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The Research Grants Council of Hong Kong
NSFC/RGC Joint Research Scheme
Joint Completion Report

(Please attach a copy of the completion report submitted to the NSFC by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Preparation of High Performance Cathodes for Li-S Batteries and Their Property and Mechanism Study: Enhancement of Electron and Lithium Ion Transmission and Anchoring of Polysulfides

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Guohua CHEN (Prof.)	Yuanfu DENG (Prof.)
Post	Chair Professor	Professor
Unit / Department / Institution	Mechanical Engineering/ The Hong Kong Polytechnic University	Chemistry and Chemical Engineering/ South China University of Technology
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Co-investigator(s) *(with title and institution)*	N.A.	N.A.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	1 Jan 2017		
Project Completion date	31 Dec 2020		
Duration *(in month)*	48		
Deadline for Submission of Completion Report	31 Dec 2021		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. Prepare hetero-atom(s) doped carbons (HCs) with micro- and meso-pores to enhance the conductivity and lithium ion (Li+) transmission and to anchor sulfur/polysulfides for S/HCs cathode materials during the discharge/charge cycles;
2. Modify S/HCs cathode materials by lithium ion conductor (LIC) coating for further enhancement of Li+ transmission, adsorption and anchoring of sulfur/ polysulfides of the cathode materials;
3. Investigate the diffusion of intermediate products, interface structure and phase transformation of S/HCs@LIC during cycling by simulation, in-situ/ex-situ physicochemical and electrochemical characterizations, and reveal the mechanism of polysulfide anchoring;
4. Fabricate the large-capacity prototype Li-S batteries using S/HCs@LIC cathode materials, and investigate the impacts of the particle size of S/HCs@LIC's, electrode compositions (S/HCs@LIC, conductor, binder and additives), polysulfide absorbents and fabrication process on the porous structure and interface properties of the as-prepared electrodes, the electron and Li+ transfer, and electrochemical performance of the batteries;
5. Fabricate S/HCs@LIC cathode materials with a specific capacity of $\geq$ 1000 mAh g^{-1} based on S mass (700 mAh g^{-1} based on S/HCs@LIC mass) and a capacity retention ratio of over 80% after 1000 cycles at 1 C rate (1600 mA g^{-1}), and provide electrodes based on S/HCs@LIC active material for practical applications of Li-S batteries.

5.2 Revised Objectives

N.A.

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

A dual function cathode consisting of WS_2 and porous carbon nanosheets was synthesized. The composite depicted very strong affinity toward lithium polysulfides with rapid transport of lithium ions. The cathode demonstrated excellent cycling stability and rate capability by delivering a reversible specific capacity of 419mAh/g at 8C after 500 cycles with low capacity fading at 0.04% per cycle. At high sulfur loading of 4.7mg/cm^2 , it delivered 3.4 mAh/cm^2 areal capacity after 100 cycles at 0.5C. The synergistic effect of strong chemical interaction between lithium polysulfides and WS_2, and the superior electronic conductivity of carbon nanosheets are found responsible. The EIS analysis shows that even after 400 cycles, the interfacial and charge transfer resistances only increased by 1.2 and 1.7Ω, respectively, describing faster electrochemical kinetics by inhibiting the formation of insulating layer of lithium sulfide (Li_2S). Impressively, the electrode has a low decay rate of 0.048% per cycle over 1000 cycles at 1 C current rate. (Majumdar et al., 2019 - JES). An intrinsically polar MoS_2 /g-C_3N_4 was also designed as the sulfur host. The strong chemical interaction of lithium polysulfides with MoS_2 and nitrogen rich g-C_3N_4 restrict the shuttling effect of polysulfides, showing comparable performance to that of WS_2/C. (Majumder et al., 2019, -JPS)

A nitrogen doped porous carbon polyhedron coupled with a well distributed α-CoS/Co heterostructure mediator was designed and prepared. It exhibits high sulfur utilization with a 1611.4 mAh/g first discharge capacity and a low decay rate of 0.042% per cycle at 0.5 C for over 800 cycles. The interaction between polysulfide and the cathode surface was investigated using density functional theory (DFT) calculations. It is found that α-CoS in the heterostructure has a strong adsorption with soluble polysulfides, and Co metal particles facilitate the fast conversion of polysulfides. (Gu et al., 2019)

Three nitrogen-doped porous carbons (NDPCs) with the ultrahigh specific surface areas were prepared via a one-step activation of the biomass waste. The higher volume ratio of marco-mesopores to micropores of the substrate can greatly enhance the rate capability of the S/NDPC cathodes, due to the improved electrolyte penetration. Meanwhile, the higher nitrogen content of the NDPC improved the cycle stability of the S/NDPC cathode. It exhibits specific capacities of 926.1 and 815.8 mAh/g at 0.5 and 1.0 C rate, respectively, with a capacity fading rate of only 0.067% per cycle after 500 cycles at 1.0 C. (Wang et al., 2019)

Commercial separator was modified with different functional materials to improve the performance of the Li-S batteries by using $Co(OH)_2$@CNF/KB (Yang et al. 2018), carbon nanofiber/CoS/Ketjen black (Yang et al., 2019- CEJ), carbonized polydopamine (C-PDA)-coated hollow carbon nanofibers (CNFs) with TiO_2 nanoparticles (Yang et al., 2019 EA), nitrogen-enriched hierarchical porous carbon (Wang et al., 2020) or crosslinked triazine frameworks (Zhu et al., 2021).

For the anode part, 2D porphyrin paddle-wheel frameworks-3 (PPF-3) microsheets were designed as a scaffold for uniform Li deposition. (Liu et al., 2021). A conducting and flexible polymer EDOT-PDMS was synthesized to improve the cycling performance of high-capacity Si anode with very good results obtained (Wang et al., 2021). TiO_2 nanorods with the controlled phase compositions were prepared for anode of LIBs (Gao et al., 2018).

Li-S pouch cell has been fabricated in collaboration with a spin-off company of the PI with capacity of 400 mAh and estimated energy density of >350 Wh/kg and redox cycling stability of over 200 cycles with coulombic efficiency>99%. One patent is under preparation.

The prepared functionalized porous carbon was found to be good materials for the fabrication of supercapacitors with five high quality papers published as some extra related research outputs, as seen in Zou et al., (2018; 2019; 2020); Tan et al., (2020), Huang et al., (2020).

Potential for further development of the research and the proposed course of action *(maximum half a page)*

For Li-S battery to be commercialized, the problems regarding the shuttle effect from the cathode part has sufficient approaches to solve it. As shown in the present study, various porous carbons with functionalized surface and the modified separator can provide very satisfactory results. However, in order for the potential of Li-S to be fully realized, the stable operation of Li metal anode remains a question to be answered. This is an internationally challenging problem. The PI has been trying to build different Cu current collectors, or to modify the surface of the Li metal foil to improve the performance of Li metal anode through the suppression of dendrite formation, or avoiding the penetration of the separator by the dendrites formed. However, there are much more to be done in terms of materials synthesis, mechanistic understanding of the deposition and stripping of Li during charging/discharging, and especially the large-scale operation with not highly excess Li supply and lean electrolyte, in order to have high energy density. Another hot research area related to Li-S is the solid or semi-solid (gel) electrolyte utilization. It requires high Li^+ conducting materials at room temperature with very good interfacial adherence with cathode and anode.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

Lithium-sulfur battery has the advantage of high energy density and low cost. It has not been commercialized because of the short service life problem caused by sulfur cathode as well as Li metal anode. For the former, the polysulfides formed during discharge can dissolve in liquid electrolyte and diffuse to anode side without going through the necessary redox reaction. For the latter, the formation of Li dendrite remains a problem. This research focused on solving the problems at the cathode by developing porous carbon to anchor the lithium polysulfides. Different chemicals were embedded on the surface of the porous carbon to enhance the interaction between the surface and polysulfides such as N, CoS, WS_2. The porous carbon can be derived from carbon containing chemicals or pyrolysed biomass. Physical, chemical and electrochemical analysis reveal the mechanism for the improvement. The porous carbon can be a good host for sulphur cathode with excellent energy density obtained, well over two times of the currently available lithium ion batteries. Li-S pouch cell made to provide about 400 Wh/kg energy with reasonable stability with the modified commercial separator. With the improvement of Li metal anode, the commercialization of Li-S battery is possible in near future.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s) ***(bold** the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	Title and Journal/Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*					
2018				Yang, YB; Zhang, LT ; Xu, H ; Qin, XS ; Deng, YF*; Chen, GH*,	Net-Structured Filter of $Co(OH)_2$-Anchored Carbon Nanofibers with Ketjen Black for High Performance Li-S Batteries, ACS SUSTAINABLE CHEMISTRY & ENGINEERING, 6(12) (2018)17099-17107	2018	https://pubs.acs.org/doi/full/10.1021/acsusche meng.8b04468	Yes
2018				Zou, K.X. ; Deng, Y.F.*; Chen, J.P;.; Qian, Y.X.; Wang, Y.W.; Li, Y.W.; Chen, G.H.	Hierarchically porous nitrogen-doped carbon derived from the activation of agriculture waste by potassium hydroxide and urea for high performance supercapacitors Journal of Power Sources 378 (2018) 579–588 DOI: 10.1016/j.jpowsour.2017.12.081	2018	https://www.sciencedirect.com/science/article/pii/S0378775317316890?via%3Dihub	Yes

2018				Man Gao, Yubo Bao, Yunxian Qian*, Yuanfu Deng*, Yingwei Li, and Guohua Chen	Porous Anatase-TiO2(B) Dual-Phase Nanorods Prepared from in Situ Pyrolysis of a Single Molecule Precursor Offer High Performance Lithium-Ion Storage Inorganic Chemistry 57 (2018) 12245−12254 DOI: 10.1021/acs.inorgchem.8b01948	2018	https://pubs.acs.org/doi/10.1021/acs.inorgchem.8b01948	Yes
2019				Zou, K.X. ; Tan, H.Q.; Wang, L.M.; Qian, Y.X.*; Deng, Y.F.*; Chen, G.H.	Biomass waste-derived nitrogen-rich hierarchical porous carbon offering superior capacitive behavior in an environmentally friendly aqueous $MgSO_4$ electrolyte, Journal of Colloid and Interface Science 537 (2019) 475–485 DOI: 10.1016/j.jcis.2018.11.050	2018	https://www.sciencedirect.com/science/article/pii/S0021979718313364X?via%3Dihub	Yes

2019				Wang, S.X.; Zou, K.X.; Qian, Y.X.; Deng, Y.F.*; Zhang L.; Chen, G.H.	Insight to the synergistic effect of N-doping level and pore structure on improving the electrochemical performance of sulfur/N-doped porous carbon cathode for Li-S batteries Carbon 144 (2019) 745-755 doi.org/10.1016/j.carbon.2018.12.113	2018	https://www.sciencedirect.com/science/article/pii/S0008622318312533?via%3Dihub	Yes
2019				Yang, YB ; Xu, H.; Wang, S.X.; Deng, Y.F.*; Qin, X.Y.; Qin, X.S.; Chen, G.H.*	N-doped carbon-coated hollow carbon nanofibers with interspersed TiO2 for integrated separator of Li-S batteries, ELECTROCHIMICA ACTA 297(2019) 641-649 DOI: 10.1016/j.electacta.2018.12.009	2018	https://www.sciencedirect.com/science/article/pii/S0013468618327075	Yes
2019				Majumder, S.; Shao, M.H.; Deng, Y.F.; Chen, G.H.*	Two Dimensional WS2/C Nanosheets as a Polysulfides Immobilizer for High Performance Lithium-Sulfur Batteries, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 166 (2019) A5386-A5395 DOI: 10.1149/2.0501903jes	2018	http://jes.ecsdl.org/content/166/3/A5386.full.pdf	Yes

2019				Gu, S.; Bai, Z.W.; Majumder, S; Huang, B.L. and Chen, GH*	In Situ Grown α-CoS/Co Heterostructrue on Nitrogen Doped Carbon Polyhedron Enabling Trapping and Catalysis of Polysulfides as Cathode towards High Performance Lithium Sulfur Battery, Nanoscale, 43(2019)20579-20588, doi.org/10.1039/C9NR07249G		https://pubs.rsc.org/en/content/articlelanding/2019/NR/C9NR07249G#!divAbstract	Yes
2019				Yang, YB; Wang, S.X., Zhang, L.T., Deng, YF*; Xu, H., Qin, X.S. and Chen, GH*	CoS-interposed and Ketjen black-embedded carbon nanofiber framework as a separator modulation for high performance Li-S batteries, Chemical Engineering Journal, 2019, 369(2019) 77-86. **DOI:** 10.1016/j.cej.2019.03.034		https://www.sciencedirect.com/science/article/pii/S1385894719304991	Yes
2019				Majumder, S; Shao, MH; Deng, YF; Chen, GH,	Ultrathin Sheets of MoS2/ g-C3N4 Composite as a Good Hosting Material of Sulfur for Lithium-Sulfur Batteries, Journal of Power Sources, 431(2019)93-104, doi.org/ 10.1016/j.jpowsour.2019.05.045		https://www.sciencedirect.com/science/article/pii/S0378775319306032?via%3Dihub	Yes

2020				Wang, S., Liu, X., Zou, K., Deng, Y.F.*, Chen, G.H.	Toward a practical Li-S battery enabled by synergistic confinement of a nitrogen-enriched porous carbon as a multifunctional interlayer and sulfur-host material, Journal of Electro-analytical Chemistry, 858 (2020) Article number 113797, DOI: 10.1016/j.jelechem.2019.113797		https://www.sciencedirect.com/science/article/pii/S1572665719310653	Yes
2020				Tan, HQ; Huang, H ; Guan, ZX ; Qian, YX ; Deng, YF* ; Chen, GH	Understanding of the effect of nitrogen-doping level and micropore volume ratio on the capacitive performance of N,S-codoped hierarchically porous carbon, ELECTROCHIMICA ACTA, 354(2020), Article Number: 136639, DOI: 10.1016/j.electacta.2020.136639		https://www.sciencedirect.com/science/article/pii/S0013468620310 32X	Yes
2020				Zou, KX; Guan, ZX; Deng, YF*; Chen, G.H.,	Nitrogen-rich porous carbon in ultra-high yield derived from activation of biomass waste by a novel eutectic salt for high performance Li-ion capacitors, Carbon, 161 (2020) 25-35; DOI: 10.1016/j.carbon.2020.01.045		https://www.sciencedirect.com/science/article/pii/S0008622320300452	Yes

2020				Huang, H; Tan, HQ; Zou, KX; Deng, YF*; Chen, G.H.,	An environmentally friendly strategy to prepare nitrogen-rich hierarchical porous carbon for high-performance supercapacitors, Chemical Communications, 56 (2020) 2182-2185; DOI: 10.1039/c9cc08854g		https://pubs.rsc.org/en/content/articlepdf/2020/cc/c9cc08854g	Yes
2021			✔	Yanan Zhu, Yuanfu Deng and Guohua Chen*	Highly crinkled and inter-connected nitrogen, oxygen and sulfur co-doped carbon nanosheets modified separator for improved lithium-sulfur batteries, *For Journal of Materials Chemistry A*		Yes	Yes
2021			✔	Yutong Liu, Junye Cheng, Qiang Liu, Yuanfu Deng and Guohua Chen*	Metal organic framework microsheets scaffold for stable lithium metal anode, *For Chemical Comm*		Yes	Yes
2021			✔	Jingwei Wang, Shenhua Song*, Yuanfu Deng and Guohua Chen*	Conductive and flexible coating of Si nanoparticles for the anode in Li-ion batteries *For Journal of Materials Chemistry A*		Yes	Yes

9. Recognized international conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*
August/2017 /HK	Two Dimensional MoS2/C composite as a potential cathode material for Lithium-sulfur batteries	The 17th Congress of Asian-Pacific Confederation of Chemical Engineering	2018	Yes	Yes
August/2017 /HK	CoS-interposed and Ketjen Black-Embedded Carbon Nanofiber Framework as a Separator Modulation in Li-S Batteries	The 17th Congress of Asian-Pacific Confederation of Chemical Engineering	2018	Yes	Yes
June/2018/ Seattle	Ultrathin Sheets of MoS_2/g-C_3N_4 Composite as a Promising Cathode Hosting Material of Sulphur for Lithium-Sulphur Batteries with Long Cycle Life and High Rate Capability	The 229 ECS Meeting	2018	Yes	Yes
June/2018/ Kyoto	Two Dimensional WS_2/C Nanosheets as a Polysulphide Immobilizer for High Performance Lithium-Sulphur Batteries	The 19th International Meeting on Lithium Batteries	2018	Yes	Yes

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Yuebin Yang	PhD	September 1, 2014	August, 2017
Qing Li	MPhil	September 1, 2016	August, 2017
Soumyadip Majumder	PhD	September 1, 2015	August, 2019
Yutong Liu	MPhil	September 1, 2017	August, 2020
Jingwei Wang	PhD	September 1, 2018	December, 2020

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

The PI received the following recognitions:

- Merit Award of Research, Faculty of Engineering, HKPolyU 2020
- Top 100 Most Influential Materialists in China 2019
- Alumnus of the Year, Dalian University of Technology 2019
- Endowed Otto Poon Charitable Professor 2019

During this period of time, the PI also received following related research grants award:

Project Title and Duration	**Grant Source**	**Amount HKD**
Power-based high value and smart energy system for drones (2021-2022)	GD STC	1,100,000
Investigation and Preparation of Long Cycle Life and Intrinsic Safe Lithium-Sulfur Batteries (2019-2021)	GD STC	3,888,889
高性能锂硫电池体系与关键材料研究 Research on High-performance Lithium-sulfur Battery System and Key Materials (2019-2021)	Shenzhen STIC	3,341,400
Advanced Electrode Materials for High Performance Electrochemical Batteries (2020-2022)	HK Scholar	378,000
Large-size Lithiophilic Two-dimensional Metal Organic Frameworks on a Current Collector to Stabilize Lithium Deposition for Lithium Metal Batteries (2019-2021)	PolyU Postdoc	766,000

Notably, the project "Investigation and Preparation of Long Cycle Life and Intrinsic Safe Lithium-Sulfur Batteries (2019-2021)" is part of a 25 million RMB project funded by GD STC for a demonstration of Li-S powered EV with the indigenous technologies. The Co-I of this project is also a partner of this project.

12. Statistics on Research Outputs *(Please ensure the summary statistics below are consistent with the information presented in other parts of this report.)*

	Peer-reviewed journal publications	Conference papers	Scholarly books, monographs and chapters	Patents awarded	Other research outputs (Please specify)
No. of outputs arising directly from this research project [or conference]	17	4	0	0	0