Communication

Electrochemical Properties of Iron Oxides as High-Capacity Negative Electrodes for Lithium Secondary Batteries

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α-Fe$_2$O$_3$ fine powder that the particle size is ca. 0.3 μm were estimated as negative electrode materials for lithium cells using lithium-ion conductive organic electrolytes. The sheet-type electrodes were fabricated by using the two differential binder solutions of conventional polyvinylidene fluoride (PVDF) and polyamic acid solutions dissolved in N-methyl pyrrolidinone (NMP). The electrodes exhibited high capacities of over 1000 mAh g$^{-1}$ corresponding to 6 Li per Fe$_2$O$_3$ at potentials ranging from the open circuit potential to 0.005 V (vs. Li/Li$^+$) in the first charging (lithium insertion) process. First discharge capacities during lithium extraction process exhibited high capacities of over 700 mAh g$^{-1}$. However, cycle life of α-Fe$_2$O$_3$ electrodes made using the conventional binder (PVDF) solution was poor. On the other hand, Fe$_2$O$_3$ electrodes made using polyamic acid solution showed better cycling performance than electrodes made from the PVDF binder solution during charge-discharge cycles and high charge-discharge efficiencies (coulombic efficiencies) over 85%. We suggest that new binders will be needed to improve cycle performance and first charge-discharge efficiencies of high-capacity iron oxide negative electrodes.

Key Words: Lithium Secondary Batteries, Negative Electrode, Iron Oxide, Polyamic Acid

1 Introduction

Lithium ion batteries based on the C/LiCoO$_2$ with high energy densities have been developed as small energy devices for mobile electronic devices such as cellular phones and notebook computers. Recently, there has been a rapid development of large lithium ion batteries as energy devices for electric vehicles. Graphite negative electrode is achieving theoretical capacity. Research and development of the high capacity negative electrode materials such as alloys and oxides are carrying out in the world-wide. These alloys undergo large volume changes during lithium insertion-extraction. In general, although the volume change of oxide materials during lithium insertion-extraction is smaller than that of alloy electrodes, the first charge-discharge efficiency of the former is larger than that of the latter. Iron oxides are inexpensive and harmless materials, so it would be very interesting if they could be used to develop electrode materials for large lithium ion batteries.

Many researchers have reported that α-Fe$_2$O$_3$ worked as high-capacity active materials in lithium cells.1-37 Poizot et al. reported that nanosized transition metal oxides worked as high-capacity negative electrode materials because the transition metal oxides enable an electrochemical conversion reaction such as M$_2$O + 2yLi$^+$ + 2y e$^- \Leftrightarrow xM + yLi_2O$ (transition metal M = Fe, Co, Ni, Cu etc.).4 We have reported that α-Fe$_2$O$_3$ fine powder were synthesized by mechanical milling of α-FeOOH and the α-Fe$_2$O$_3$ electrodes made using the binder solutions of conventional polyvinylidene fluoride (PVDF) worked as high-capacity negative electrode materials but the electrodes showed a poor cycle life.5 Recently, Jing Li et al. described the importance of binder choice of α-Fe$_2$O$_3$ electrode material demonstrating large volume expansion during conversion reaction with lithium.27

In this study, we compared charge-discharge behavior for α-Fe$_2$O$_3$ sheet-type electrodes made using the two differential binder solutions of conventional polyvinylidene fluoride (PVDF) and polyamic acid dissolved in N-methyl pyrrolidinone (NMP).

2 Experimental

The test electrode was prepared from α-Fe$_2$O$_3$ powder (85 wt % by weight), acetylene black powder (5 wt % by weight), and binder (10 wt % by weight). The α-Fe$_2$O$_3$ powder and acetylene black powder were added to polyvinylidene fluoride (PVDF) binder solution or polyamic acid (Binder A) binder solution dissolved in N-methyl pyrrolidinone (NMP). After the mixture was painted uniformly on a copper sheet, it was dried at about 80°C in air and pressed for use as a working electrode. Then the electrodes were dried in a vacuum at 120°C. A lithium sheet (approximately 500 μm thick) was used as a counter. The electrolyte was 1 mol dm$^{-3}$ LiPF$_6$ in an organic liquid mixture consisting of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 volume ratio). The charge-discharge tests with a constant current density were carried out by using the 2032 coin cells at room temperature. The charge-discharge cut-off voltage was 0.005 and 3.0 V versus Li/Li$^+$.

3 Results and Discussion

Figure 1 shows first charge-discharge curves for α-Fe$_2$O$_3$/PVDF and α-Fe$_2$O$_3$/Binder A electrodes. “Binder
A" will exit as intermediates of polyimide under this experimental condition. We suggested that a part of polyamic acid should be imidized by heat treatment. At presence, it is not clear about ratio of imidization of polyamic acid working as binder. In addition, molecular structures of “Binder A” may vary with electrochemical reaction of α-Fe₂O₃ electrode for charge-discharge. We are investigating electrochemistry behavior (e.g. lithium insertion-extraction) of “Binder A” in detail. The charge-discharge curves are similar at the two electrodes under constant current density of 0.2 mA cm⁻². Charge capacity (lithium insertion process) and discharge capacity (lithium extraction process) of α-Fe₂O₃/PVDF electrode are ca. 1000 mAh g⁻¹ and 600 mAh g⁻¹, respectively. On the other hand, those of α-Fe₂O₃/Binder A are ca. 1200 mAh g⁻¹ and 840 mAh g⁻¹, respectively. The electrodes exhibited high capacities of over 1000 mAh g⁻¹ corresponding to 6 Li per Fe₂O₃ at potentials ranging from the open circuit potential to 0.005 V (vs. Li/Li⁺) in the first charging process. The capacities of α-Fe₂O₃/Binder A electrode were higher than those of α-Fe₂O₃/PVDF electrode. First coulombic efficiencies of α-Fe₂O₃/PVDF and α-Fe₂O₃/Binder A electrodes were ca. 59% and ca. 70%, respectively. The improvement of electrode properties, such as capacity and coulombic efficiency, was confirmed on sheet-type electrode prepared by using polyamic acids dissolved in N-methyl pyrrolidinone (NMP). Though α-Fe₂O₃/PVDF electrode lost its original shape, there was no apparent change in α-Fe₂O₃/Binder A. The adhesion of the active material to current collector would have been improved.

Figure 2 shows discharge capacity degradation of α-Fe₂O₃/PVDF and α-Fe₂O₃/Binder A sheet-type electrodes. For α-Fe₂O₃/PVDF electrode, a remarkable drop capacity was confirmed. On the other hand, α-Fe₂O₃/Binder A electrode showed an excellent cycle performance with high capacity of 730 mAh g⁻¹ during 30 cycles.

First charge-discharge curves of α-Fe₂O₃/Binder A electrodes when the discharge current densities are changed into 0.01, 0.05, and 0.2 mA cm⁻² under constant charge current density of 0.2 mA cm⁻² are shown in Fig. 3. Both discharge capacity and the coulombic efficiencies were plotted as a function of discharge current densities in Fig. 4. The discharge capacity has decreased with an increase in the discharge current density. The coulombic efficiencies at discharge current densities of 0.01, 0.05, and 0.2 mA cm⁻² shows ca. 87, 75 and 71%, respectively. The coulombic efficiency has increased with the decrease in the discharge current density. The coulombic efficiency of the α-Fe₂O₃ electrode indicated a value close to the coulombic efficiency of natural graphite negative electrode (ca. 90%). It might have been shown that the α-Fe₂O₃ negative electrode materials with a conversion reaction had excellent electrochemical reversibility and high coulombic efficiency during first cycle, compared with high-capacity oxide negative electrodes such SnO-based glass (amorphous). The discharge capacity more than the theoretical capacity of 1007 mAh g⁻¹ according to conversion reaction was indicated during
Fig. 4 The dependence of discharge capacities and the coulombic efficiencies for discharge current density of α-Fe$_2$O$_3$/Binder A electrodes.

Fig. 5 The relationship between cycle performance and sheet thickness of α-Fe$_2$O$_3$/Binder A electrodes.

current density of 0.01 mA cm$^{-2}$. The possibility of a reversible electrochemical reaction by the interaction of electrolyte and the electrode was suggested. We are examining the electrochemistry behavior on interphase of electrode/electrolyte.

Figure 5 shows the relationship between cycle performance and thickness of the electrodes. Since thin electrode shows an excellent cycle performance, it would be very important to carry out optimization of the electrode structures.

α-Fe$_2$O$_3$ sheet-type electrodes made using polyamic acid binder are one of the promising candidates as conversion negative electrodes for lithium secondary batteries. At present we are investigating the function of the binder in α-Fe$_2$O$_3$ sheet-type electrode and making clear the mechanism of the electrode reaction.

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References

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