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(please insert ref. above)

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

Three Dimensional Graphene/Metal Oxide (Sulfide) Composite Nanoarchitectures for Anode Applications in Li-ion Batteries

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

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Prof. Quan LI	Prof. Yanglong HOU
Post	Professor	Professor
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Co-investigator(s) *(with title and institution)*	/	/

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	2014/01/01	NA	NA
Project Completion date	2017/12/31	NA	NA
Duration *(in month)*	48	NA	NA
Deadline for Submission of Completion Report	2018/12/31	NA	NA

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. Developing 3D networked electrode of branched metallic nanowire arrays/graphene directly on metallic current collectors. Root-branched short metal nanowire arrays will be firstly grown onto metallic current collectors (e.g. Cu), on top of which the 3D graphene network will be fabricated via solvothermal method. The entanglement between the branched nanowire array and the graphene at the graphene/current collector interface would fix the 3D graphene networks directly onto the metallic current collectors, providing a simplest device configuration, as the cell can be assembled free of additional binders and additives. Manipulating the porosity of the 3D graphene network will be performed, as it relates to both the effective filling of the active materials and the mechanical stability of the whole anode. Doping of the graphene will be carried out to further improve its electrical properties. The chemical composition, phase, morphology and the conductivity of the 3D networked nanoelectrode will be examined as functions of the growth parameters.

2. Developing 3D graphene-metal oxide (sulfide) composite structures on the prepared nanoelectrode (branched metallic nanowire arrays/3D graphene) for Li-ion battery anode. Two growth methodologies, i.e., electroplating and wet chemistry, will be employed to deposit the active materials (metal oxide (sulfide)) on the existing 3D networked graphene electrode. The two methods will be evaluated regarding the metal oxide (sulfide) filling capacity in the 3D graphene electrode and the controllability of the active material amount, size, morphology and its interfacing with the graphene. Compositional and structural characterizations will be carried out as functions of the deposition parameters. In particular, the interface and the possible coupling between the graphene and metal oxide (sulfide) will be examined.

3. Proto-type cells will be assembled. Electrochemical property of the anode will be evaluated by its charge/discharge capacity at specific charging/discharging rates and number of cycling. The structural parameters associated with the optimized anode performance will be identified, and the correlation between the 3D composite nanoarchitectures configuration and the anode's electrochemical performance will be established, serving as guidelines for the development of new generation of Li-ion battery anode with high capacity and long cycling life. Performance comparison of the anodes made from 3D composite architecture and the 2D layered graphene/metal oxide (sulphide) will be made, and possible new microscopic mechanism that lead to the improved anode performance will be identified.

5.2 Revised Objectives

Date of approval from the RGC: NA__________________

Reasons for the change: NA____

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1.
2.
3. ....

6. Research Outcome

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

We have adopted two different approaches in creating the three dimensional graphene/metal oxide (sulfide) composite nanoarchitectures for anode applications in Li-ion batteries. In order to obtain graphene-based composites, we choose two different types of graphene, that is, reduced graphene oxide (rGO) and graphene foam (GF) grown by chemical vapor deposition. Graphene oxide is hydrophilic, so it can be easily mixed with active materials. As a comparison, the natural 3D network of GF can be employed as the current collector itself, allowing electroplating of active materials. The different characteristics of the two types of graphene decides the different approaches when using them to build the 3D architecture to host the active materials, and achieve binder/additive free graphene-based electrodes--we develop electrophoresis to prepared rGO-based composite [Huang et al., Journal of Power Sources, 2015], while electroplating is employed for fabrication of graphene foam (GF)-based composite [Huang et al., Nano Energy, 2017].

rGO/LiFePO4 (LFP) composite have been fabricated using electrophoresis. A 3D substrate, carbon cloth, is employed as the current collector. EIS studies reveal lower charge transfer resistance and more effective Li^+ diffusion associated with the 3D current collector configuration, as compared to that employing conventional 2D Al foil. The rGO serves as further bridge/secondary structure in addition to the primary 3D current collector provided by carbon cloth. Nevertheless, the enhancement resulted from rGO would saturate when adequate network is available [Huang et al., Journal of Power Sources, 2015].

On the other hand, electrophoresis process of GO and LFP requires the presence of Mg^{2+} to modify the surface charge of GO and LFP. Other than its role of improving the adhesion of both GO and LFP to the current collector in the electrophoresis process, we found that the introduction of Mg^{2+} also affect the electrochemical performance of the final electrode. Largely improved rate performance of the composite electrode is achieved when introducing Mg^{2+} into LFP/rGO composite (on 3D networked substrate). It is ascribed to enhanced reduction of Fe^{2+} to Fe^0 in the simultaneous presence of Mg^{2+} and rGO, leading to significantly enhanced electronic conductivity [Huang et al., Journal of Power Sources, 2017].

In developing GF based composite electrode, Fe_3O_4 are employed as the active material. The GF-Fe3O4 composite is successfully fabricated by an electroplating process, which results in a binder/additive free, yet mechanically robust composite anode. The GF-Fe3O4 composite electrode delivers a good cycling performance (~1220 mA h g-1 at 1 A g-1 after 500 cycles) and excellent rate capability (~500 mA h g-1 at 5 A g-1). The presence of graphene effectively enhances the charge transport in the electrode, resulting in large capacity and outstanding rate performance. The synergistic effect of the composite is enabled by the intimate coupling between the Fe_3O_4 nanoparticles and the GF in the composite sample, as suggested by the NEXAFS results. The cycling induced capacity increase of the GF-Fe_3O_4 composite is observed and ascribed to the electrolyte reaction, activation of GF and the decomposition of lithium oxide that occurs during the cycling of composite [Huang et al., Nano Energy, 2017].

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

Despite the exciting observation of the cycling enhanced capacity in the GF-Fe_3O_4 composite, the exact chemical and/or electrochemical reaction that took place during the cycling process of GF-Fe3O4 composite and the evaluation of the catalytic roles of Fe3O4 and graphene in the corresponding reactions remain unclear, and the understanding of which may be relevant to key issues in Li-air batteries or fuel cells. Operando NEXAFS or in-situ TEM can be employed to examine the dynamic evolution of electronic structure, microstructure and morphology directly related to the changes within the GF-Fe3O4 composite during cycling. These characterization methods help to obtain a thorough understanding on the reaction mechanisms of GF-Fe3O4 during electrochemical cycling.

7. The Layman's Summary

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

The high specific capacity associated with many metal oxides (sulfides) makes them a most promising category of anode candidate for Li-ion batteries. Nevertheless, this family of materials suffers from low cyclability as a result of the materials' low electrical conductivity and/or volume change during cycling. In this project, we have addressed this problem by constructing a binder/additive free three dimensional graphene-metal oxides (sulfides) composite electrode by developing two effective methods, that is, electrophoresis based on graphene oxide flakes and electroplating/wet chemistry based on three dimensional graphene foams. In both cases, we found that the effective graphene network and intimate contact formed between the graphene and the active materials are keys to the high capacity, high rate performance and long cycle life of the composite electrode. What is particularly worth noting is the observed cycling enhanced capacity in the graphene-Fe_3O_4 composite. Introducing 3D graphene foam promotes the cycling induced capacity enhancement of the Fe3O4 electrode. The presence of graphene effectively promotes the electrolyte reactions and reversible formation/decomposition of lithium oxide. At the same time, activation of GF also occurs in the presence of Fe3O4 nanoparticles, further increases the capacity of the nanocomposite.

<u>Part C: Research Output</u>

8. Peer-reviewed journal publication(s) arising <u>directly</u> 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)*	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)*						
2015	/	/	/	Yuan Huang, Hao Liu, Y.-C. Lu, Yanglong Hou, Quan Li*	Electrophoretic lithium iron phosphate/reduced graphene oxide composite for lithium ion battery cathode application/ **Journal of Power Sources** 284, 236-244, 2015	2016	Yes	Yes	No

2015	/	/	/	Nasir Mahmood, Jinghan Zhu, Sarish Rehman, Quan Li , Yanglong Hou*	Control over large-volume changes of lithium battery anodes via active–inactive metal alloy embedded in porous carbon/ **Nano Energy** 15, 755–765, 2015	No	Yes	No	No
2017	/	/	/	Yuan Huang, Hao Liu, Li Gong, Yanglong Hou , Quan Li*	A simple route to improve rate performance of LiFePO4/reduced graphene oxide composite cathode by adding Mg2+ via mechanical mixing/ **Journal of Power Sources** 347, 29-36, 2017	No	Yes	Yes	No
2017	/	/	/	Yuan Huang, Zihan Xu, Jiangquan Mai, Tsz-Ki Lau, Xinhui Lu, Yao-Jane Hsu, Yongsheng Chen, Alex Chinghuan Lee, Yanglong Hou, Ying Shirley Meng, Quan Li*	Revisiting the origin of cycling enhanced capacity of Fe3O4 based nanostructured electrode for lithium ion batteries/ **Nano Energy**, 41, 426–433, 2017	No	Yes	Yes	No

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)*	Accessible from the institutional repository *(Yes or No)*
04/2015/ San Francisco	Electrophoretic $LiFePO_4$/reduced graphene oxide composite cathode for Li-ion battery with high active material content	2015 MRS Spring Meeting	2016	Yes	Yes	No
05/2015/ Chicago	Electrophoretic LiFePO4/ graphene composite for Li-ion battery cathode application	2015 ECS Meeting	2016	Yes	Yes	No

10/2015/ Hong Kong	Three-dimensional architectures for Li-ion battery electrode	International Society of Electrochemistry 2015 Satellite Meeting	2016	Yes	Yes	No
12/2015/ Dubai	Three Dimensional Graphene Foam as current collector for Lithium Ion Batteries Applications	4th Nano Today Conference	2016	Yes	Yes	No

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
HUANG Yuan	PhD	July 2014	July 2016

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

Nil