RGC Ref.: M-PolyU503/13
(please insert ref. above)

The Research Grants Council of Hong Kong
SRFDP & RGC ERG Joint Research Scheme
Completion Report

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

Part A: The Project and Investigator(s)

1. Project Title

High Performance Aqueous Rechargeable Battery Based on Anodic Compound Electrodes

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

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Dr Huang Haitao	Prof. Wei Bingqing
Post	Associate Professor	Professor
Unit / Department / Institution	Department of Applied Physics The Hong Kong Polytechnic University (PolyU)	School of Materials Science and Engineering, Northwestern Polytechnical University (NPU)
Contact Information	Tel : (852) 2766 5694 haitao.huang@polyu.edu.hk	Tel : +86-029-88460204 weib@udel.edu
Co-investigator(s) *(with title and institution)*	Dr Yip Chao Tung / PolyU Mr Huang Chun / PolyU	Dr Xie Keyu, Mr Sun Zhen, Ms. Li Lu, Ms. Luo Huijuan, Ms Yu Haiyan / NPU
PhD student(s) (with period of involvement)	Dr Guo Min, full-time PhD student at PolyU from 1 Jan 2014 to 31 Dec 2014 Dr Liu Yan, full-time PhD student at PolyU from 1 Jan 2014 to 31 Dec 2016	Dr Hu Jingzhi, full-time PhD student at NWPU from 1 Sep. 2014 Dr Qi yaqing, full-time PhD student at PolyU from 1 Sep. 2015

Note: The Hong Kong project team must involve at least one research postgraduate student pursuing a Doctor of Philosophy degree at the UGC-funded university (PhD student) at any time throughout the project period.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted*)
Project Start date	1 Jan 2014	N/A	N/A
Project Completion date	31 Dec 2016	N/A	N/A
Duration *(in month)*	36 months	N/A	N/A
Deadline for Submission of Completion Report	31 Dec 2017	N/A	N/A

Part B: The Completion Report

5 Project Objectives

5.1 Objectives as per original application

1. To have a deeper understanding on the anodization mechanism of non-valve metal in order to achieve controllable growth of the electrode material.
2. To configure the novel $Ni(OH)_2$/Ni-TiO_2/Ti batteries and to study their structure-property relationship.
3. To have a deeper understanding on the multi-ion energy storage mechanism.

5.2 Revised Objectives

Date of approval from the RGC: _____

Reasons for the change: _____

_____

N/A

6. Research Outcome

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

A novel hierarchical nanotube array (NTA) with nickel–cobalt metallic core and nickel–cobalt layered double hydroxide shell (Ni-Co@Ni-Co LDH), is grown on carbon fiber cloth (CFC) for high-performance battery-type supercapacitors. The synthesized electrode shows high capacitance of 2200 F g^{-1} at a current density of 5 A g^{-1}, while 98.8% of its initial capacitance is retained after 5000 cycles. When the current density is increased from 1 to 20 A g^{-1}, the capacitance loss is less than 20%, demonstrating excellent rate capability. A highly flexible all-solid-state battery-type supercapacitor is successfully fabricated with Ni-Co LDH NTAs/CFC as the positive electrode and electrospun carbon fibers/CFC as the negative electrode, showing a maximum specific capacitance of 319 F g^{-1}, a high energy density of 100 Wh kg^{-1} at 1.5 kW kg^{-1}, and good cycling stability (98.6% after 3000 cycles) (***Adv.Funct.Mater.*** **27**, 1605307, 2017).
Various kinds of nanostructured electrodes were synthesized and characterized, such as, dendritic Ni@NiO core/shell electrode fabricated by electrodeposition in a Ni-free electrolyte (***J.Mater.Chem.A*** **4**, 15049, 2016), $Cu(OH)_2$ nanobelt array electrode deposited on commercial Dacron cloth (***J.Mater.Chem.A*** **4**, 14781, 2016), flexible $NiCo_2O_4$ nanograss@carbon fiber electrode (***Electrochimi.Acta*** **211**, 411, 2016), flexible and wearable fiber shaped copper hexacyanoferrate electrode (***J.Mater.Chem.A***, 4, 4934, 2016), porous NiO electrode (***Nanoscale*** **8**, 11256, 2016 and ***J.Mater.Chem.A*** **4**, 8211, 2016), and iron oxide nanotube array electrode (***Corros.Sci.*** **88**, 66, 2014). Those electrodes were fabricated by anodization or electrodeposition and showed excellent electrochemical performance, due to enlarged active surface area for charge storage and shortened ion diffusion path for charge transport, which are the principles guiding our design of electrode structures.
Hollow nanotubes of N-doped carbon deposited on CoS is enabled by the simultaneous use of three functionalities of polyacrylonitrite (PAN) nanofibers: 1) a substrate for loading active materials, 2) a sacrificial template for creating hollow tubular structures, and 3) a

precursor for in situ nitrogen doping. The charge storage mechanism for Li and Na ions in CoS is shown to be the conversion reaction $2A^{+}+2e^{-}+CoS \rightarrow Co+A_2S$ with A=Li or Na.
A novel TiO_2 three-dimensional (3D) anode with an aligned TiO_2 nanotube/nanoparticle heterostructure (TiO_2 NTs/NPs) is developed by simply immersing as-anodized TiO_2 NTs into water and further crystallizing the TiO_2 NTs by post-annealing. The heterostructure, with its core in a tubular morphology and with both the outer and inner surface consisting of nanoparticles, is confirmed by FESEM and TEM. A reversible areal capacity of 0.126 $mAh \cdot cm^{-2}$ is retained after 50 cycles for the TiO^2 NTs/NPs heterostructure electrode, which is higher than that of the TiO_2 NTs electrode (0.102 $mAh \cdot cm^{-2}$ after 50 cycles). At the current densities of 0.02, 0.04, 0.06, 0.08, 0.10 and 0.20 $mA \cdot cm^{-2}$, the areal capacities are 0.142, 0.127, 0.117, 0.110, 0.104 and 0.089 $mAh \cdot cm^{-2}$, respectively, for the TiO_2 NTs/NPs heterostructure electrode compared to the areal capacities of 0.123, 0.112, 0.105, 0.101, 0.094 and 0.083 $mAh \cdot cm^{-2}$, respectively, for the TiO_2 NTs electrode. The enhanced electrochemical performance is attributed to the unique microstructure of the TiO_2 NTs/NPs heterostructure electrode with the TiO_2 NT core used as a straight pathway for electronic transport and with TiO_2 NP offering enhanced surface areas for facile Li^{+} insertion/extraction. The results described here inspire a facile approach to fabricate a 3D anode with an enhanced electrochemical performance for lithium-ion microbattery applications (***Nanotech.*** **25**, 455401, 2014).

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

The energy storage devices we fabricated have the potential for flexible energy storage device applications. Future work includes the development of better electrode and electrolyte. The design of the electrode should consider the optimization of mass flow in the porous channels of electrode. The Murray's law can be adopted in the future design of electrode structure. Moreover, solid-state electrolyte can be used to enhance the cell voltage and avoid leakage problems.

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)

Aqueous rechargeable lithium batteries, with high-safety, low-cost and high-rate capability, are attractive electrochemical energy storage devices. However, their energy density is limited by low voltage, low capacity and the electrode fabrication method. Based on our recent success in the fabrication of hierarchical $Ni(OH)_2$ and TiO_2 nanotube array as the electrode for electrochemical energy storage via the anodization method, we proposed a novel aqueous rechargeable battery which uses anodic $Ni(OH)_2$/Ti and anodic TiO_2/Ti as the positive/negative electrodes and mixed LiOH/KOH solution as the aqueous electrolyte. Efforts were devoted to the optimization of anodization technique on valve and non-valve metals, to the study of formation mechanism and to the development of new fabrication technique of flexible electrode with controllable structure and hence controllable performance. The relationship between the battery architecture and its electrochemical performances were established and the energy storage mechanism was studied. The proposed project sheds light on the design and development of novel high-performance aqueous rechargeable lithium batteries.

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)*	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)*						
2017				**Y.Liu**, N.Fu, G.Zhang, M.Xu, W.Lu, L.Zhou and **H.Huang***	"Design of Hierarchical Ni-Co@Ni-Co Layered Double Hydroxide Core-Shell Structured Nanotube Array for High-Performance Flexible All-Solid-State Battery-Type Supercapacitors" ***Adv.Funct.Mater.*** **27**, 1605307		Yes	Yes	Yes
2016				**Y.Liu**, N.Fu, G.Zhang, W.Lu, L.Zhou and **H.Huang***	"Ni@NiO Core/Shell Dendrites for Ultra-Long Cycle Life Electrochemical Energy Storage", ***J.Mater.Chem.A*** **4**, 15049		Yes	Yes	Yes
2016				S.Lei, Y.Liu, L.Fei, R.Song, W.Lu, L.Shu, C.L.Mak*, Y.Wang and **H.Huang***	"Commercial Dacron Cloth Supported $Cu(OH)_2$ Nanobelt Arrays for Wearable Supercapacitors", ***J.Mater.Chem.A*** **4**, 14781		Yes	Yes	Yes
2016				S.T.Senthilkumar, N.Fu, Y.Liu, Y.Wang, L.Zhou and **H.Huang***	"Flexible Fiber Hybrid Supercapacitor with $NiCo_2O_4$ Nanograss@Carbon Fiber and Bio-Waste Derived High Surface Area Porous Carbon", ***Electrochimi.Acta*** **211**, 411		Yes	Yes	Yes
2016				L.Wang, G.Zhang*, Y.Liu, W.Li, W.Lu and **H.Huang***	"Facile Synthesis of a Mechanically Robust and Highly Porous NiO Film with Excellent Electrocatalytic Activity towards Methanol Oxidation", ***Nanoscale*** **8**, 11256		Yes	Yes	Yes
2016				G.Zhang*, L.Wang, Y.Liu, W.Li, F.Yu, W.Lu and **H.Huang***	"Cracks Bring Robustness: a Pre-Cracked NiO Nanosponge Electrode with Greatly Enhanced Cycle Stability and Rate Performance", ***J.Mater.Chem.A*** **4**, 8211		Yes	Yes	Yes
2016				S.T.Senthilkumar, J.Kim, Y.Wang, **H.Huang*** and Y.Kim*	"Flexible and Wearable Fiber Shaped High Voltage Supercapacitors Based on Copper Hexacyanoferrate and Porous Carbon Coated Carbon Fiber Electrodes", ***J.Mater.Chem.A***, 4, 4934		Yes	Yes	Yes
2015				S.T.Senthilkumar, Y.Wang and **H.Huang***	"Advances and Prospects of Fiber Supercapacitors", ***J.Mater.Chem.A*** **3**, 20863		Yes	Yes	Yes
2014				**K.Xie***, **M.Guo**, W.Lu and **H.Huang***	"Aligned TiO_2 Nanotube/Nanoparticle Heterostructures with Enhanced Electrochemical Performance as Three-Dimensional Anode for Lithium-Ion Microbatteries", ***Nanotech.*** **25**, 455401		Yes	Yes	Yes
2014				**K.Xie***, **M.Guo**, **H.Huang***, and Y.Liu	"Fabrication of Iron Oxide Nanotube Arrays by Electrochemical Anodization", ***Corros.Sci.*** **88**, 66		Yes	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.)*

N/A

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)*

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
Guo Min	PhD	2011.10.06	2014.10.05/ 2015
Liu Yan	PhD	2013.06.14	2017.06.13/ 2017

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

N/A