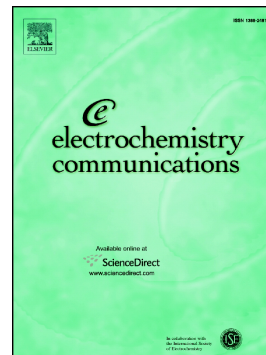


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Jiechen Lu, Shin-ichi Nishimura, Atsuo Yamada

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Abstract

Phosphate compounds have been intensively investigated as cathode materials for sodium ion batteries. Here we report the synthesis and electrochemical performance of a novel iron-rich sodium iron orthophosphate. This new compound was synthesized by a conventional solid state reaction method, and was found to be electrochemically active, delivering a reversible capacity of 85 mAhg^{-1} at an average voltage of *c.a.* 3.0 V vs. Na/Na⁺. Besides, the desodiated phase can be (de)intercalated by lithium ions when assembled into a lithium cell. Our discovery will open up the scope of phosphate family and reveal the importance of off-stoichiometric compounds as cathode materials.

Introduction

Towards the goal of realizing a sustainable and green society, efficient and economic electric energy storage is one of major challenges. In this context, rechargeable lithium ion batteries are considered as the most competitive candidates due to their great success in consumer electronics. Over the past few years, their applications in electric vehicles and stationery electric storage for power grids have entered into the fast growing stage. However, due to limitation and unevenly distribution of lithium reserves, there is a constant concern that the costs of lithium ion batteries will dramatically increase, impeding the development of the market. Therefore, cheaper and more available alternatives are in urgent demand. The analogues of lithium ion batteries, sodium ion batteries, have attracted renewed interest recently owing to the abundance of sodium reserves. Although heavier Na⁺ ion and lower operating voltage make sodium ion batteries slightly less efficient than lithium ion batteries[1], sodium ion batteries are considered as an economic and sustainable choice among the post lithium ion battery approaches.[2–4]

Enlightened by the rich experience of materials research in lithium ion batteries, a variety of cathode compounds for sodium ion batteries have been continuously found. They are mainly categorized into layered oxides[5–11] (*e.g.* Na_xCoO₂, O3-Na_xFe_{1-y}Co_yO₂, P2-Na_xMn_{1/2}Fe_{1/2}O₂) and polyanionic compounds[12–16] (*e.g.* Na₂FePO₄F, Na₄Fe₃(PO₄)₂P₂O₇ and Na₂FeP₂O₇). Compared with the former one, polyanionic compounds are advantageous in the respect of cycling life and safety owing to their stable three dimensional polyanionic frameworks. To reduce the costs of cathode materials avoiding to use expensive transition metals such as cobalt and nickel, our effort has been devoted to identify new iron-based polyanionic compounds such as Na₂FeP₂O₇[15,16] and alluaudite Na_{2.56}Fe_{1.72}(SO₄)₃[17–19].

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