



Synthesis and charge-discharge properties of LiF-NiO composite as a cathode material for Li-ion batteries



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HIGHLIGHTS

- LiF-NiO composites are synthesized by the mechanical milling of LiF and NiO.
- The composites prepared by milling for more than 72 h form a solid solution.
- LiF and NiO milled individually do not exhibit a noticeable discharge capacity.
- The discharge capacity of the LiF-NiO composites increases with the milling time.
- XPS suggests Ni ions are oxidized/reduced repeatedly during charging/discharging.

ARTICLE INFO

Article history:

Received 27 June 2016

Received in revised form

10 August 2016

Accepted 22 August 2016

Keywords:

Cathode materials

Lithium-ion secondary battery

Mechanical milling

Solid solution

ABSTRACT

LiF-NiO composites in a molar ratio of 1:1 are synthesized by the mechanical milling of equal amounts of LiF and NiO for 12–144 h. The synthesized composites are investigated by XRD, charge-discharge measurements, and XPS. The XRD peaks of NiO broaden with an increase in the milling time, while those of LiF disappear. Rietveld analysis shows that the LiF-NiO composites prepared by milling for more than 72 h form a solid solution and that the arrangement of Li⁺ and Ni²⁺ ions in them is disordered. The LiF and NiO samples milled individually do not exhibit a noticeable discharge capacity, while the composites show a large one. Further, the discharge capacity of the LiF-NiO composites increases with the milling time, with the composite prepared by milling for 144 h exhibiting a discharge capacity of 216 mA h g⁻¹ and an average voltage of 3.53 V at 0.05 C for voltages of 2.0–5.0 V. The XPS data suggest that the Ni ions are probably oxidized and reduced repeatedly during the charge-discharge process and that the Ni²⁺ ions are partially oxidized to Ni³⁺ ions during charging to 5.0 V.

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1. Introduction

In recent years, high-performance batteries have attracted a lot of interest, and many such batteries have been developed for commercial use. Rechargeable lithium-ion batteries are being studied extensively, especially because they exhibit the highest specific energy among the various rechargeable batteries available and can be used as large-scale energy-storage devices for powering hybrid and electric vehicles [1,2]. Commercial lithium-ion batteries

use lithium transition metal oxides, such as LiCoO₂, LiMn₂O₄, and LiFePO₄, as the cathode material [3–5]. However, to improve the energy density of these batteries further, the development of alternative cathode materials with high capacities and better voltage characteristics is important.

Metal trifluorides, such as iron fluoride and manganese fluoride, show large theoretical capacities and have been examined thoroughly as positive electrode materials. Iron trifluoride, FeF₃, is one such compound that shows a high energy density and can thus be used as an iron-based electrode material [6]. However, FeF₃ and MnF₃ do not contain Li⁺ ions, and these compounds must be pre-doped with Li, in order to be made suitable for use as cathode materials for general Li-ion secondary batteries. LiF-Fe and LiF/Fe/

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graphene composites, which have been synthesized and characterized previously, show high discharge capacities [7,8]. On the other hand, FeF_3 is an insulator owing to the strongly ionic nature of the Fe-F bond. Therefore, composites of FeF_3 and conductive carbon were synthesized and subjected to annealing for short periods. This enhanced the electrode properties of FeF_3 and resulted in a high discharge capacity [9,10]. In a previous study, FeF_3 was oxidized partially by calcination for a short period in air. This improved the rate capability and cycling performance of FeF_3 as a cathode material without requiring the formation of a composite of conductive carbon and FeF_3 [11]. The partial oxidation of FeF_3 produced a thin layer of Fe_2O_3 , which increased the conductivity of FeF_3 . In addition, it has been reported that NiO-doped NiF_2 exhibits a higher discharge potential and better reversibility than pristine NiF_2 , owing to the increase in the electronic conductivity because of the doping [12].

In this study, we fabricated LiF-NiO composites by the mechanical milling of LiF and NiO and investigated their charge-discharge characteristics at room temperature. NiO does not exhibit a discharge capacity at voltages higher than 3 V (versus Li/Li⁺). Therefore, LiF was added to increase the discharge capacity at higher voltages as well as to increase the energy density, such that the composites would be suitable for use as cathode materials in Li-ion secondary batteries. The structures of the composites were investigated by XRD analysis. The progression of the reaction resulting from the milling process and the arrangement of the Li⁺ and Ni²⁺ ions in the composites were investigated based on a Rietveld analysis of the XRD patterns. Finally, ex-situ XPS was performed to study the oxidation states of the Ni ions during the charge-discharge process.

2. Experimental

The LiF-NiO composites were synthesized by subjecting equal amounts of LiF and NiO to 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 12–144 h in an Ar atmosphere. A zirconia vessel and ball were used to perform the planetary ball milling. LiF and NiO were also milled individually for 72 h using the same process. The obtained samples were characterized by XRD analysis and SEM. The powder XRD patterns were recorded using a Rigaku Rad-B system with Cu-K α radiation, while SEM (S-3000E; Hitachi High-Technologies Co.) imaging was performed to observe the morphologies of the samples. Further, the diffraction data were analyzed using the Rietveld method [13].

The charge-discharge measurements were performed using a stainless steel cell for voltages of 2.0–5.0 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%). To study the dependence of charge-discharge capacities on the upper limit of the charging voltage, the upper limit was changed from 4.0 to 5.3 V on charging the test cell. As mentioned previously, XPS was performed to examine the valence states of Ni; a Kratos AXIS ULTRA DLD system with a monochromatic Al K α X-ray source was employed for the purpose.

3. Results and discussion

3.1. XRD patterns and SEM images

Fig. 1 shows the XRD patterns of the LiF-NiO composites synthesized by milling for various durations as well as those of LiF and

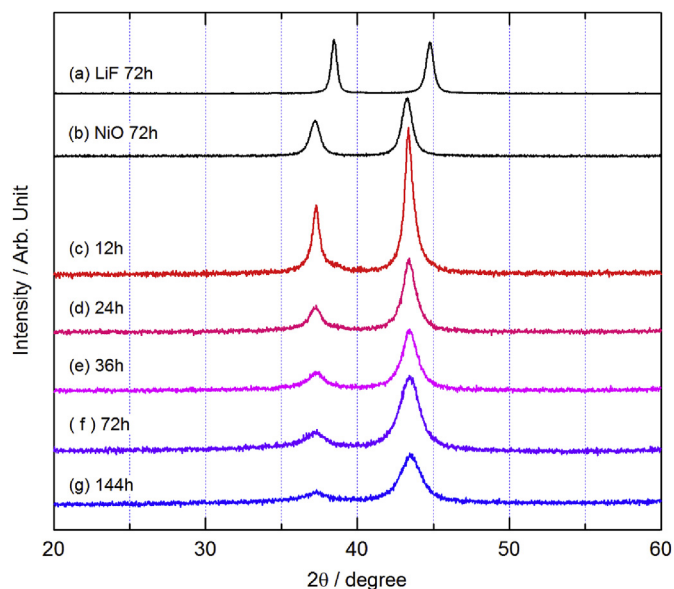


Fig. 1. XRD patterns of the LiF-NiO composites, LiF, and NiO.

NiO. The source materials, LiF and NiO, were milled individually for 72 h each. The crystal structures of LiF and NiO were of the rock-salt type, with that of NiO being a little distorted. The lattice constant of LiF (4.027 Å) was smaller than that of NiO (4.177 Å). The XRD patterns of LiF and NiO obtained after milling (see (a) and (b) in Fig. 1) contained only diffraction peaks related to LiF and NiO, respectively, with the peaks becoming broader after the milling process.

The LiF-NiO composites were synthesized by milling equal amounts of LiF and NiO for 12–144 h. The XRD pattern of the LiF-NiO composite milled for 12 h (see (c) in Fig. 1) contained only two peaks. The intensities of the peaks of the composites decreased and their linewidth increased with an increase in the milling time, as can be seen from (c)–(g), indicating that the composite particles became finer with the increase in the milling time. SEM images of the LiF-NiO composites formed by milling for 24, 72, and 144 h are shown in Fig. 2.

It can be seen that the particle size of the composites became smaller with the milling time, in keeping with the XRD results. In Fig. 1, the diffraction peak at $2\theta = 37^\circ$ corresponds to the (111) plane of the rock-salt type crystal lattice and that at 43° to the (200) plane. The ratio of the intensities of the (111) and (200) peaks also decreased with the milling time. In the case of Li-doped NiO, it has been observed that the peak intensity ratio of (111)/(200) decreases with the amount of Li doped [14]. The intensities of the XRD peaks were not affected significantly when the O^{2-} ions were substituted by F^- ions. This indicated that the decrease in the (111)/(200) peak intensity ratio was caused by the replacement of the Ni^{2+} ions with the Li^+ ions, which resulted in the LiF-NiO composite becoming a solid solution. To examine the occupancy of the Li ions at the Ni sites, a Rietveld analysis was performed on the XRD data; the results for the composite formed by milling for 144 h are shown in Fig. 3. The thermal parameter was fixed while the lattice constants and the occupancy of the Ni sites were refined in the Rietveld analysis. NiO has two Ni sites and their coordinates were (0, 0, 0) and (0.5, 0.5, 0); however, their occupancy values were set to be the same. R_{wp} , R_{B} and R_{e} are reliability factors used for Rietveld refinement. The R_{wp} , R_{B} , and $S (=R_{\text{wp}}/R_{\text{e}})$ values were estimated to be 11.1%, 2.73%, and 1.06, respectively, from the analyses. The lattice constants of this sample were found to be $a = 5.86(7)$ Å and $c = 7.23(9)$ Å. These values were a little smaller than those of NiO, which were $a = 5.911$ Å and $c = 7.225$ Å. However, the extent of

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