

Electrochemical Characterization of Novel Cathode Active Materials for Sodium-ion Battery

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<https://hdl.handle.net/2324/1807080>

出版情報 : 九州大学, 2016, 博士 (工学), 課程博士
バージョン :
権利関係 :

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Name

論 文 名 : Electrochemical Characterization of Novel Cathode Active Materials for Sodium-ion
Battery

(ナトリウムイオン電池用新規正極活物質の電気化学特性)

Title

区 分 : 甲

Category

論 文 内 容 の 要 旨

Thesis Summary

As the most popular energy storage technology, rechargeable Li-ion batteries (LIBs) have been widely used in portable electronic devices. Their application fields have been expanding to larger scale devices such as electric vehicles (EVs) and a smart grid system utilizing renewable and sustainable green energies. This movement is considered as a feasible solution to take a step toward more environmentally friendly society, and regarded to be truly helpful for relieving energy crisis and global energy gap between countries. Under these circumstances, large numbers of researches have been conducted to introduce LIBs into the systems to facilitate clean energy technologies. However, when the energy storage system is enlarged, cost performance becomes a more dominant factor rather than electrochemical performance, and hence, inexpensive batteries, which can be derived from low cost and abundant materials, become more and more desirable. Rechargeable sodium-ion batteries (SIBs) have been, therefore, actively studied for the recent past few years and regarded as an alternative candidate to LIBs due to the abundant reserve and even-distribution of Na resources. Since the energy density of SIBs always falls in short compared to that of LIBs because Na has higher standard electrode potential and heavier atomic weight than Li, development on performance of known materials and/or research of new active materials for SIBs is needed to be emphasized on whether they show high working voltage and/or large discharge capacity.

The reported cathode active materials with relatively good electrochemical properties for SIBs can be categorized to some special material groups, and their common features are an open structure capable enough to accept large sodium ions. Among them, fluorophosphates materials shows higher working voltage than other materials such as layered transition metal oxide because of inductive effect from PO_4 units and high electronegativity of F. We hence have taken a particular interest in $\text{Na}_3\text{M}_2(\text{PO}_4)_2\text{F}_3$ which have open structure consisting of corner-sharing matrix made up with VO_6 octahedras

and PO₄ tetrahedras. In addition, we also search cathode materials with large discharge capacity from organic components which have multi redox functional groups. Organic compounds with lamellar stacking structure may also play as suitable sodium insertion hosts due to their low density and stacking structure. In this paper, we will present electrochemical property and structural evolution of Na₃M₂(PO₄)F₃ (M = Ti, V, and Fe) during cycles in Chapter 2. In addition, Na₂C₆O₆ and their analog will be discussed as a new cathode material for SIBs in Chapter 3 and their structure change during cycle will be also presented in Chapter 4.

In chapter 1, the basic principles of secondary batteries will be explained, and the brief introduction of sodium ion batteries including methodologies and previous studies.

In chapter 2, the synthesis and electrochemical properties of Na₃M(PO₄)F₃ (M = Ti, V, and Fe) materials will be discussed in half and full cell configurations. In this research, Na₃V(PO₄)F₃ achieved repeatable discharge capacity of ca. 120 mA g⁻¹ with average working voltage close to 4.0 V, exhibiting strong possibility to become a candidate as a high voltage cathode material for SIBs. Its good electrochemical sodiation and desodiation behaviors during cycles could be explained by investigating the structural evolution of Na₃V₂(PO₄)F₃ investigated with using ex-situ XRD measurement. The volume change of Na₃V₂(PO₄)F₃ structure after being charged to 4.3 V was less than 2.5%, which leads good cycle performance even under the continuous insertion/extraction of large Na ions.

In chapter 3, in the first part, the history of organic cathode materials for sodium ion batteries will be briefly introduced, and then electrochemical properties of Na₂C₆O₆ will be discussed in half and full cell conditions. Since Na₂C₆O₆ delivered large reversible capacity over 200 mAh/g attributable to multiple electron reactions, Na₂C₆O₆ analogs of Na₂C₅O₅, Na₂C₄O₄, and K₂C₆O₆ were also investigated for additional works. Unlike the expectation, only Na₂C₆O₆ and Na₂C₅O₅ have brought positive results as active materials for SIBs. Generally speaking, charge and discharge mechanism for organic cathode materials has been discussed with organic redox chemistry based on molecule and reactivity of functional groups. Although all materials have redox functional group of C=O bonds and get categorized with oxocarbon group, the studied materials showed all inconstant electrochemical behaviors. This result suggests the electrochemical sodium insertion and extraction by redox reaction in these oxocarbons would be more complicated than the past explanation in organic active materials.

In order to elucidate the charge and discharge behaviors in Na₂C₆O₆, the structural change of Na₂C₆O₆ during electrochemical cycle (sodiation/ disodiation) will be discussed based on the observation by Fourier transform infrared spectroscopy, X ray diffraction, and ¹³C and ²³Na nuclear magnetic resonance in chapter 4. In this work, we observed electron localization above C₆O₆ rings in association with sodiation into Na₂C₆O₆, and the crystal structure of Na₂C₆O₆ also transformed to new structure. The strong electron localization emerged after Na₂C₆O₆ structure transforms to a new phase of Na_{3.5}C₆O₆ where distortion and/or difference in crystal growth are suggested by obtained ex-situ XRD patterns.

In chapter 5, the summary of this research and conclusions will be noted.