

# **Phosphate-Based Cathode Materials for Rechargeable Batteries**

A thesis presented for the award of the degree of

**Doctor of Philosophy**

from

**University of Technology Sydney**

by

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May, 2018

## **CERTIFICATE OF ORIGINAL AUTHORSHIP**

I, Katja Ramona Kretschmer, certify that the work presented in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

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Katja Ramona Kretschmer

Sydney, Australia

May, 2018

## **DEDICATION**

This thesis is dedicated to my family. Thank you for all your love and support.

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## ABSTRACT

The design of electrode materials depends critically on understanding the underlying electrochemical processes. Material composition, morphology, structure, and preparation method affect and can alter electrochemical performance of electrochemically active materials. In this research project, a series of phosphate-based polyanionic electrode materials have been fabricated and their electrochemical properties for the use in lithium-ion and sodium-ion batteries are evaluated.

We successfully prepared carbon-coated  $\text{LiFePO}_4$  cathode materials by industrial ball milling and a solid-state reaction with  $\text{Li}_2\text{CO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ , and  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  as starting materials. Soluble starch as the primary carbon source was investigated for its capability of generating a highly graphitic carbon coating, whilst sufficiently controlling the crystal growth of  $\text{LiFePO}_4$ . XRD analysis, Raman spectroscopy, and electrochemical testing revealed the significant impact of the amount of starch added to the pre-sintered precursor on phase purity, carbon quality, and electrochemical performance of the final  $\text{LiFePO}_4/\text{C}$  composite. The optimum soluble starch content to achieve a highly  $\text{sp}^2$ -coordinated carbon coating is 10 wt%, which enabled our  $\text{LiFePO}_4/\text{C}$  composite to achieve competitive reversible capacities as well as improved rate performance

The spray method is well-trusted in practical applications, such as food manufacturing, fertilizers, oxide ceramics, and pharmaceuticals. The ability to produce uniformly spherical particle clusters ranging from nano- to micrometre in size is one of the main advantages of this method, which is immensely important for large scale production of electrochemically active materials for the energy storage market. In this report, we systematically evaluated spray-drying conditions and equipment settings in regards to electrochemical performance of carbon coated  $\text{LiFePO}_4$  cathode materials. In an optimisation trial, the most suitable process conditions for the precursor materials and spray-dryer model used to prepare pure and practical  $\text{LiFePO}_4$  cathode materials were identified. The impact

of different organic additives on the resulting particle morphology of the final product was also investigated. It was found that the addition of polyvinyl alcohol (PVA) generates particle clusters that provide a high tap density product without sacrificing electrochemical performance. The  $\text{LiFePO}_4$  cathode material prepared with the addition of PVA achieved remarkable rate performance results and could maintain a capacity of  $113.95 \text{ mA h g}^{-1}$  at 10C.

Lithium-ion batteries (LIBs) are widely implemented to power portable electronic devices and are increasingly in demand for large-scale applications. One of the major obstacles for this technology is still the low cost-efficiency of its electrochemical active materials and production processes. In this work, we present a novel impregnation–carbothermal reduction method to generate a  $\text{LiFePO}_4$ –carbon paper hybrid electrode, which does not require a metallic current collector, polymeric binder or conducting additives to function as a cathode material in a LIB system. A shell of  $\text{LiFePO}_4$  crystals was grown *in situ* on carbon fibres during the carbonization of microcrystalline cellulose. The  $\text{LiFePO}_4$ –carbon paper electrode achieved an initial reversible areal capacity of  $197 \mu\text{A h cm}^{-2}$  increasing to  $222 \mu\text{A h cm}^{-2}$  after 500 cycles at a current density of  $0.1 \text{ mA cm}^{-2}$ . The hybrid electrode also demonstrated a superior cycling performance for up to 1000 cycles. The free-standing electrode could be potentially applied for flexible lithium-ion batteries.

Sodium-ion batteries (NIBs) are an emerging technology, which can meet increasing demands for large-scale energy storage. One of the most promising cathode material candidates for sodium-ion batteries is  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  due to its high capacity, thermal stability, and sodium (**Na**) superionic conductor 3D (NASICON)-type framework. In this work, the authors have significantly improved electrochemical performance and cycling stability of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  by introducing a 3D interconnected conductive network in the form of carbon fibre derived from ordinary paper towel. The free-standing  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ –carbon paper ( $\text{Na}_3\text{V}_2(\text{PO}_4)_3@CP$ ) hybrid electrodes do not require a metallic current collector, polymeric binder, or conducting additives to function as a cathode material in an

NIB system. The  $\text{Na}_3\text{V}_2(\text{PO}_4)_3@\text{CP}$  cathode demonstrates extraordinary long-term cycling stability for 30 000 deep charge– discharge cycles at a current density of  $2.5 \text{ mA cm}^{-2}$ . Such outstanding cycling stability can meet the stringent requirements for renewable energy storage.