K⁺- β -Ferrite as a New Cathode Active Material for Lithium Secondary Battery

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Abstract. The possibility of K⁺- β -ferrite (K_{1.33}Fe₁₁O₁₇) as a cathode active material for lithium secondary battery was investigated. It was confirmed that lithium ions certainly inserted into K⁺- β -ferrite. Li content y in Li_yK_{1.33}Fe₁₁O₁₇ was increased up to 6.79. Most of lithium ions seem to enter into γ -Fe₂O₃ layers of K⁺- β -ferrite, because alkali layers could contain only 2 alkali ions for Fe₁₁O₁₇. According to the cyclic voltammogram, good reversibility was observed in insertion and extraction of lithium ions. The discharge potential decreased to 1.5V vs. Li/Li⁺ and the charge potential increased to 4.5V vs. Li/Li⁺. The capacity of K⁺- β -ferrite has reached 200Ah/kg.

1. INTRODUCTION

Recently, many researches of cathode active materials for lithium secondary batteries are carried out widely. Iron compounds [1] have attracted a great deal of research because of its economical and environmental advantages in comparison with the conventional cathode active materials, such as LiCoO₂, LiNiO₂, and V₂O₅. In addition, the iron compounds have a possibility of lowering the battery cost. K⁺- β -ferrite is a β -alumina analogue and has a layer structure consisting of potassium layers and γ -Fe₂O₃ layers [2]. The composition of K⁺- β -ferrite is written as K_{1+x}Fe₁₁O₁₇ (x=0.2-0.5). On the other hand, it is well known that lithium ions are inserted into the defect spinel γ -Fe₂O₃ by the reduction of Fe³⁺ [3]. The γ -Fe₂O₃ layer in K⁺- β -ferrite is constructed from only four layers of close-packed oxygen. Therefore, a large amount of lithium ions is expected to be smoothly inserted into γ -Fe₂O₃ layers through the loose packed potassium layer. Generally, extraction of lithium ions from γ -Fe₂O₃ is very slow. However, γ -Fe₂O₃ layer in K⁺- β -ferrite is very thin (ca. 6 Å). The extraction of lithium ions from γ -Fe₂O₃ layer is also expected to be smoothly performed in K⁺- β -ferrite.

In the present work, lithium insertion and extraction for K⁺- β -ferrite and discharge/charge test for the lithium secondary battery were performed, using electrochemical cell.

2. EXPERIMENTAL

K₂CO₃ and α -Fe₂O₃ powders were mixed with the composition of K⁺- β -ferrite. The mixed powder was calcined at 900°C for 1 hr and the powder was then heated at 1200°C for 5 hr to produce K_{1.33}Fe₁₁O₁₇.

The electrochemical insertion of lithium ions into K⁺- β -ferrite was examined using a two-electrode cell. The cathode consisted of K⁺- β -ferrite powder (90wt%) and an acetylene black powder (10wt%) (total weight: 120mg). The lithium anode and the cathode were separated by glass-fiber pads that had been saturated with the electrolyte 1M solution of LiClO₄ in propylene carbonate (PC). The cell was discharged under a constant resistance at 25°C. A three-electrode cell for cyclic voltammetry (C.V.) and for constant current test was also constructed. The working electrode and cathode consisted of a pressed powder pellet containing K⁺- β -ferrite (20 mg), an acetylene black powder (15.0mg), an artificial graphite powder (5.0mg), and PTFE binder (16.0mg). The current collector was an Mo mesh (1.0cm²). The counter and reference electrode were made by pressing lithium lump onto expanded Ni mesh. The discharge and charge test was carried out at a constant current density of 0.1mA/cm². All cells were constructed in a glove box with Ar

atmosphere.

3. RESULTS AND DISCUSSION

3.1 Lithium insertion into $K^+ - \beta$ - ferrite

The discharge curves of the test cell under 50 and 100k Ω loads at 25°C are respectively shown in Figure 1. The open - circuit voltage of the test cell indicated 3.3V. Connecting a constant resistance between anode and cathode, Fe^{3+} in $K_{1.33}Fe_{11}O_{17}$ is reduced to Fe^{2+} . At the same time, lithium ions are inserted into $K_{1.33}Fe_{11}O_{17}$ from the electrolyte. This lithium insertion reaction can be written as

In the case of 50k Ω , the cell voltage slowly decreased to 1.7V and kept to this value until 11400min. At this point, the Li content y in equation (1) was calculated by the current integration as 2.60, which was in agreement with that obtained by atomic absorption analysis. Each peak of the x-ray diffraction pattern of lithium inserted $K_{1.33}Fe_{11}O_{17}$ was still sharp. This means that lithium ions enter into $\gamma - Fe_2O_3$ layers of $K_{1.33}Fe_{11}O_{17}$ without destruction of the β - structure. Most of lithium ions seem to enter into $\gamma - Fe_2O_3$ layers of $K_{1.33}Fe_{11}O_{17}$, because alkali layers theoretically contain only 2 ions for $Fe_{11}O_{17}$.

3.2 Insertion/extraction of Li in $K^+ - \beta$ - ferrite and capacity of the cell

Figure 2 shows cyclic voltammogram of $K_{1.33}Fe_{11}O_{17}$ in 1M $LiClO_4$ PC electrolyte. Good reversibility was observed in the C. V. curves. Except for 1st cycle, every reduction curve was almost same. The quantity of electricity corresponding to the redox reaction was not decreased after 10th cycle. Figure 3 shows the discharge/charge curves for $Li/K_{1.33}Fe_{11}O_{17}$ secondary cell. The discharge curve was characterized by the potential plateau at ca. 1.5V vs. Li/Li^+ . The discharge capacity shown in Fig. 3 has reached 200 Ah/kg, which corresponds to the amount of Li insertion $y=6.79$ in $Li_yK_{1.33}Fe_{11}O_{17}$. The β -structure was still not destroyed in the x-ray diffraction pattern of discharged $K^+ - \beta$ - ferrite. The charge potential was within the electrochemical potential window of the electrolyte. It is concluded that $K^+ - \beta$ - ferrite is considered to be one of the promising cathode materials for lithium secondary battery.

References

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Figure 1: Discharge curves for $Li/K_{1.33}Fe_{11}O_{17}$ cell at 25°C. (a) 100k Ω , (b) 50k Ω .

Figure 2: Cyclic voltammograms for $K_{1.33}Fe_{11}O_{17}$ at 25°C. Sweep rate : 2 mV s⁻¹. Sweep range : 1.9 ~ 4.5V vs. Li/Li^+ .

Figure 3: Discharge and charge curves for $Li/K_{1.33}Fe_{11}O_{17}$ secondary cell at 25°C. Current Density : 0.1mA · cm⁻².