ADVANCED ELECTRODE MATERIALS FOR LITHIUM- AND POTASSIUM-BASED ENERGY STORAGE DEVICES

A thesis presented for the award of the degree of

Doctor of Philosophy

from

University of Technology Sydney

By

Shuoqing Zhao, B. Eng., M. Sc.

September, 2021

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Shuoqing Zhao, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledgement. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

Shuoqing Zhao

Production Note:
Signature removed prior to publication.

Sydney, Australia

September 2021

ACKNOWLEDGEMENTS

It has been four years since I was enrolled as a Ph.D. candidate in University of Technology Sydney (UTS) for the autumn of 2017. Due to the impact of COVID-19, up until now, I am still stranded in China and cannot return to Australia to get together with my friends. It is a really difficult and painful period, during which I have suffered from depression and the tragic loss. However, I should also embrace to this special experience and really appreciate the valuable help from my family members, friends and UTS.

Firstly, I express sincere thanks to my supervisor, Professor Guoxiu Wang, for his encouragement, invaluable suggestions and selfless assistance throughout my Ph.D. study at UTS.

Secondly, many thanks to my co-supervisor Dr. Bing Sun and Dr. Jane Yao for their kind help and support, which smoothly assisted my work in laboratory as well as my daily life in Sydney.

I would like to acknowledge my colleagues at UTS, Dr. Hao Liu, Dr. Dawei Su, Dr. Jinqiang Zhang, Dr. Yufei Zhao, Dr. Dong Zhou, Dr. Pan Xiong, Dr. Liubing Dong, Dr. Huajun Tian, Dr. Xin Guo, Dr. Weizhai Bao, Dr. Tuhin Sahu, Dr. Kang Yan, Dr. Xingxing Yu, Dr. Yi Chen, Dr. Xiaochun Gao, Mr. Fan Zhang, Mr. Tianyi Wang, Miss Ziqi Guo, Miss Pauline Jaumaux, Mr. Javad Safaei, Miss Yuhan Xie. Their kind collaboration and assistance were helpful.

Also, I want to thank my friends, Mr. Feng Liu, Mr. Tiexin Li and Dr. Jianjia Zhang, we shared a lot of happy memories in Sydney.

In addition, I appreciate the administrative and technical support from Miss Elizabeth Gurung Tamang, Dr. Ronald Shimmon, Dr. Linda Xiao, Miss Katie McBean, Mr. Geoff McCredie and Mr. Herbert Yuan, Mr. Iurii Bodachivskyi.

The financial support from Australian Rail Manufacturing Cooperative Research Centre (RMCRC) and UTS (International Research Scholarship) helped me completing my Ph.D. study, which is highly acknowledged.

Last but not the least, I would like to thank my family members for their wholly warm support throughout my life.

STATEMENT OF FORMAT

This is the statement indicating that seven published works are included in this doctoral thesis. Three review papers are referred to 1.2, 1.3, 1.4, 1.5 and 1.7 in the introduction. Four original published works are referred to chapter 3, chapter 4, chapter 5 and chapter 6. The related publications in this thesis are listed as follows:

1. Title: **Reaction Mechanisms of Layered Lithium-Rich Cathode Materials for High-Energy Lithium-Ion Batteries**. Authors: **Shuoqing Zhao**, Kang Yan, Jinqiang Zhang, Bing Sun and Guoxiu Wang. Journal: *Angew. Chem. Int. Ed.*, 2020, 202000262. DOI: 10.1002/anie.202000262. This work is referred to **1.2**, **1.3** and **1.4** in the introduction.
2. Title: **Towards High-energy-density Lithium-ion Batteries: Strategies for Developing High-capacity Lithium-rich Cathode Materials**. Authors: **Shuoqing Zhao**, Ziqi Guo, Kang Yan, Shuwei Wan, Fengrong He, Bing Sun and Guoxiu Wang. Journal: *Energy Stor. Mater.*, 2021, 34, 716-734. DOI: 10.1016/j.ensm.2020.11.008. This work is referred to **1.5** in the introduction.
3. Title: **The Rise of Prussian Blue Analogs: Challenges and Opportunities for High-Performance Cathode Materials in Potassium-Ion Batteries**. Authors: **Shuoqing Zhao**, Ziqi Guo, Kang Yan, Xin Guo, Shuwei Wan, Fengrong He, Bing Sun and Guoxiu Wang. Journal: *Small Structures*, 2020, 2000054. DOI: 10.1002/sstr.202000054. This work is referred to **1.7** in the introduction.

4. Title: **Aegis of Lithium-Rich Cathode Materials via Heterostructured $LiAlF_4$ Coating for High-Performance Lithium-Ion Batteries**. Authors: **Shuoqing Zhao**, Bing Sun, Kang Yan, Jinqiang Zhang, Chengyin Wang and Guoxiu Wang. Journal: *ACS Appl. Mater. Interfaces*, 2018, 10 (39), 33260-33268. DOI: 10.1021/acsami.8b11471. This work is referred to **Chapter 3**.

5. Title: **Construction of Hierarchical $K_{1.39}Mn_3O_6$ Spheres via AlF_3 Coating for High-Performance Potassium-Ion Batteries**. Authors: **Shuoqing Zhao**, Kang Yan, Paul Munroe, Bing Sun and Guoxiu Wang. Journal: *Adv. Energy Mater.*, 2019, 9 (10), 1803757. DOI: 10.1002/aenm.201803757. This work is referred to **Chapter 4**.

6. Title: **$K_2Ti_2O_5$@C Microspheres with Enhanced K^+ Intercalation Pseudocapacitance Ensuring Fast Potassium Storage and Long-Term Cycling Stability**. Authors: **Shuoqing Zhao**, Liubing Dong, Bing Sun, Kang Yan, Jinqiang Zhang, Shuwei Wan, Fengrong He, Paul Munroe, Peter H. L. Notten and Guoxiu Wang. Journal: *Small*, 2020, 16 (4), 1803757. DOI: 1906131. This work is referred to **Chapter 5**.

7. Title: **Phosphorus and Oxygen Dual-doped Porous Carbon Spheres with Enhanced Reaction Kinetics as Anode Materials for High-performance Potassium-ion Hybrid Capacitors**. Authors: **Shuoqing Zhao**, Kang Yan, Jiayu Liang, Qinghong Yuan, Jinqiang Zhang, Bing Sun, Paul Munroe and Guoxiu Wang. Journal: *Adv. Funct. Mater.*, 2021, 2102060. DOI: 10.1002/adfm.202102060. This work is referred to **Chapter 6**.

RESEARCH PUBLICATIONS

1. **Zhao, S.**; Yan, K.; Zhang, J.; Sun, B.*; Wang, G.*, Reaction Mechanisms of Layered Lithium-Rich Cathode Materials for High-Energy Lithium-Ion Batteries. *Angewandte Chemie International Edition* **2021**, 60 (5), 2208-2220.
2. **Zhao, S.**; Yan, K.; Liang, J.; Yuan, Q.; Zhang, J.; Sun, B.*; Munroe, P.; Wang, G.*, Phosphorus and Oxygen Dual-doped Porous Carbon Spheres with Enhanced Reaction Kinetics as Anode Materials for High-performance Potassium-ion Hybrid Capacitors. *Advanced Functional Materials* **2021**, 2102060, DOI: 10.1002/adfm.202102060.
3. **Zhao, S.**; Guo, Z.; Yan, K.; Wan, S.; He, F.; Sun, B.*; Wang, G.*, Towards high-energy-density lithium-ion batteries: Strategies for developing high-capacity lithium-rich cathode materials. *Energy Storage Materials* **2021**, 34, 716-734.
4. **Zhao, S.**; Guo, Z.; Yang, J.; Wang, C.; Sun, B.*; Wang, G.*, Nanoengineering of Advanced Carbon Materials for Sodium-Ion Batteries. *Small* **2021**, 2007431.
5. **Zhao, S.**; Guo, Z.; Yan, K.; Guo, X.; Wan, S.; He, F.; Sun, B.*; Wang, G.*, The Rise of Prussian Blue Analogs: Challenges and Opportunities for High-Performance Cathode Materials in Potassium-Ion Batteries. *Small Structures* **2021**, 2 (1), 2000054.
6. **Zhao, S.**; Dong, L.; Sun, B.*; Yan, K.; Zhang, J.; Wan, S.; He, F.; Munroe, P.; Notten, P. H. L.; Wang, G.*, $K_2Ti_2O_5$@C Microspheres with Enhanced K^+ Intercalation Pseudocapacitance Ensuring Fast Potassium Storage and Long-Term Cycling Stability. *Small* **2020**, 16 (4), 1906131.
7. **Zhao, S.**; Yan, K.; Munroe, P.; Sun, B.*; Wang, G.*, Construction of Hierarchical $K_{1.39}Mn_3O_6$ Spheres via AlF_3 Coating for High-Performance Potassium-Ion Batteries. *Advanced Energy Materials* **2019**, 9 (10), 1803757.
8. **Zhao, S.**; Sun, B.*; Yan, K.; Zhang, J.; Wang, C.; Wang, G.*, Aegis of Lithium-Rich Cathode Materials via Heterostructured $LiAlF_4$ Coating for High-Performance Lithium-Ion Batteries. *ACS Applied Materials & Interfaces* **2018**, 10 (39), 33260-33268.
9. Yan, K.; **Zhao, S.**; Zhang, J.; Safaei, J.; Yu, X.; Wang, T.; Wang, S.; Sun, B.*; Wang, G.*, Dendrite-Free Sodium Metal Batteries Enabled by the Release of Contact Strain on Flexible and Sodiophilic Matrix. *Nano Letters* **2020**, 20 (8), 6112-6119.
10. Guo, Z.; **Zhao, S.**; Li, T.; Su, D.*; Guo, S.; Wang, G.*, Recent Advances in Rechargeable Magnesium-Based Batteries for High-Efficiency Energy Storage. *Advanced Energy Materials* **2020**, 10 (21), 1903591.
11. Yan, K.; Wang, J.; **Zhao, S.**; Zhou, D.; Sun, B.*; Cui, Y.*; Wang, G.*, Temperature-Dependent Nucleation and Growth of Dendrite-Free Lithium Metal Anodes. *Angewandte Chemie International Edition* **2019**, 58 (33), 11364-11368.
12. Tian, H.; Wang, T.; Zhang, F.; **Zhao, S.**; Wan, S.; He, F.; Wang, G.*, Tunable porous carbon spheres for high-performance rechargeable batteries. *Journal of Materials Chemistry A* **2018**, 6 (27), 12816-12841.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

With the growing demand for high-energy-density lithium-ion batteries, layered lithium-rich cathode materials with high specific capacity and low cost have been widely regarded as one of the most attractive candidates for next-generation lithium-ion batteries. However, issues such as voltage decay, capacity loss and sluggish reaction kinetics have hindered their further commercialization for decades. Herein, we propose a heterostructured $LiAlF_4$ coating strategy to overcome those obstacles. The as-developed lithium-rich cathode material shows a high reversible capacity and ultralong cycling stability. The enhanced performances can be attributed to the introduction of the lithium-ion-conductive nanolayer and the generation of nonbonding O^{n-} species in the active material lattice, which enable rapid and effective lithium ions transport and diffusion.

Considering the increasing cost and uneven distribution of lithium resources, potassium-ion batteries are attracting great interest for emerging large-scale energy storage, owing to their advantages such as low cost and high operational voltage. Herein, the synthesis of hierarchical $K_{1.39}Mn_3O_6$ microspheres as cathode materials for potassium-ion batteries is reported. Additionally, an effective AlF_3 surface coating strategy is applied to further improve the electrochemical performance of $K_{1.39}Mn_3O_6$ microspheres. The as-synthesized AlF_3 coated $K_{1.39}Mn_3O_6$ microspheres show a high reversible capacity, excellent rate capability, and cycling stability. *Ex situ* X-ray diffraction measurements reveal that the irreversible structure evolution can be significantly mitigated via surface modification.

As for anode materials, it is reported on carbon-coated $K_2Ti_2O_5$ microspheres (S-KTO@C) synthesized through a facile spray drying method. Taking advantages of both the porous microstructure and carbon coating, S-KTO@C shows excellent rate capability and cycling stability as an anode material for PIBs. As a proof of concept, a potassium-ion hybrid capacitor shows a high energy density, high power density, and excellent capacity retention.

Phosphorus/oxygen dual-doped porous carbon spheres, which possess expanded interlayer distances, abundant redox active sites and oxygen-rich defects, were also prepared in this thesis. The as-developed anode material shows superior electrochemical performances. *In situ* Raman spectroscopy and density functional theory calculations further confirm that the formation of P-C and P-O/P-OH bonds not only improves structural stability, but also contributes to a rapid surface-controlled potassium adsorption process. A potassium-ion hybrid capacitor was assembled by a dual-doped porous carbon sphere anode and an activated carbon cathode, which holds great promise as next-generation energy storage devices.