM image in Figure 1e shows that the Ni$_2$P crystals are well dispersed with a diameter of 8 nm. The lattice space of about 0.22 nm corresponds to the (111) lattice plane of Ni$_2$P. Further element mapping images in Figure 1f strongly confirms that the Ni$_2$P nanoparticles are uniformly distributed on the rGO sheets. A good distribution of polar nanoparticles will gain a good uniformity and stability of property, which are good for the stable of reaction for lithium–sulfur battery.[4c,11] And also the nano-scale of polar particle decoration can dramatically create the adsorption activity, but do not sacrifice too much on the specific energy density of host material.[12]

To further confirm the species change of the host material during the fabrication, XRD data are efficiency to point out the phase transformation. The XRD patterns of the synthesized Ni$_2$P/PrGO is shown in Figure 2a. The diffraction peaks of all of the XRD patterns can be directly indexed to the hexagonal Ni$_2$P phase and are in agreement with the corresponding JCPDS card (lattice parameters $a = b = 5.856$ Å, $c = 3.382$ Å, $\gamma = 120^\circ$, P-62m space group, JCPDS 74-1385). The weak diffraction peaks are owing to the Nano-crystallization and low content of Ni$_2$P nanoparticles. By compared with the XRD patterns of Ni-precursor/rGO (Figure S2, Supporting Information), these observations demonstrated that the successful conversion from Ni-precursor into Ni$_2$P during phosphorization process. Figure S3 in the Supporting Information shows the XRD pattern of Ni$_2$P/rGO, which confirm the changing of atmosphere by forming the Ni$_2$P after 300 °C have barely effect on the phase transformation of Ni-precursor. According our previous research, the phase change from Ni-precursor into Ni$_2$P basically happen in low temperature phosphorization.[8,13]

The pore structure of Ni$_2$P/PrGO is characterized by N$_2$ adsorption/desorption isotherms test with a high specific
surface area of 392.6 m$^2$ g$^{-1}$ and pore volume of 0.357 cm$^3$ g$^{-1}$. It is noted that the type IV isotherms curve with distinct hysteresis loop shows its mesoporous characteristic features (Figure 2b), which shows it mesoporous behavior. The pore structure is further supported by the Barrett-Joyner-Halenda (BJH) pore size distribution curve with the average pore diameter of 4.64 nm as demonstrated in Figure 2c. The isotherms results of bare rGO are demonstrated in Figure S4 in the Supporting Information without good hysteresis loop and pore distribution. By comparing with the sorption isotherms results, Ni$_2$P/PrGO shows much higher specific surface area and pore volumes. That caused by the anchored Ni$_2$P nanoparticles into the graphene sheets, which strongly prevent the aggregation of composite material.[14] These results confirm the Ni$_2$P nanoparticle have good ability on prevention of the structure shrink during the material preparation as same as most of others nano materials.[15] The structure stability and its pore structure is important for its electrochemical behavior. These physical structures with high pore volumes derived from wrinkle structure will ensure that the Ni$_2$P/PrGO host has enough stable interspace to accommodate activated sulfur species in good during the battery lifetime. And the abundant internal reaction area is good for reaction, electron exchange and its transfer by forming fast conductive bulk network.[16] The Raman spectrum of two samples confirm the similar typical pattern of graphene. The slight increased of Id:Ig of Ni$_2$P/PrGO to Ni$_2$P/rGO (which increase from 0.931 to 0.992) might cause by the intense graphitization by reductive PH$_3$ atmosphere which may further reduce the GO to graphene sheets during the high temperature anneal process. Higher graphitized rGO may has some benefit on the cathode performance contribution but the EIS result (Figure 3f) has confirm that ohm resistance has no apparent changes.

To fill the sulfur into the host material, a thermal diffusion method was used to fabricate the S@Ni$_2$P/PrGO, S@Ni$_2$P/rGO, and bare S@rGO composite for comparison. All the thermal diffusion procedures are based on the same weight ratio (1:3) of host materials and sulfur in a sealed vessel. Thermogravimetric analysis (TGA) in Figure 2d was used to determine the mass percent of sulfur after annealing.

![Figure 3](image-url)
of sulfur in such composite. The weight loss at 200–350 °C confirmed that the sulfur content of S@Ni2P/PrGO is about 73.32%. Figure S6 in the Supporting Information demonstrates the TGA curve of S@Ni2P/rGO and S@rGO with the sulfur mass loss of 71.92% and 65.54%, respectively. The data shows that even the composite which has been sealed in the same mass ratio, vessel and same procedure, the sulfur content still have slight change. These changes cause by the different pore structure as rGO is poor of its BET result (Figure S4, Supporting Information).

All the samples of sulfur cathode material have been assembled as coin-type batteries to study its electrochemical performances. Figure 3a demonstrates the cycle performance of S@Ni2P/PrGO, S@Ni2P/rGO and S@rGO for 300 cycles at 0.2C (IC = 1675 mA g⁻¹) in the voltage range of 1.6–3.0 V. The S@Ni2P/PrGO shows a reversible discharge capacity of 1254.6 mAh g⁻¹ for initial and maintains 897.1 mAh g⁻¹ over 300 cycles. It is worthy mentioned that, by compared with a discharge capacity of S@Ni2P/rGO (512.2 mAh g⁻¹ for initial, 1185.2 at top, and 824.2 mAh g⁻¹ over 300 cycles), such higher reversible capacity and capacity retention after long cycle process reveal the deepened of reaction depth and prolonged lifespan. The S@Ni2P/PrGO presents slightly capacity increased as shown at about 150 cycles, which is likely cause by the higher sulfur areal loading (1.169 mg cm⁻²) by compare with the S@Ni2P/rGO (0.985 mg cm⁻²). The testing was controlled at same electrolyte addition amount which is 35 µL mg⁻¹. The high sulfur loading and thick electrode needs extra time (during the whole electrode lifespan) for electrolyte deeply infiltration which may delay the specific capacity drop or slightly increased at some stage. The abundant electrolyte for Ni2P/PrGO sample may cause more polysulfide dissolve and the shuttle effect may delayed appear. Although the Ni2P/PrGO shows slightly different of the curve shape but its specific capacity retention (71.5% for 300 cycles) still slightly higher than the Ni2P/rGO electrode (69.5% for 300 cycles). The XRD patterns for the electrode after cycles (Figure S7, Supporting Information) has confirmed that the Ni2P has not occurring on the reaction with sulfur and maintain its original phase. The charge/discharge profiles of S@Ni2P/PrGO in different cycles are illustrated in Figure S8 in the Supporting Information. For S@rGO without Ni2P nanoparticle embedded into, despite these composites reach high electrochemical activity in initial, the speedy capacity decay demonstrates a weakened cycle life owing to the lack of polar surface to trap polysulfides. [4c,11,17] It is notable that the S@Ni2P/PrGO still maintain good rate performance even the sulfur area loading up to 2.7 mg cm⁻² as shown in Figure S9 in the Supporting Information. The electrode demonstrates 1076.9 mAhg⁻¹ at 0.2C at beginning, and following 963.6, 897.1, 811.9, 749.5 mAhg⁻¹ under 0.5C, 1C, 2C, 3C, respectively. After the current shift back to 0.2C, the electrode still remains high specific capacity of 1010.6 mAhg⁻¹ which confirm the reversible rate performance for the electrode.

Charge and discharge voltage profiles of the Li–S batteries with S@Ni2P/PrGO electrode and S@Ni2P/rGO electrode at the 100th cycles are illustrated in Figure 3b, and the S@rGO is in Figure S10 in the Supporting Information. All the curves show the typical discharge/charge profiles between 1.6 and 3.0 V (versus Li⁺/Li). In addition, the potential difference between redox plateau of the S@Ni2P/PrGO is 220 mV, which is much lower than the S@Ni2P/rGO of 290 mV. These data prove that the polarization and reaction barriers of S@Ni2P/PrGO are much lower than those of S@Ni2P/rGO. Furthermore, to clearly show the activator barrier during charge process, the charge profiles of S@Ni2P/PrGO and S@Ni2P/rGO has amplified in Figure 3c. The S@Ni2P/rGO cathode exhibits a high potential barrier at about 104.1 mV in the initial charging process, indicating a sluggish activation process with high charge transfer resistance. However, the S@Ni2P/PrGO dramatically reduces the height of the potential barrier to 80.6 mV. Notably, for the second plateau of discharge process, it is evident that the specific capacity contribution of S@Ni2P/PrGO is much higher than S@Ni2P/rGO. Further gathered statistical capacity distribution data of S@Ni2P/PrGO, S@Ni2P/rGO and S@rGO (Figure 3d) show that the capacity contribution ratio of S@Ni2P/PrGO and S@Ni2P/rGO is 1:2.10 and 1:1.62 respectively, which strongly prove the enhancement effect of Ni2P/PrGO. Notably even the capacity contribution ratio of S@rGO has reached 1:2.40, however, owing to the lack of adsorption ability by the nonpolar host material, the specific capacity has shriveled totally. These typical signals strongly confirm that the break bond reaction of polysulfides (Li₂Sₓ, 8 > x > 4) during discharge process and reconstruction reaction of lithium sulfide (Li₂Sₓ/Li₂S) during charge process are all significantly enhanced. The reason on the enhancement of the electrochemical behaviors needs to be studied. In order to evaluate the electrochemical activity of Ni2P/PrGO and Ni2P/rGO, cyclic voltammograms (CVs) were tested at a low scan rate of 0.1 mV s⁻¹ (Figure 3e). The CV curve of S@Ni2P/PrGO and S@Ni2P/rGO are illustrated in Figure S11 in the Supporting Information and Figure S12 in the Supporting Information respectively. For both materials, the second CV cycle also overlaps well with the fifth cycle, indicating a constant suppression on electrochemical polarization of the Ni2P host. Obviously, two cathodic peaks at 2.1–2.4 V and 1.6–2.1 V were observed, which corresponded to the two-step sulfur reduction from elemental sulfur to soluble polysulfides and subsequent generation of solid Li2S2 and Li2S. [18] The cathodic peak potential of two materials is no obvious difference. However, consistent with aforementioned slow redox kinetics of polysulfides on graphene surface, Ni2P/PrGO based sulfur cathode exhibited double anodic peaks as well as gentle polarization, which demonstrates the better reversibility of reaction at a given scan rate. Furthermore, the distinguishable positive shift in anodic peaks of Ni2P/PrGO indicates the higher activity of Ni2P/PrGO electrode toward the polysulfides conversion process (Table S1, Supporting Information). These peak shifts typically indicate a decrease in cell polarization, which is in good agreement with galvanostatic charge/discharge profiles shown in Figure 3b.

Electrochemical impedance spectroscopy (EIS) tests further be pointed out to better understand the charging reaction dynamic enhancement of the Li–S cell by different host materials. While the Nyquist plots of two cathode material were consistent at discharged state (Figure 3f), the diameter of the two semicircles (R1 and R2) can be qualitatively described as the charge transfer resistance of the electrolyte interface and reduction production of Li2S or Li2S2 which remarkably influence the reaction kinetics at charge process. The inset shows the relevant equivalent circuit. It is notable that the small impedance
response of S@Ni$_2$P/PrGO is greatly facilitated due to the vigorous kinetics and lower charge-transfer resistance, as revealed by the small semicircular loop in the high-medium frequency region. Based on the EIS test, the enhancement of the electrochemical performance cause by the reinforcement of the reaction kinetic owing to the reduction of the reaction resistance.[8,19] However, this single static EIS analysis at discharged state is unrepresentative and not strong enough to explain the increased behavior for the entire cycle life of the battery.

To further point out the enhanced reaction kinetics in different electrochemistry reaction depth, in situ EIS tests of S@Ni$_2$P/PrGO and S@Ni$_2$P/rGO during charge and discharge process are demonstrated in Figure 4. Typically, all the EIS tests are be operated during the cycling process of the batteries without break. To minimize the influence on the cycling process and to maximize the distinction of the charge transfer resistance, the EIS tests were operated under the high frequency zone over 100 Hz with the same break period, and low C rate at 0.1C for the batteries. Figure 4a,b,d,e are four clusters of in situ Nyquist plots in different reaction depth under charge and discharge process of S@Ni$_2$P/PrGO and S@Ni$_2$P/rGO. Each EIS plots can be recognized as semicircle which the beginning on Z' axe can be marked as the internal resistance ($R_u$) of the battery, and the diameter of the semicircle can be regarded as the charge transfer resistance ($R_{ct}$). By extract the data of $R_u$ and $R_{ct}$ with real-time charge/discharge profile, Figure 4c,f illustrate the changing of $R_u$ and $R_{ct}$ in different reaction step. By comparing with two profiles, the $R_u$ of two electrodes have similar changing tendency by increasing at beginning and decreasing in the end. That means the medium-chain polysulfides (Li$_2$S$_4$, Li$_2$S$_6$) has low conductivity by comparing with short-chain polysulfides (Li$_2$S, Li$_2$S$_2$) and long-chain polysulfides (Li$_2$S$_8$, S$_8$). The charge transfer resistance of two electrodes is quite different. Obviously, the $R_{ct}$ of the S@Ni$_2$P/PrGO is much smaller than the S@Ni$_2$P/rGO all the time. That means S@Ni$_2$P/PrGO have higher reaction ability than S@Ni$_2$P/rGO. Also by focus on the in situ changing profile of the $R_{ct}$ of S@Ni$_2$P/PrGO, it can be recognized that the reaction of medium-chain polysulfides is the biggest puzzle than another form of polysulfides due to its highest charge transfer resistance. That gives us another sight by enhancing the reaction kinetics of the medium polysulfides, which might the crucial importance to further develop new catalytic material and new structure. All in all, the in situ EIS test of two electrodes shows that the enhancement of the electrochemical behavior is attributed by the enhanced of the charge transferability. By thinking about the preparation procedure, these behavior changes might cause by the different linkage between polar material and nonpolar substrate during high temperature anneal process with the change of the atmosphere.

To get further knowledge of the linkage between Ni$_2$P nanoparticle and graphene sheets, the XPS test is necessary to gain the inside view of the host material, of which we could find out the connection between different chemical bound and electrochemical behavior. For this paper, we do test the Ni$_2$P/PrGO, Ni$_2$P/rGO as comparison sample and PrGO as a blank sample. The preparation of PrGO as a blank sample demonstrate in the experiment section. The XPS board scan spectrum of S@Ni$_2$P/PrGO is illustrating in Figure 5a with obvious C, O, Ni, P elements peak. To get the precise analysis, all the XPS data are revised by the main carbon 1s peak with a binding energy of 284.8 eV. As Figure S13 in the Supporting Information demonstrating, except the carbon 1s peaks of 284.8 eV, all the carbon peaks could be separated as another two part of peaks of about 286.0 and 288.3 eV, which consist with C–O bound and C = O group.[17b,20]
The oxygen binding energy is much meaningful. Figure 5b demonstrates the fitting peaks of three samples. All samples could be recognized as two peaks at about 531.5 and 533.3 eV, which correspond to C=O and C—O bound respectively. However, not like Ni2P/rGO, the PrGO and Ni2P/PrGO are all fitted with an unrecognized peak at about 532 eV which consist the binding energy of P—O.[21] The peak details are demonstrated in Table S2 in the Supporting Information. The top of P—O binding energy of Ni2P/PrGO is also much higher than PrGO significantly. The upper result clearly demonstrates the chemical linkage between P element and reduced graphene oxide which form P—O bound to reinforce the contact relationship between two different species of Ni2P and rGO. By thinking the same C—O binding energy at 533.25 eV of Ni2P/PrGO and Ni2P/PrGO, the Ni2P/PrGO shows unique C = O—P chemical bond which speed up the electron transfer between polar and nonpolar material.

Figure 5c,d shows the P peak and Ni peak of Ni2P/PrGO and Ni2P/rGO with blank Ni2P as the comparison. The Ni 2p peaks of Ni2P/PrGO and Ni2P/rGO confirm that the binding energy got redshift (Table S3, Supporting Information). The opposite result also is pointed out by P 2p peak (Table S3, Supporting Information). The XPS spectrum of P 2p has been identified as three parts of peaks which are relevant with P 2p3/2, 2p1/2 and P—O bond. The P binding energy of Ni2P/rGO has no difference with pure Ni2P reference, which means the Ni2P nanoparticles on Ni2P/rGO maintain its original electron state. However, all the peaks of Ni2P/PrGO shows blueshift which confirm the P element states has been changed due to the different thermal treatments. Also the Ni2P/PrGO shows higher P—O bound areal than Ni2P/rGO which demonstrates the increasing of the P—O connection. The upper result confirms that due to the linkage between the Ni2P and the graphene, the electronic state of Ni2P has been changed. Based on the upper result, we theoretical contribute the good performance from the different treating process from Ni-precursor/rGO to Ni2P/PrGO. The high-temperature phosphating reaction under 600 °C gives precursor another opportunity to form a linkage of P—O bound by the reduction of PH3. Then the Ni2P nanoparticle could be anchored onto the graphene sheet by comparing with weak interaction of Ni2P/rGO (Figure 5e). Considering the special chemical bond structure test by XPS analysis, we consider that the enhancement of charge process should be attributed by the intense reaction kinetics while Ni2P nanoparticle anchoring on graphene sheet with P—O bond (Ni2P/PrGO) compared with simple composite structure (Ni2P/rGO). Such bond gets close electric contact between polar material (Ni2P) to a nonpolar conductive material (graphene), which enhance the electron conductivity from two part of materials and finally reveal the enhancement of the electrochemical performance by strength the reaction ability.

It should be pointed out that although the excellent performance of S@Ni2P/PrGO coin-type cell has already been gained, our materials displayed an outstanding capacity and lifespan in large-scale test. The Al-plastic film soft package battery of S@Ni2P/PrGO cathode with lithium foil as anode was assembled (Figure 6a; for fabrication details see Experimental Section in Supporting Information). Figure 6a displays the cycling...
performance of the soft package Li–S battery at 0.15C between 1.6 and 3.0 V. For initial, it exhibits a discharge capacity of 24.3 mAh with corresponding specific capacity of 1109 mAh g⁻¹ (based on sulfur mass). After 150 cycles, the reversible capacity of the battery is still as high as 174 mAh with the low capacity decay ratio of 0.19%. Figure 6b shows the discharge/charge profiles of the soft package Li–S battery at the 100th cycle. Two couple reaction plateaus can be clearly observed, which has dramatically distinguished two reaction step of soft package Li–S battery. Such lower potential difference of 36 mV and 106 mV for different reaction step demonstrate higher reaction activity of this type of cathode material. Furthermore, the distinguishable length ratio of two plateau of soft package Li–S battery is 1:2.59, which is much approach the theoretical value (1:3). By comparing with peer’s work (Table S4, Supporting Information), this value demonstrates that such high reversible process and deepened reaction depth are strengthened during charge/discharge process. The contribution ratios of capacity in different reaction depth are given in the inset of Figure 6b. Considering the relatively enlarged scale effect of from coin-type cell to soft package battery, such electrochemical behavior would be considered to be excellent.

3. Conclusion

In summary, we find out that there are some principles on the design of hybrid host material to touch better electrochemical behavior. The linkage state between polar material and non-polar host should be connected in good to meet the fast charge transfer requirement. By this special connection, the enhanced reaction activity of the host material and decreased reaction barrier can meet faster reaction speed. For this example, the Ni₂P/PrGO material shows enhanced specific capacity of 1254.6 mAh g⁻¹ than Ni₂P/rGO at 0.2C. The soft pack battery also shows good lifespan over 150 cycles with 0.19% capacity drop for each cycle. The pack shows an even and electrochemical activity improved reaction plateau (ΔE = 106 and 36 mV for two plateau) both charge and discharge process. These designs are important for most of the hybrid host materials cause by the multiple reaction dynamic and its real reaction place for polysulfides. The in situ EIS tests further show the tough period for lithium–sulfur battery is during the reaction of medium-chain polysulfides, which is important to touch higher reaction depth and reversible energy density. By contribute with the special linkage state, in situ EIS test confirm that the improved chemical bond connection between polar material and non-polar material has dramatically drop the charge transfer resistance. Such special catalyst and designed linkage state of host materials need to be considered to touch higher requirement of these reaction dynamic needs. And further theoretical calculation for these low activated polysulfides are necessary for further study and design.

4. Experimental Section

Materials: Ni(NO₃)₂·6H₂O, methenamine, Hexamethylenetetramine, sulfur was purchased from Aladdin Ltd (Shanghai, China). Concentrated H₂SO₄, KMnO₄, NaNO₃, graphite, HCl, H₂O₂ were bought from Kermel Chemical Corporation (Tianjin, China). Ethanol was purchased from the Tianjin Chemical Corporation. All chemicals were used as received without further purification. The water use throughout all experiments was purified through a Millipore system (18.25 MΩ).

Synthesis of GO Solution: GO was synthesized according to the modified Hummer’s method.[21] In an Erlenmeyer flask placed in an ice bath with 3 g nature flake graphite, 300 mesh, with 99% metals basis and 1.5 g NaNO₃ was mixed under stirring in 100 mL concentrated H₂SO₄. 12 g KMnO₄ was added very slowly and cooling was continued for 2 h after addition. The solution was then heated in a water bath to 35 °C for the 30 min. After heating, the solution was added followed by slow addition of 25 mL 30% H₂O₂. The precipitate was isolated by centrifugation, washed with 0.1 M H₂SO₄ and then washed four times with 1 M HCl. And then the GO solution was transferred in a dialysis bag and wash for two weeks. After then, the GO solution was transferred to a glass bottle. The concentration of prepared GO solution was about 1.5 mg mL⁻¹.

Synthesis of Ni₂P/PrGO: Ni₂P/PrGO was synthesized by simple hydrothermal reaction, freeze drying and phosphorization processes step-by-step:

a. Stand-by Ni-HMT solution: First, 1.45 g Ni(NO₃)₂·6H₂O, 1.4 g Hexamethylenetetramine (HMT) and following 10 mL distilled water was added into a 20 mL beaker. After stirring for 20 min, the uniformed solution was transferred into a glass bottle and sealed tightly named Ni-HMT.
b. Ni-precursor/rGO: 10 mg Sodium Dodecyl Sulfonate (SDS) was slowly added into a 40 mL Teflon container pre-filled with stirred 30 mL GO solution of 1.5 mg mL⁻¹. After stirring for 10 min, 0.2 mL Ni-HMT was added into the GO solution drop-by drop. After stirring for another 10 min, the container was then transferred to a stainless-steel autoclave and kept in an electric oven at 180 °C for 12 h. After cooling to room temperature naturally, the precipitate was separated by filtration, washed several times with distilled water and frozen by liquid nitrogen. To prevent it aggregation, the frozen Ni-precursor/rGO was put into a freeze dryer for two days.

c. NiP/rGO: To obtain the NiP/rGO, the as-obtained Ni-precursor/rGO was then annealed at 300 °C in PH₃/Ar gas flow for 2 h. After that, the temperature of furnace increases to 600 °C with a heating rate of 10 °C min⁻¹ and keep it another 2 h to further reform the structure and crystal texture. After that, the furnace naturally cooled to ambient temperature. For NiP/rGO, the same anneal process was used, but without PH₃ flow at high-temperature part over 350 °C.

d. PrGO: To get the blank PrGO sample for XPS analysis, the GO solution was sealed into a stainless-steel autoclave and kept in an electric oven at 180 °C for 12 h. After cooling to room temperature, the product been put into a freeze dryer until its fully dried. The phosphorization process was the same with the preparation of the NiP/rGO.

**Synthesis of S@NiP/PrGO: **Thermal diffusion method was used to fabricate the S@NiP/PrGO composite. The as-prepared NiP/PrGO and sulfur were ground together, heated to 160 °C in a sealed reactor, and keep there for 24 h to facilitate sulfur diffusion into the host structure.

**Characterization: **Phase analysis was obtained by powder X-ray diffraction which was operated by a X-ray diffractometer (Panalytical X’pert pro) as Cu Kα X-ray radiation (λ = 1.5418 Å). The model of field-emission electron microscopy was Hitachi SU8010. The working voltage was 15 kV. The transmission electron microscopy was operated on a Tecnai G2 F30, working voltage of 200 kV. The model for nitrogen adsorption isotherm test was Micromeritics ASAP 2020 adsorption analyzer at 77 K. The sample was thermal pre-treated at 150 °C for 6 h. The thermogravimetric analyses (TGA) was processed via Linseis STAPT 1600 at stabled N2 flow. The heating rate was 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was performed at room temperature to analyze the electrode and contents of element.

**Assemble of Soft Package Li–S Battery: **For the fabrication of soft package Li–S battery: first, the cathode with the suitable length was spread on a glass plate; then the twice length separator membrane was folded in double and cover the cathode; third the lithium foil was injected with suitable amount of electrolyte and sealed in vacuum. The total mass of the assembled soft package Li–S battery was 4.41 g.

**Electrochemical Measurement: **All the electrochemical test were based on a coin-type (CR 2025) cell. The prepared S@NiP/PrGO was first mixed with Super P and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The weight ratio for homogeneous slurry was 8:1:1. The slurry coating on the Al foil was processed by coaters which control slit within 100 and 300 um. The coated electrode were dried in oven at 60 °C for 12 h and further vacuum it for another 12 h to remove the solvent and moisture. The cells were assembled with the sulfur electrode as the working electrode, the metallic lithium plate as counter electrode. The separator was a trilayer polypropylene-polyethylene-polypropylene (PP/PE/PP) membrane (Celgard 2300). The electrolyte was 1 mol L⁻¹ lithium bis(trifluoromethanesulfonimide)ilide (LiTFSI) in 1,3-dioxolane (DOL) and dimethoxy methane (DME) (1:1 in volume) with 2 wt% LiNO₃ as an additive. The testing cells assembly was operated in a glovebox which protected under pure Argon atmosphere. The oxygen and moisture for the glovebox was controlled under 0.5 ppm. The cyclic voltammetry was tested on a CHI 710e electrochemical works station which manufactured by CH Instruments Inc., Shanghai. The scanning potential between 1.6 and 3.0 V at scanning rate of 0.1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) test was tested on PARSTAT 2273 which was manufactured by Princeton Applied Research, USA. The testing frequency range was 1 MHz–1 Hz. The galvanostatic charge-discharge test were operated at a Neware battery-testing system. The current were calculated by different C rate in need.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was funded by the Bryden Centre project and China Scholarship Council (CSC) for providing a scholarship at the Queen’s University Belfast. The Bryden Centre (Project ID VA5048) was supported by the European Union’s INTERREG VA Programmed, managed by the Special EU Programmed Body (SEUPB). The authors thank for the soft pack battery assembling help by Rui Guo in Shanghai space power research institute. The views and opinions expressed in this paper do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB).

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

binding structure, electrochemical reaction kinetics, graphene, lithium–sulfur battery, Ni₃P

Received: November 3, 2021
Revised: January 12, 2022
Published online: February 24, 2022
