Synthesis and charge-discharge properties of 2LiF-NiF₂ composite and Li₂NiF₄ as a cathode material for Li-ion batteries.

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2LiF-NiF₂ composites are synthesized by the mechanical milling of LiF and NiF₂ in a molar ratio of 2 : 1 for 72 h, and Li₂NiF₄ are synthesized by calcination at 673 K. The synthesized samples are investigated by XRD, cyclic voltammetry, and charge-discharge measurements. XRD peaks of the 2LiF-NiF₂ composite are broad and the discharge capacity is 44 mAh/g at 0.05 C for voltages of 2.0–4.8 V. After calcination, the XRD peaks become sharp and most peaks are agreement with Li₂NiF₄. Li₂NiF₄ obtained by calcination shows a discharge capacity of 96 mAh/g at 0.05 C and 118 mAh/g at 0.02 C for voltages of 2.0–4.8 V. 2LiF-NiO composites are also obtained by the milling of LiF and NiO in a molar ratio of 2 : 1 for 72 h, and shows a discharge capacity of 146 mAh/g. The discharge capacity of 2LiF-NiO at 3C was maintained that of 70 % of 0.1C.

Key words: Cathode material, Lithium-ion secondary battery, Mechanical milling, Composite material

1. INTRODUCTION

Lithium-ion secondary batteries exhibit the highest specific energies of the various secondary batteries and have been extensively studied in recent years to use as large-scale energy-storage devices such as electric vehicles [1,2]. Now commercial lithium-ion batteries use the lithium transition metal oxides and the lithium transition metal phosphate, such as LiCoO₂, LiMn₂O₄, and LiFePO₄, as a cathode material [3–6]. Metal trifluorides, such as iron fluoride and manganese fluoride, show large theoretical capacities and have been studied thoroughly as cathode materials. Iron trifluoride, FeF₃, is one such compound that shows a high energy density and can be used as an iron-based electrode material [7,8]. FeF₃ is an insulator due to the strong ionicity of the Fe–F bond. Therefore, a composite of FeF₃ and conductive carbon is synthesized and annealed for a short time to improve the electrode characteristics of FeF₃, and showed a high discharge capacity [9–11]. Previous studies have shown that partial oxidation of FeF₃ improved the rate capability and cycle performance of FeF₃ as a cathode material without requiring the formation of a composite of conductive carbon and FeF₃ [12]. Partial oxidation generated a thin layer of Fe₂O₃ which increases the conductivity of FeF₃, indicating that the presence of oxides can result in high discharge capacities. However, FeF₃ and MnF₃ do not include Li⁺ ions and these compounds must be pre-doped with of Li, in order to be made suitable for use as cathode materials for general Li-ion secondary batteries. LiF-Fe composites have been synthesized and characterized to produce materials that can be used in the cathodes of Li-ion secondary batteries [13]. On the other hand, Li₂NiF₄ and LiMnF₄ are known as transition metal fluorides containing Li⁺ ion. The charge-discharge process with conversion reaction of Li₂NiF₄ synthesized by the spray pyrolysis is reported [14]. In this study, composites of LiF and NiF₂ were prepared by milling

and studied by XRD and charge-discharge characteristics. The characteristics of Li₂NiF₄ synthesized at low temperature by using the LiF-NiF₂ composite as a raw material were also investigated. In addition, a composite of LiF-NiO having a composition ratio of Li and Ni of 2 : 1 was prepared, and characteristic changes due to partial oxidation were investigated.

2. EXPERIMENTAL

NiF₂ was obtained by adding Ni(OH)₂ to an aqueous HF solution and evaporating the solvent. The 2LiF-NiF₂ and 2NiF-NiO composites were synthesized by subjecting LiF and NiF₂ or NiO in a molar ratio of 2 : 1 to a mechanical ball-milling, which was performed using a planetary ball-milling apparatus (P-7; Fritsch Japan Co., Ltd.) at a rotational speed of 650 rpm for 72 h in an Ar atmosphere. A zirconia vessel and ball were used to perform the planetary ball milling. The obtained samples were characterized by XRD analysis were recorded using a Rigaku Rad-B system with Cu-Kα radiation. Li₂NiF₄ was obtained by calcination of the 2LiF-NiF₂ composites at 673 K in vacuum. The charge-discharge measurements were performed using a stainless-steel cell for voltages of 2.0 – 4.8 V (versus Li/Li⁺). The test cell was composed of a sheet of the synthesized composite as the cathode, a piece of lithium foil as the anode, and 1 M LiPF₆-EC/DEC (1:1 by volume) as the electrolyte. The cathode sheet was fabricated using the synthesized composite sample (70 wt.%), KETJENBLACK (20 wt.%), and polyvinylidene fluoride (10 wt.%).

3. RESULTS AND DISCUSSION

3.1 XRD patterns of 2LiF-NiF₂

Figure 1 shows XRD patterns of obtained samples. The XRD pattern of (a) and (b) are those of the LiF-NiF₂

composites obtained by the mechanical milling of LiF and NiF₂ for 12 hours and 72 hours. LiF and NiF₂ peaks were observed except for NiF₂ (001) diffraction peak for these composites as shown in Figure 1 (a) and (b). In our studies on other composites, it has been shown that the diffraction peaks are broadened due to crystal distortion by long-time milling and that the structure became similar to the rock-salt type from the original structure [15,16]. It is considered that the diffraction peaks became broad and NiF₂ (001) peak disappeared due to similar change in NiF₂. No significant change in the XRD pattern was observed due to the difference in the milling time. The XRD pattern of Figure 1(c) was obtained in the composite annealed at 673 K for 1 minute after milling for 72 hours. The diffraction peaks became sharp as compared with before annealing. The peaks indicated by circles in Figure 1(c) was the diffraction peaks of Li₂NiF₄, and it was found that the objective Li₂NiF₄ was synthesized although there was a small amount of impurity peak. Milling of LiF and NiF₂ generated a new diffraction peak, and annealing of the milled sample yielded Li₂NiF₄. Therefore, it is considered that most of the diffraction peaks in Figure 1 (a) and (b) correspond to those of Li₂NiF₄ and the 2theta is slightly different from those of crystalline Li₂NiF₄ due to the disorder of cation sites and the milling.

Fig. 1 XRD patterns of the 2LiF-NiF₂ composites milled for (a)12h and (b)72h, and (c) annealed at 673 K. Circles indicate the peaks of Li₂NiF₄, and triangles indicate the peaks of LiF.

3.2 Charge-discharge measurements of 2LiF-NiF₂

The charge-discharge performances of the 2LiF-NiF₂ composites milled for 72 h and annealed at 673 K after milling for 72 h, respectively, were tested by fabricating half-cells using Li metal sheet as the anode. Figure 2 shows the discharge curves for the 1st and 2nd cycle at 0.05 C rate, and 3rd and 4th cycle at 0.02 C. Only a small discharge capacity could be observed in the measurement at higher C-rate. The discharge capacity was about 40 mA h g⁻¹ for the sample milled for 72 h and 117 mA h g⁻¹ for the annealed sample. Large discharge capacity could be confirmed for some composites in our previous study, but in this LiF-NiF₂, enough discharge could not be confirmed by the milling process alone. As shown in the powder XRD measurement results mentioned above, Li₂NiF₄ was produced by annealing. The Li₂NiF₄ seems to show a larger discharge capacity than the sample of only grinding and mixing. However, high voltage and discharge curve with obvious plateau as observed in typical oxide cathode materials was

not obtained. When all the lithium ions in the sample contribute to charge-discharge process, the theoretical discharge capacity is 360.8 mAh/g. The obtained discharge capacity in this measurement was very low. This is considered to be due to the low electron conductivity of the fluoride, 2LiF-NiF₂ composite and Li₂NiF₄, whose value was measured to be less than 10⁻⁷ S/cm. In order to improve electron conduction paths in the active material, conductive carbon was increased or complexed, but they did not lead to an increase in discharge capacity.

Fig. 2. Charge-discharge curves of the 2LiF-NiF₂ composites formed by (a)milling for 72 h and (b) annealing at 673 K at a 0.05 C (1st and 2nd cycle) and 0.02 C (3rd and 4th cycle) rate.

3.3 Synthesis and XRD of 2LiF-NiO

2LiF-NiF₂ composite and Li₂NiF₄ showed very low electric conductivity. In order to improve the electrical conductivity, we attempted to synthesize 2LiF-NiO composite in which NiF₂ was replaced by NiO. Higher electrical conductivity than 2LiF-NiF₂ is obtained by the replacement, and it is expected that the discharge characteristics will be improved. Figure 3 shows XRD patterns of 2LiF-NiO composite obtained by the mechanical milling of LiF and NiO (LiF : NiO = 1:2) for 72 hours and those of the source materials, LiF and NiO. As shown in Figure 3, the diffraction peaks of 2LiF-NiO are broad, and each diffraction peak is located between the corresponding diffraction peaks of NiO and LiF. SEM measurement and element mapping of this composite confirmed that Ni, O, and F ions distribute uniformly and

that there is no segregation of LiF or NiO. The crystal structures of LiF and NiO are both rock salt type structures, and it is considered that LiF and NiO formed a solid solution by ball milling, and their diffraction peaks shifted. Furthermore, the diffraction peak intensity of the (111) plane at $2\theta = 38^\circ$ became much weaker than that of the (200) plane at $2\theta = 44^\circ$, which also suggests the formation of a solid solution. When Rietveld analysis is performed on the diffraction pattern of 2LiF-NiO shown in Figure 3, the occupancy of Li^+ ion and Ni^{2+} ion at the cation site of rock salt type structure were evaluated to be 0.61 and 0.39, respectively, and they were close to composition ratio of 2LiF-NiO composite. The difference from the composition ratio may indicate that a small amount of LiF which cannot form the solid solution remains.

Fig. 3 XRD patterns of the 2LiF-NiO composite milled for 72 h, LiF, and NiO.

Fig. 4. Charge-discharge curves of the 2LiF-NiO composites at 0.1 C.

3.4 Charge-discharge measurements of 2LiF-NiO

Figure 4 shows the charge-discharge curves of the 2LiF-NiO composite at 0.1 C. The initial discharge capacity is 146 mAh/g. This discharge capacity was large compared to LiF-NiF₂ before substitution, and the voltage of discharge was also high. It is considered that the discharge characteristics are improved because the electric conductivity of composite is increased and a solid solution with LiF is formed by substituting NiF₂ of 2LiF-NiF₂ with NiO. XPS measurements of the composite before and after

the charge-discharge measurement showed that Li was desorbed and Ni^{2+} was oxidized to Ni^{3+} in the charge process, and the reverse reaction proceeded in the discharging process. As expected from the discharge capacity, the presence of Ni^{4+} was not confirmed. Figure 5 shows the discharge curves of 2LiF-NiO composite at 0.1, 0.2, 0.5, 1, 2, and 3 C rates, and the plots of discharge capacity against cycles. The discharge curves of the 2LiF-NiO composite varies with rate, as shown in Figure 5(a), and the discharge capacities of 106 and 64 mAh/g are obtained at 1 and 3 C, respectively. The discharge capacity decreased and the discharge curve became linear with the increase of the rate. The rate capability of the 2LiF-NiO composite were 73 % at 1 C and 44 % at 3 C, and the discharge capacity of 13th and 14th cycles at 0.1 C was held 93 % of the 1st cycle as shown in Figure 5(b). In the 2LiF-NiF₂ composite and Li₂NiF₄ sample, the discharge capacity was obtained very small at higher rate more than 0.1C. The rate capability of the 2LiF-NiO composite was considerably higher than those. Comparing the DC conductivity of only the composite before the addition of the conductive carbon(KB), the conductivity of the 2LiF-NiO composite was more than 10^{-5} S/cm and over 100 times those of LiF-NiF₂ composite and Li₂NiF₄. Therefore, since the conductivity of the 2LiF-NiO composite is considerably higher, the rate characteristic of this composite is considered to be superior to that of 2LiF-NiF₂ and Li₂NiF₄ cathode.

Fig. 5. Discharge curves(a) and discharge capacity(b) of the 2LiF-NiO composites at various rates.

4. Conclusions

2LiF-NiF₂ and 2LiF-NiO were fabricated by the mechanical milling of LiF and NiF₂ or NiO. Li₂NiF₄ was obtained by annealing of 2LiF-NiF₂ composite. In the XRD measurement of 2LiF-NiO, the diffraction peaks of LiF and NiO were integrated by ball milling, and it was found that solid solution of the 2LiF - NiO was formed. In the charge-discharge measurement, the discharge capacity of 2LiF-NiF₂ and Li₂NiF₄ was lower than 100 mAh/g even at 0.05 C and became much lower in higher rate. These low discharge capacities are considered to be due to low electric conductivity. On the other hand, in the 2LiF-NiO composite, the discharge capacity was 146 mAh/g at 0.1 C, and the average discharge voltage was 3.57 V. It is considered that the formation of a solid solution made it possible to charge and discharge process at a high potential. The charge-discharge measurement of the 2LiF-NiO composite showed that the discharge capacity at 3C was maintained that of 70 % of 0.1C and the rate capability were also high.

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