RGC Ref. No.:
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(please insert ref. above)

RESEARCH GRANTS COUNCIL
COMPETITIVE RESEARCH FUNDING SCHEMES FOR THE LOCAL SELF-FINANCING DEGREE SECTOR

FACULTY DEVELOPMENT SCHEME (FDS)

Completion Report
(for completed projects only)

Submission Deadlines:	*1. Auditor's report with unspent balance, if any: within **six** months of the approved project completion date.* *2. Completion report: within **12** months of the approved project completion date.*

Part A: The Project and Investigator(s)

1. Project Title

Development of fluorinated Si/C composites with porous and micro/-nanoarchitectures for advanced lithium ion batteries

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

Research Team	Name / Post	Unit / Department / Institution
Principal Investigator	Lu Xiaoying/Assistant Professor	Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong
Co-Investigator(s)	Denis, Yu Yau Wai/ Associate Professor David, Lou Xiong Wen/Professor	School of Energy and Environment, City University of Hong Kong School of Chemical and Biomedical Engineering, Nanyang Technological University
Others	Prof. Michael K.H. Leung/Professor Dr. Yuanyuan Tang/Assistant Professor	School of Energy and Environment, City University of Hong Kong School of Environmental Science and Engineering, Southern University of Science and Technology

3. Project Duration

	Original	**Revised**	**Date of RGC / Institution Approval** *(must be quoted)*
Project Start Date	2017/01/01	N.A.	N.A.
Project Completion Date	2018/12/31	2019/06/30	2018/10/02 (by Institution)
Duration *(in month)*	24 months	30 months	2018/10/02
Deadline for Submission of Completion Report	2019/12/31	2020/06/30	2018/10/02

Part B: The Final Report

5. Project Objectives

5.1 Objectives as per original application

1. To develop fluorinated Si/C composites with porous and micro-/nanoarchitectures by nano-bubble-assisted templates followed by spray-pyrolysis to produce a designed structure;
2. To characterize and optimize the physical properties of fluorinated Si/C composites to achieve high areal capacity, excellent rate capability and a long life cycle;
3. To gain fundamental understandings of the relationship between physical and electrochemical properties;
4. To transfer the knowledge gained in this research to undergraduates by developing teaching materials and Final Year Project (FYP) topics.

5.2 Revised objectives

Date of approval from the RGC: N.A.

Reasons for the change: N.A.

1.

2.

3. ....

5.3 Realisation of the objectives
(Maximum 1 page; please state how and to what extent the project objectives have been achieved; give reasons for under-achievements and outline attempts to overcome problems, if any)

All the objectives proposed in this project are achieved with the below explanations.

For objective 1, fluorinated Si/C composites with porous and micro-/nanoarchitectures were synthesized by electrospraying of polyvinylidene difluoride (PVDF) and silicon particles, followed by chemical stabilization and pyrolysis processes. To achieve the desirable micro/nanostructures, we found that proper treatment of Si/PVDF precursors with tetrabutylammonium bromide (TBAB) played crucial roles in maintaining the unique micro-/nanoarchitectures during pyrolysis treatment. Material morphological analysis indicated that particle size of Si was estimated to be ~100 nm and carbon fibers was about micron-scale in length. The control experiment also suggested that micro-/nanoarchitectures could be collapsed by high temperature pyrolysis, if no chemical stabilization treatment of PVDF/Si precursor was applied. For achieving porous structure, due to the pyrolysis treatment in nitrogen atmosphere, PVDF polymer was completely decomposed into carbonaceous materials and possible HF by-products. The particle size of silicon could be further reduced by the etching reaction between Si and the by-products, which could lead to the formation of porous structure and fluorinated property in Si/C composites. Nitrogen adsorption-desorption experiment at 77K further confirmed that the as-prepared Si/C composites showed a typical Barrett-Joyner-Halenda (BJH) pore size of ~3.8 nm.

For objective 2, in order to understand physical properties of the as-prepared Si/C composites, we employed a series of advanced material characterization techniques including field emission scanning electron microscope (FE-SEM), high resolution transmission electron microscope (HRTEM), powder X-ray diffractometer (XRD), element mapping, X-ray photoelectron spectroscopy (XPS), Raman spectroscope and nitrogen adsorption-desorption isotherm etc. Also, we evaluated electrochemical performance of fluorinated Si/C composites in coin cells by repeated charge-discharge cycles, using battery testers. The applied charge-discharge current density was 1 A g^{-1} for cycling performance test. For rate capability measurement, various current densities were employed to evaluate electrochemical performances of Si/C composite materials. These excellent electrochemical results confirmed that high capacity, excellent rate capability and long-life cycle were achieved with our Si/C composites.

For objective 3, based on the above material characterizations and performance evaluation, we established the relationship between physical and electrochemical properties, from the views of morphologies, microstructure, crystal phases, element distribution, valence states, specific surface area and pore size distributions etc. We found that micro-/nanoarchitectures could significantly enhance electron transport behaviors and improve ion diffusion in electrochemical process.

For objective 4, we developed four final year projects (FYP) for undergraduate students of Technological and Higher Education Institute of Hong Kong (THEi). The FYP topics and undergraduate names are listed as below: preliminary study of silicon-carbon composite anodes for lithium ion batteries (Sin Chung Yin), silicon carbon material development for lithium-ion batteries (Wong Sung) and synthesis of fluorinated silicon/carbon composites with porous and micro/nanostructure for high energy density lithium-ion batteries (Wong King Wai).

5.4 Summary of objectives addressed to date

Objectives *(as per 5.1/5.2 above)*	**Addressed** *(please tick)*	**Percentage Achieved** *(please estimate)*
1. To develop fluorinated Si/C composites with porous and micro-/nanoarchitectures by nano-bubble-assisted templates followed by spray-pyrolysis to produce a designed	✓	100%

structure;		
2. To characterize and optimize the physical properties of fluorinated Si/C composites to achieve high areal capacity, excellent rate capability and a long life cycle;	✓	100%
3. To gain fundamental understandings of the relationship between physical and electrochemical properties;	✓	100%
4. To transfer the knowledge gained in this research to undergraduates by developing teaching materials and Final Year Project (FYP) topics.	✓	100%

6. Research Outcome

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

In this project, we successfully developed a series of high-capacity anode materials with porous and micro-/nanoarchitectures and demonstrated their excellent electrochemical performances for lithium-ion battery applications. Specifically, we synthesized sea urchin-like $NiCo_2O_4$ and found that it could exhibit high reversible capacity of 663 mAh g^{-1} after 100 cycles at a current density of 100 mA g^{-1}. Rate capability measurement indicated that average capacities of 1085, 1048, 926, 642, 261, and 86 mAh g^{-1} could be achieved by varying current densities e.g. 100, 200, 500, 1000, 2000, and 3000 mA g^{-1}, respectively [J1]. In addition, we successfully prepared one dimensional Co_3O_4 nanorods with micro-/nanoarchitectures and electrochemical performance results suggested that an initial discharge capacity of 1343.8 mAh g^{-1} was achieved at a current density of 500 mAh g^{-1} and high capacity retention was achieved with 500 mA g^{-1} for 200 cycles [J2]. Besides that, we further fabricated *calliandra*-like $MnCo_2O_{4.5}$ anode materials with micro/nanostructures and confirmed their superior electrochemical lithium storage performances. For example, excellent specific capacity (e.g. 1301 mAh g^{-1}@500 mA g^{-1}), good cycling performance and rate capability (e.g. 966 mAh g^{-1}@3000 mA g^{-1}) [J3]. We found that micro-/nanoarchitectures could play crucial roles in electrochemical processes. This is because microscale dimension was advantageous for electron transport and nanoscale dimension was favorable for lithium ion diffusion. The details of these high-capacity anodes with porous and micro-/nanoarchitectures were delivered in conferences [C1 and C2]. On the basis of the above findings, we further explored Si/C composites with porous and micro-/nanoarchitectures as anode materials for advanced lithium-ion battery application.

The fluorinated Si/C composites were synthesized by electrospraying of polyvinylidene difluoride (PVDF) and silicon particles, followed by chemical stabilization and pyrolysis processes. The detail of synthesis procedures and findings were also delivered in conferences [C3 and C4]. We optimized synthesis parameters (e.g. Si contents, applied voltage and dosing speed etc.) and found that chemical stabilization process played crucial roles in achieving micro-/nanoarchitectures. Morphological analysis suggested that nanoparticles of ~100 nm was uniformly encapsulated in fibrous carbon to form micro-/nanoarchitecture. Element mapping implied the uniform distribution of silicon, carbon, fluorine, and oxygen atoms in the as-prepared Si/C composites. In addition, nitrogen adsorption-desorption isotherm revealed that BET surface area and BJH pore size of Si/C composites were around 708.6 m^2 g^{-1} and 3.8 nm, respectively. The above physiochemical features could be utilized to explain the electrochemical performances.

To demonstrate potential application in lithium-ion batteries, we conducted battery performance evaluation of Si/C composites in standard coin cells (CR 2032) with a voltage window of 0.005 V~3.0 V *vs.* Li^+/Li. When a current density of 1000 mA g^{-1} was applied to Si/C composite anode materials, a high reversible specific capacity of ~2313 mAh g^{-1} was achieved with 200 charge-discharge cycles. In order to proof the excellent rate capability, high current densities e.g. 0.5, 1, 2, 5, 10 and 20 A g^{-1} were applied to rate capability evaluation, specific capacities were achieved at about 2788, 2108, 1740, 1512, 1371 and 1179 mAh g^{-1}, respectively. The excellent cyclability and rate capability of the as-prepared Si/C composites were attributed to the following features: (1) porous structure could effectively accommodate the volume variation during charge-discharge cycles; (2) micro-/nanoarchitectures could significantly enhance the electron transport and ion diffusion in the electrochemical environment; (3) the presence of fluorine element in Si/C composites could provide good affinity to fluoride-containing electrolyte.

Overall, the major findings were already published in 4 journal papers and presented in 5 conferences. One more journal paper related to Si/C composites will be submitted for publication.

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

Potential for further development of this research is summarized as below:
- The synthesis strategies of anode materials with porous and micro-/nanoarchitectures developed in this project can be applied to other energy storage materials for performance enhancement of electrochemical processes;
- Theoretical knowledge of fluorinated Si/C composites with porous and micro-/nanoarchitectures can be further investigated with *in-situ* electrochemical characterization techniques (e.g. Raman, X-ray diffraction, Fourier-transform infrared spectroscopy etc.) and computational quantum mechanical modelling; and
- The promising results of high-capacity Si/C anode materials can be further extended to investigate the recycling and reuse of silicon-based solar cell panels for development of high-performance energy storage materials.

7. Layman's Summary

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

With the pursuit of high-energy-density and fast-charging lithium-ion batteries, traditional anode materials with a low specific capacity (e.g. 372 mAh g^{-1}) and poor rate capability cannot meet the future technological demands. Thus, developing high-performance anode materials is of paramount importance for the next-generation LIBs. In this project, high-capacity anode materials with porous and micro-/nanoarchitectures, which could deliver at least two times higher specific capacity than graphite anode, was successfully developed by rational structure design for lithium-ion batteries. The crucial treatment, namely chemical stabilization, was identified for realizing micro/nanoarchitecture under thermal treatment. Also, the relationship between battery performance and physicochemical properties was revealed by advanced material characterizations. The unique characteristics such as micro/nanoarchitecture and mesoporous structure could significantly improve electron transport and ion diffusion in the electrochemical environment. Also, electrochemical performance studies in standard coin cell prototypes confirmed the potential applications of high-capacity anode materials for achieving long cycle life and high rate capacity. Overall, this project demonstrated the excellent electrochemical performance of anode materials with unique physiochemical properties for next-generation lithium-ion batteries.

Part C: Research Output

8. Peer-Reviewed Journal Publication(s) Arising Directly From This Research Project

(Please attach a copy of the 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) *(denote the correspond-ing 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 RGC *(Yes or No)*	Accessible from the Institutional Repository *(Yes or No)*
Year of Publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*						
2018	**2018**	**N.A.**	**N.A.**	**Bin Wang, Xiao-Ying Lu*, Chi-Wing Tsang*, Yuanhao Wang, Wai Kuen Au, Hongfan Guo, Yuanyuan Tang**	Charge-driven self-assembly synthesis of straw-sheaf-like Co3O4 with superior cyclability and rate capability for lithium-ion batteries, Chemical Engineering journal, Volume 338, 15 April 2018, Pages 278-286	**2018**	No	Yes	Yes
2019				Bin Wang, Chi-Wing Tsang, Ka Ho Li, Yuanyuan Tang, Yanping Mao, Xiao-Ying Lu	Synthesis of Sea urchin-like $NiCo_2O_4$ via Charge-driven Self-assembly Strategy for High Performance Lithium-ion Batteries, Nanoscale Research Letters, (2019), 14:6	2018	No	Yes	Yes
2019				Bin Wang, Shifeng Wang, Yuanyuan Tang, Yaxiong Ji, Wei Liu, Xiao-Ying Lu	Hydrothermal Synthesis of Mesoporous Co_3O_4 Nanorods as High Capacity Anode Materials for Lithium Ion Batteries, Energy Procedia 158 (2019) 5293-5298.	No	Yes	Yes	Yes
2019				Bin Wang, Shifeng Wang, Yuanyuan Tang, Chi-Wing Tsang,	Micro/ nanostructured $MnCo_2O_{4.5}$ Anodes with High Reversible Capacity and Excellent Rate	No	Yes	Yes	Yes

				Jinchuan Dai, Michael K.H. Leung, Xiao-Ying Lu	Capability for Next Generation Lithium-ion Batteries, Applied Energy, (2019), 252: 113452				
			✓		Synthesis of SiO_x-based Composites with High Specific Capacity, Long Cyclability and Superior Rate Capability for Lithium-ion Batteries	**No**	No	Yes	**N/A**

9. Recognized International Conference(s) In Which Paper(s) Related To This Research Project Was / Were Delivered
(Please attach a copy of each conference abstract)

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 RGC** *(Yes or No)*	**Accessible from the Institutional Repository** *(Yes or No)*
2017 June/Hong Kong Convention and Exhibition Centre	Development of Binary Metal Sea Urchin-Like Structure For Next Generation Lithium-Ion Batteries	International STEM Students' Forum 2017	2018	No	Yes	Yes
08/2018, Hong Kong	Hydrothermal Synthesis of Mesoporous Co_3O_4 Nanorods as High Capacity Anode Materials for Lithium Ion Batteries	The10th International Conference on Applied Energy (ICAE)	2018	No	Yes	Yes
08/2018, Hong Kong	PDDA-mediated Synthesis of Uniform Calliandra-like $MnCo_2O_{4.5}$ Anodes with Micro/nanostructures for Advanced Lithium-ion Batteries	The10th International Conference on Applied Energy (ICAE)	2018	No	Yes	Yes

04/2019, Hong Kong	Development of Si-based Materials Encapsulated in Carbon Fibres as High Capacity Anode for Next Generation Lithium-ion Batteries	International Conference on Applied Education, Technology and Innovation (THEi AETI 2019)	No	Yes	Yes	Yes
05/2019, Bei Jing	Synthesis of Fibrous Si/C Composite Anode Materials with Micro/nanostructures for Advanced Lithium-ion Batteries	2019 4th International Conference on Energy Materials and Applications (ICEMA 2019)	No	Yes	Yes	Yes
06/2019, Hong Kong	High Capacity and Long Cycle Performance of Fluorinated Si/C composite with Micro/nano Architectures for Advanced Lithium-ion Batteries	The 3rd International Conference on Bioresources, Energy, Environment, and Materials Technology 2019 (BEEM 2019)	No	Yes	Yes	Yes

10. Whether Research Experience And New Knowledge Has Been Transferred / Has Contributed To Teaching And Learning
(Please elaborate)

Four Final year project (FYP) topics were developed for undergraduates of Technological and Higher Education Institute of Hong Kong (THEi). Under the supervision of principle investigator, these students could gain basic knowledges of material synthesis, material characterizations, electrochemical experiments, and battery performance analysis etc.

11. 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**
	Environmental Engineering and Management	2014	2017/Graduation (title page submitted to RGC with the 2017 progress report)
	Environmental Engineering and Management	2014	2018/Graduation (title page submitted to RGC with the 2018 progress report)
	Environmental Engineering and Management	2014	2018/Graduation (title page submitted to RGC with the 2018

			progress report)
	Environmental Engineering and Management	2015	2019/undergraduate (title page submitted to RGC with the 2018 progress report)

12. Other Impact

(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, teaching enhancement, etc.)

1. Undergraduate student participated in this project successfully won Best Oral Presentation Award at International Conference on Applied Education, Technology and Innovation (AETI 2019) for his excellent performance in his final year project (FYP).
2. Some of the published journal papers were completed in collaboration with Prof. Michael K.H. Leung from School of Energy and Environment, City University of Hong Kong and Dr. Yuanyuan Tang from School of Environmental Science and Engineering, Southern University of Science and Technology.

1. **Statistics on Research Outputs**

	Peer-reviewed Journal Publications	**Conference Papers**	**Scholarly Books, Monographs and Chapters**	**Patents Awarded**	**Other Research Outputs (please specify)**	
					Type	No.
No. of outputs arising directly from this research project	4	6	0	0	N/A	

2. **Public Access Of Completion Report**
(Please specify the information, if any, that cannot be provided for public access and give the reasons.)

Information that Cannot Be Provided for Public Access	Reasons
Nil	