

Electrochemical and Thermal Properties of Electrodes for Na-ion Batteries

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主論文の要約データ

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Electrochemical and Thermal Properties of Electrodes for Na-ion Batteries

(ナトリウムイオン電池用電極の電気化学特性と熱安定性)

Li-ion batteries have the highest energy density among all commercially available alternatives. Virtually all portable electronic devices are powered by Li-ion batteries. The highest energy density of the Li-ion batteries results in further expansion to larger-scale applications such as battery-assisted bicycles, hybrid electric vehicles, electric vehicles, and load-leveling systems. Such a scaling-up requires substantial cost reduction to be feasible. The abundance of elements in the Earth's crust and their cost follow this order; $O > S > Fe > Ca > Na > \dots$. High energy density electrochemical reactions involving these five most abundant elements are under investigation for possible replacement of the high energy density but costly Li-ion batteries technology. Among these most abundant elements, Na and Na-ion batteries that could developed in the near future have the potential to offer an almost drop-down, rare-metal-free replacement for Li-ion batteries technology. This is because the intercalation chemistry of Na^+ resembles that of Li^+ , which has been extensively investigated in the past two decades. There are however, some substantial differences between Li^+ and Na^+ electrochemistry in aprotic solvents as well.

First, the solid electrolyte interface (SEI) formation conditions in Na^+ and Li^+ organic electrolytes seem to be different. While SEI is known to form readily in Li^+ electrolytes, its formation is questionable in Na^+ electrolytes. Since SEI formation is one of the key factors for the stability and cycle life of the state-of-the-art Li-ion batteries, further substantial efforts are necessary to understand the SEI formation mechanism in the Na^+ case.

Upon charging, the cathode of the typical Li-ion batteries or Na-ion batteries gradually increases its oxidation power, while the anode gradually accumulates Li or Na and in most cases becomes a powerful reducing agent. These two highly active electrodes are separated by a very thin polymer membrane (ca. 10 μm). If the temperature of a fully charged Li-ion battery rises for some reason such as an external or internal short circuit,

exothermic reactions may be triggered in an event described as a thermal runaway. In the worst-case scenario, this may result in a battery fire or explosion. Scaling up is particularly difficult in the cases of Li-ion batteries and Na-ion batteries because heat dissipation is proportional to the surface/volume ratio of the battery. With the increase in the physical dimensions of the batteries, heat dissipation is hindered and larger battery packs are considered more dangerous, as evidenced by the recent Tesla and Boeing 787 Dreamliner safety issues involving their Li-ion batteries packs. On the other hand, Na-ion batteries are still in their infancy and the safety evaluations of this chemistry have not been conducted in detail. My thesis aims to provide some essential information regarding the relatively new Na-ion chemistry and compare it with the already well-known Li-ion chemistry. The thesis is structured as follows.

Chapter 1 outlines the basic principles of Li-ion batteries and introduces the need to study their Na-ion counterparts.

Chapter 2 compares LiCoO₂, the most popular cathode for portable electronic devices in Li-ion batteries, with NaFeO₂, a candidate cathode for Na-ion batteries. Historically, NaFeO₂ was described prior to LiCoO₂, and both compounds are in a structural, adopting the same R-3m (No. 166) crystallographic space group. NaFeO₂ was prepared by means of solid-state reaction. It was charged to net composition Na_{0.58}FeO₂ and its thermal stability was investigated. An exothermic peak was observed above 300 °C, while the LiCoO₂ exothermic heat appears at a lower onset temperature, to 250 °C. In both cases, exothermic heat is caused by oxidation of the electrolyte from oxygen released by the charged cathode material. Higher onset temperature and lower total heat release by Na_{0.58}FeO₂ compared with LiCoO₂ make NaFeO₂ and its derivatives safe cathode candidates for Na-ion batteries.

Chapter 3 is devoted to Mn-doped Na_xFeO₂ derivatives, i.e., compounds with the general formula Na_xFe_yMn_{1-y}O₂. Mn doping was considered important to increase the reversible capacities and cycle lives of these cathodes. P2-phase compositions

$\text{Na}_{2/3}\text{Fe}_y\text{Mn}_{1-y}\text{O}_2$ ($y = 1/3, 1/2, \text{ and } 2/3$) were prepared by a solid-state reaction method. It was found that compositions with $y = 1/3, 1/2$ adopt pure P2-phase structure, while $y = 2/3$ contains an impurity phase and cannot be prepared in a pure P2 form. Therefore, Mn is considered a P2 phase promoter and stabilizer because pure P2- $\text{Na}_{2/3}\text{FeO}_2$ does not exist. $\text{Na}_{2/3}\text{Fe}_y\text{Mn}_{1-y}\text{O}_2$ phases are interesting from a fundamental viewpoint because during charging first Mn^{3+} is oxidized to Mn^{4+} at potential below 4.1 V vs. Na/Na^+ , and when the charging potential exceeds 4.1 V, Fe is oxidized from Fe^{3+} to the unstable high-spin-state Fe^{4+} . These results were confirmed by XAS spectroscopy. The thermal behavior of various states of charge of $\text{Na}_x\text{Fe}_{1/3}\text{Mn}_{2/3}\text{O}_2$ was studied in detail. As expected, charging, i.e., lower x , results in larger heat generation. Although the heat release itself was comparable to or even exceeded that of the reference $\text{Li}_{0.5}\text{CoO}_2$ material, there was no heat release below 330 °C. In addition, the exothermic peaks were not sharp, but relatively broad, which means heat dissipation might be eased in comparison with $\text{Li}_{0.5}\text{CoO}_2$.

Chapter 4 focuses on the heat stability of hard carbon C1600 used as an anode for Na-ion batteries. Only hard carbons with faulty structures and wide intercalation spaces can be used as anodes for Na-ion batteries because large Na^+ ions cannot intercalate in the interlayer spaces of highly crystallized graphite and thus can be used only as anodes for Na-ion batteries. In fact, five types of hard carbons, prepared in the temperature range 1000 - 2000 °C, have been reported so far. Samples prepared at 1600 °C are superior because they have the largest reversible capacity. Four types of electrolyte were investigated in this study: 1 M $\text{NaClO}_4/\text{EC-DMC}$, 1 M NaClO_4/PC , 1 M $\text{NaPF}_6/\text{EC-DMC}$, and 1 M NaPF_6/PC . The 1 M $\text{NaClO}_4/\text{EC-DMC}$ electrolyte showed the best electrochemical performance, i.e., the highest reversible capacity and best cycle life. However, perchlorate-based organic electrolytes are generally considered inappropriate for large-scale applications. Accordingly, NaPF_6 shows smaller exothermic heat generation at the expense of reduced electrode performance.

Chapter 5 summarizes the data obtained in this thesis.