Investigations on intercalation cathodes for sodium-ion batteries

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論 文 の 内 容 の 要 旨

論文題目　Investigations on intercalation cathodes for sodium-ion batteries
（ナトリウムイオン電池正極としてのインターカレーション材料の研究）

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Currently, Lithium-ion batteries (LIBs) are used as the main power sources in portable devices owning to their high energy density and good reversibility. However, high cost drags LIBs from the major electric suppliers for large-scale applications. Sodium-ion batteries (NIBs) have emerged as an attractive alternative recently due to the natural abundance of sodium and the comparable electrochemical properties.

However, NIBs are still far from the target to replace LIBs for large-scale application. The main problems include limited electrochemical performance and safety. This thesis focuses on NIBs cathode materials to solve these problems.

Cathode materials in NIBs mainly employ intercalation-type compounds currently, and can be divided into two main groups, polyanionic compounds and transition metal oxides. As the first part of this work, $Na_{2-x}M_{1+x/2}P_2O_7$-type (M= Fe, Mn, Mg…) polyanionic compounds were investigated. Our group has recently reported $Na_2FeP_2O_7$ as a promising cathode material for NIBs. This material shows a moderate redox voltage (~3 V) and excellent rate capability; 85% capacity retains even at a high rate of 5C. Chapter 3 focuses on the safety property on $Na_2FeP_2O_7$. As the unstable charged state, the desodiated $NaFeP_2O_7$ has been obtained with chemical oxidation. Its thermal stability has been checked with in-situ high temperature XRD and TG-DSC in the temperature range of 298~873 K. Only a polymorphic transition from the pristine $NaFeP_2O_7$ (space group: P -1) to monoclinic phase (P 2_1/c) was observed, no decomposition with oxygen evolution occurs. These results confirmed the very high thermal stability of $Na_2FeP_2O_7$ as a NIBs cathode material. Combining with the fair electrochemical performance, $Na_2FeP_2O_7$ was proven as a potential candidate for practical application.

To understand the high rate capability in $Na_2FeP_2O_7$, Chapter 4 deals with the ionic conduction properties in $Na_{2-x}M_{1+x/2}P_2O_7$-type compounds. Because the redox activity of transition metal would introduce additional defects in the crystal structure, and affect the as-measured conduction properties, the intrinsic conductivity can hardly be obtained. Therefore, a transition metal free analog, $Na_{2-x}Mg_{1+x/2}P_2O_7$, was selected. The crystal structure was refined with Rietveld refinement of Synchrotron XRD pattern, and the ionic conduction mechanism was elucidated.

The chapter 5 focuses on the cathode material with enhanced capacity. An ordered transition metal oxide, $Na[Na_{1/3}Ru_{2/3}]O_2$, has been investigated to utilize oxygen redox reaction strongly hybridized with Ru 4d orbital. It was obtained with thermal decomposition of Na_2RuO_4 and has honeycomb-like arrangement of Na and Ru on the $Na_{1/3}Ru_{2/3}$ layers. This material delivers a high capacity of ca. 180 mAh/g with partial contribution from oxygen redox, proving our original concept.