論文の内容の要旨

Phase diagram, transport property and materials exploration of iron-based cathode materials for lithium/sodium ion batteries

（リチウム・ナトリウムイオン電池用鉄系正極材料の相図、輸送特性、及び新規材料探索に関する研究）

氏名　盧　潔晨

Introduction

Rechargeable lithium ion batteries, as the key components of consumer electronic devices, electric vehicles and electric energy storage systems, are now penetrating into our modern life. Up-to-date lithium ion batteries are ten times cheaper than the first commercial ones introduced by Sony in 1991. But further reducing their costs seems to be extremely hard due to the limitation and high price of raw materials. One of the most promising strategies to reduce the costs is to use transition metal iron instead of cobalt as the redox center. Iron is the fourth most abundant in the earth's crust and the price is 1/100 of that of cobalt. Besides, iron is nontoxic and benign to the environment. Another possible strategy to reduce the costs is to change the charge carrier from expensive Li to cheap Na. Although the voltage and capacity will be slightly reduced, the costs will be greatly cut down. In the field of large-scale stationery energy storage, sodium ion battery is considered to be a very promising candidate.

In this research, two typical intercalation frameworks (olivine and alluaudite) are investigated as the cathodes for lithium/sodium ion batteries. Several basic issues such as transport property, guest ion effect on the phase diagram and polyanion substitution effect on the voltage were discussed. In part I, the reason for the high rate capability of olivine $LiFePO_4$ was clarified (topic 1). And the guest ion exchange from Li to Na in olivine framework was proved to critically change the phase diagram (topic 2). In part II, the intrinsic fast ionic transport property of SO_4-based alluaudite framework was proved, explaining the high rate capability (topic 3). In the last topic, the polyanionic solid-solution phases with tunable voltage and capacity were found in alluaudite framework (topic 4).

Part I Transport property and phase diagram of olivine AFePO$_4$ (A=Li, Na)

Topic 1: Increased conductivity in the metastable intermediate in Li$_x$FePO$_4$ electrode

Recently, using in situ X-ray diffraction during the high rate charge/discharge process, the non-equilibrium single-phase transition behavior of nanoparticle $LiFePO_4$ under high current rates was reported and metastable solid solution phases are claimed to be formed at the two-phase interface [1].

The scattering of the $LiFePO_4$ conductivity data resulting from the extrinsic effects such as carbon residue, conductive impurities and instability of the intermediate phase has troubled and confused scientists for a long time. In our present study, pure

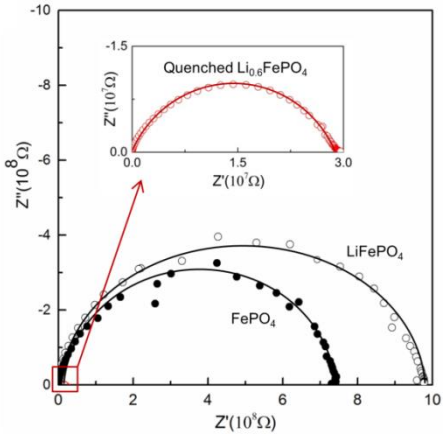

Figure 1. Representative Nyquist plots of carbon-free $LiFePO_4$, carbon-free $FePO_4$ and quenched $Li_{0.6}FePO_4$ samples at 340 K.

carbon-free $LiFePO_4$ and $FePO_4$ were prepared using carbon-free precursors and controlling sintering parameters, and the intrinsic conductivity of quenched single phase Li_xFePO_4 ($x = 0.6$) was measured for the first time.

Figure 1 shows representative Nyquist plots of carbon-free $LiFePO_4$, carbon-free $FePO_4$, and quenched $Li_{0.6}FePO_4$ samples measured at 340 K in the frequency range from 10^6 to 10^{-2} Hz. Of particular interest is that the resistance of the quenched single-phase $Li_{0.6}FePO_4$ was approximately 2 orders of magnitude smaller than those of the two end-members ($LiFePO_4$ and $FePO_4$) at 340 K. This increased conductivity of intermediate phase $Li_{0.6}FePO_4$ should be attributed to the increased carrier density resulting from mixed valence state of $Fe^{2+/3+}$ and higher Li ion/vacancy concentration.

Topic 2: Phase diagram of olivine Na_xFePO_4

Phase behavior of olivine Li_xFePO_4 has been under concentrated scrutiny. Electrochemical activity of Na_xFePO_4 in the olivine phase was first reported by Moreau *et al.* [2]. The charge/discharge profile shows two plateaus in charging and one plateau in discharging, this prompts one to assume two-phase reactions for the two plateaus in the charging curve [2], with $Na_{x\approx0.7}FePO_4$ as the intermediate phase. To our knowledge, until now there has been no in-depth discussion about the phase diagram of the $FePO_4$/$NaFePO_4$ system.

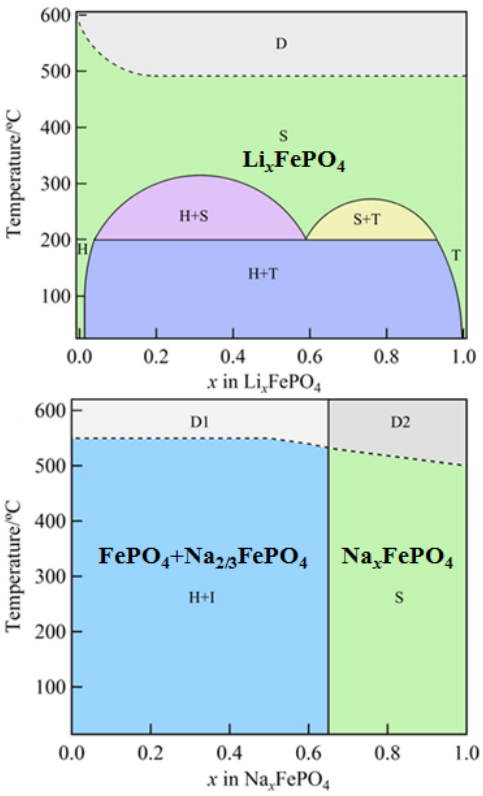

Figure 2. Phase diagram of Li_xFePO_4 and Na_xFePO_4.

Figure 2 compares the phase diagram of Li_xFePO_4 [3]and Na_xFePO_4. In $LiFePO_4$, there is a eutectic point at 2/3. When the temperature reaches above 300°C, two-end members form solid solution phases. On the contrary, in Na_xFePO_4, at room temperature, the phase diagram consists of two regions. For $x<2/3$, phase separation into $FePO_4$/$Na_{2/3}FePO_4$ was found to be favorable, while for $x>2/3$, solid-solution phase Na_xFePO_4 is the ground state. Temperature dependent XRD found that the phase diagram at room temperature firmly maintained until 500°C. Above 500°C, $NaFePO_4$ converts to the ground state maricite structure, while Na_xFePO_4 decomposes to variety of products.

Considering the lattice mismatch between two end members, we can have a more intuitive understanding of the phase diagram. The lattice shrink from $NaFePO_4$ to $FePO_4$ is much larger than Li case, It is very reasonable that there exists intermediate phase to buffer this large lattice mismatch. In sodium case the formation of intermediate phase is favored. Therefore, there phase change in Na case is different from Li case.

Part II: Alluaudite compound as sodium-ion battery cathode

Topic 3: Ionic and electronic transport in alluaudite $Na_{2+2x}Fe_{2-x}(SO_4)_3$

Recently, Yamada group reported a new alluaudite-type sulfate polyanion compound $Na_{2+2x}Fe_{2-x}(SO_4)_3$, as a promising cathode material for sodium ion batteries [4]. Without further optimization procedures

such as nanosizing and in-situ carbon coating through pyrolysis of carbon precursors, high reversible capacity of 85% and 75% of the initial capacity can be delivered at 2C and 10C, respectively. Here, we investigated the intrinsic ionic and electronic transport in this compound which explains it high-rate capability.

The temperature-dependent ionic conductivity and electronic of alluaudite $Na_{2.56}Fe_{1.72}(SO_4)_3$ in the range of 300 to 623 K was shown in figure 3a. A linear relation of log σ versus 1000/T, following the Arrhenius equation $\sigma T = \sigma_0 \exp(-E/RT)$ can be observed. The activation energy of ionic conduction was estimated to be 500 meV, close to calculated diffusion barrier between Na2 sites (550 meV). In the whole temperature range, the total conductivity of alluaudite $Na_{2.56}Fe_{1.72}(SO_4)_3$ shows approximately 2 orders of magnitude higher than the electronic conductivity, confirming that the ionic conduction dominates the transport property.

In figure 3b, as polaron hopping dominates the whole transport property of olivine $LiFePO_4$, the total conductivity and the electronic conductivity are almost identical. The activation energy was estimated to be 620 meV, and the electronic conductivity is 5×10^{-11}S/cm at room temperature. The extrapolated electronic conductivity of alluaudite $Na_{2.56}Fe_{1.72}(SO_4)_3$ at 298K is 2×10^{-9} S/cm, which is much higher than the 5×10^{-11} S/cm value of olivine $LiFePO_4$.

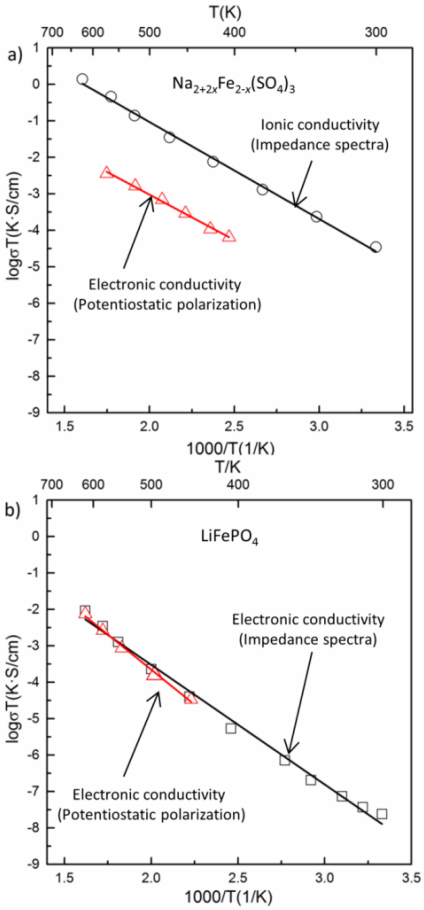

Figure 3. Temperature-dependent ionic and electronic conductivities of a) alluaudite $Na_{2.56}Fe_{1.72}(SO_4)_3$ and b) olivine $LiFePO_4$.

Topic 4: Polyanionic solid-solution cathode in alluaudite system

In the search for new intercalation frameworks for sodium ion battery, alluaudite compound has been attracting researcher's attention since it was first found in natural minerals. However, previous studies have shown that alluaudite compounds such as $NaFe_3(PO_4)_3$, $NaMnFe_2(PO_4)_3$ and $Na_2FeMn_2(PO_4)_3$ [5] can only be electrochemically cycled with low capacity (< 60mAh/g) and operating voltage (< 3.0V vs Na^+/Na).

On the contrary, recently a SO_4-based alluaudite compound $Na_{2+2x}Fe_{2-x}(SO_4)_3$ was reported [4] in our group as a promising cathode material for sodium ion batteries. The reversible capacity reaches 100mAh/g and the Fe^{3+}/Fe^{2+} redox potential is registered as the highest ever 3.8 V vs Na^+/Na due to the inductive effect of SO_4 polyanion. Enlightened by the pioneering work about tuning the redox potential by polyanion substitution in NASICON framework [6], we attempted to seek for better intercalation compounds by mixing PO_4 and SO_4 polyanions in the alluaudite framework.

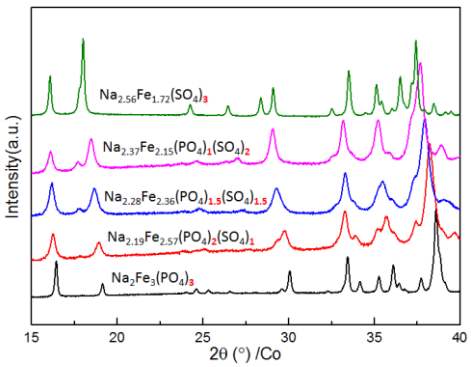

Figure 4. XRD of polyanionic solid-solution phases in alluaudite framework.

Figure 4 is the XRD after sintering at 350°C for 35 hours with various mixing PO_4:SO_4 ratio. Continuous peak shifts to lower degrees are obvious when SO_4 was introduced into alluaudite $Na_2Fe_3(PO_4)_3$. All the peaks can be indexed with the C2/c space group.

All of the polyanionic solid solution phases $Na_xFe_y(PO_4)_z(SO_4)_{3-z}$ are electrochemically active and show enhanced capacity and elevated operating voltage than pristine $Na_2Fe_3(PO_4)_3$ due to the inductive effect of SO_4. The capacity of $Na_{2.28}Fe_{2.36}(PO_4)_{1.5}(SO_4)_{1.5}$ reaches 113mAh/g, even higher than the pristine $Na_{2.56}Fe_{1.72}(SO_4)_3$.

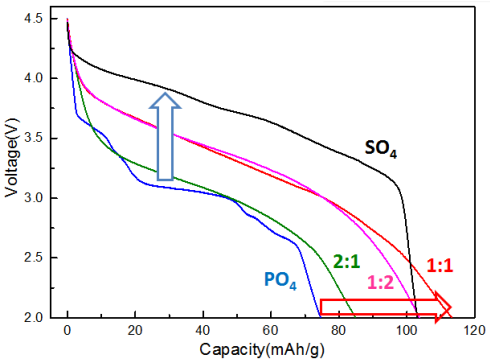

Figure 5. Charge-discharge profiles of solid-solution phases.

Conclusion

This research focuses on Fe-based cathode materials for lithium/sodium ion batteries. Two intercalation host frameworks (olivine and alluaudite) are investigated. In olivine framework, transport property of $LiFePO_4$ and phase diagram of $NaFePO_4$ was discussed. In alluaudite framework, transport property of $Na_{2.56}Fe_{1.72}(SO_4)_3$ and new polyanionic solid-solution phases $Na_xFe_y(PO_4)_z(SO_4)_{3-z}$ were explored.

In the olivine framework, it was found the single-phase transformation mechanism not only relaxes the interfacial strain energy but also enhances the intrinsic charge transport, enabling the high-rate capability of olivine Li_xFePO_4. Then we focused on the Na counterpart of olivine $LiFePO_4$. It was found that due to the larger Na^+ radius, guest ion exchange from Li to Na in the same framework results in a totally different phase diagram.

In the alluaudite framework, we investigated the intrinsic ionic and electronic conductivities. We found that alluaudite $Na_{2.56}Fe_{1.72}(SO_4)_3$ was ionic conduction and the ionic conductivity is more than 4 orders of magnitude higher than that of $LiFePO_4$, which explains its high-rate capability. In the last topic, for the first time, continuous polyanionic solid-solution phases $Na_xFe_y(PO_4)_z(SO_4)_{3-z}$ in the whole mixing ratio range can be prepared. Besides, the voltage gradually elevate when the fraction of SO_4 increases. The capacity of the polyanionic solid-solution phases $Na_xFe_y(PO_4)_z(SO_4)_{3-z}$ can also be tuned and the maximum capacity can be obtained when PO_4:SO_4=1:1.

References

[1] H. Liu, F.C. Strobridge, O.J. Borkiewicz, K.M. Wiaderek, K.W. Chapman, P.J. Chupas, C.P. Grey, Science, 344 (2014).

[2] P. Moreau, D. Guyomard, J. Gaubicher, F. Boucher, Chem. Mater., 22 (2010) 4126-4128.

[3] J.L. Dodd, R. Yazami, B. Fultz, Electrochemical and Solid State Letters, 9 (2006) A151-A155.

[4] P. Barpanda, G. Oyama, S.-I. Nishimura, S.-C. Chung, A. Yamada, Nat. Commun., 5 (2014) 4358-4365.

[5] T.J. Richardson, J. Power Sources, 119-121 (2003) 262-265.

[6] A.K. Padhi, V. Manivannan, J.B. Goodenough, J. Electrochem. Soc., 145 (1998) 1518-1520.