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Electrochemical properties of $LiNiO_2$ cathode after TiO_2 or ZnO addition

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Abstract

$LiNiO_2$ was prepared by solid state reaction, and $LiNiO_2$ was mixed with 1-, 2-, or 5 wt% TiO_2 or ZnO for the preparation of cathodes for a lithium ion battery. The electrochemical properties of the cathodes were investigated and the effects of the addition of TiO_2 or ZnO were discussed. The voltage vs. capacity curves for charge and discharge at different numbers of cycles for $LiNiO_2$, 2 wt% TiO_2-added $LiNiO_2$, and 2 wt% ZnO_2-added $LiNiO_2$ showed that in all the samples the first discharge capacity is much smaller than the first charge capacity. The addition of TiO_2 or ZnO decreased the discharge capacities, but improved the cycling performance. The discharge capacities of $LiNiO_2$ and 2 wt% TiO_2-added $LiNiO_2$ decreased as the number of cycles increased. However, the discharge capacity of 2 wt% ZnO-added $LiNiO_2$ increased overall as the number of cycles increased. The $-dx/|dV|$ vs. voltage curves for the 1st and 2nd cycles of 0, 1-, 2-, or 5 wt% TiO_2 or ZnO-added $LiNiO_2$ showed that all the samples underwent four phase transitions during charging and discharging.

Keywords: $LiNiO_2$; Oxide addition; Electrochemical properties; First charge capacity; Discharge capacity

1. Introduction

Lithium transition metal oxides such as $LiCoO_2$ [1,2], $LiNiO_2$ [3,4], and $LiMn_2O_4$ [5,6] have been investigated as cathode electrode materials for rechargeable lithium batteries. $LiCoO_2$ has been studied most intensively for the application to commercial rechargeable batteries because of its large diffusivity and high operating voltage. However, it has drawbacks that cobalt is expensive and toxic. $LiMn_2O_4$ has several advantages that Mn is less expensive than other elements and its synthesis is easy, but its cycling performance is poor. $LiNiO_2$ is considered a promising cathode material due to its large discharge capacity and low cost. However, due to the size similarity of Li and Ni (Li^+=0.72 Å and Ni^{2+}=0.69 Å), $LiNiO_2$ is practically obtained in the non-stoichiometric composition $Li_{1-y}Ni_{1+y}O_2$ [7,8] and the Ni^{2+} ions in the lithium planes obstruct movement of Li^+ ions during charge and discharge [9,10].

In order to increase the discharge capacity and improve the cycling performance and structural stability of cathode materials, various elements were substituted for the transition elements in the cathode materials, and the surfaces of cathode materials were modified. Choblet et al. [11] showed that 2 wt% TiO_2-added $LiCoO_2$ had the best cycling performance and that the phase transition voltage for discharge changed. Researches on the surface modification, in which Co_3O_4 [12], Al_2O_3 [13,14], B_2O_3 [15], MgO [16,17], TiO_2 [15] or ZrO_2 [15] was added to $LiCoO_2$, have been presented. Oh et al. [13] reported that Al_2O_3 coating increases both the surface area and the electrical conductivity of $LiCoO_2$, improves the cycle performance even at a higher cut-off charge voltage, and induces higher thermal stability. Kweon et al. [16] reported that $Li_xNi_{1-y}Co_yO_2$, of which the surface is modified by coating $Mg(OH)_2$ and further heating the coated sample, had a lowered initial discharge capacity but had an improved cycle-reversibility. Wang et al. [17] studied commercial $LiCoO_2$ surfaces modified with MgO for lithium-ion batteries, and reported that surface modification can improve the structural stability of $LiCoO_2$ without decreasing its available specific

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capacity. They attributed this improvement to the pillaring effect of the Mg^{2+} ions in the interslab space of the lattice and the protective effect of the MgO film against the escape of Co^{4+} ions from the bulk of the $LiCoO_2$ particles. Lu et al. [18] studied the anomalous capacity of $Li/Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$ cells using *in situ* X-ray diffraction, and reported that irreversible loss of oxygen from the compounds with $x < 1/2$ occurred during the first charge to 4.8 V, forming oxygen deficient layered materials, which reacted reversibly with lithium.

However, the surface modification of $LiNiO_2$ or the addition of oxides to $LiNiO_2$ was not reported. In this work, TiO_2 or ZnO was added to $LiNiO_2$ prepared by solid state reaction, and the electrochemical characteristics of the TiO_2 or ZnO-added cathode were investigated.

2. Experimental

$LiNiO_2$ was synthesized using a solid-state reaction method. $LiOH \cdot H_2O$ (Kojundo Chemical Lab. Co., Ltd, purity 99%) and $Ni(OH)_2$ (Kojundo Chemical Lab. Co., Ltd, purity 99.9%) were used as starting materials. The starting materials with a composition of $LiNiO_2$ were mixed mechanically with a SPEX mill for 1 h. The mixed material was preheated at 450 °C for 5 h in air, pressed into a pellet and then calcined at 750 °C for 30 h under oxygen stream. The $LiNiO_2$ sample, which was prepared under these conditions, showed the best electrochemical properties [19].

TiO_2 (anatase) (Aldrich Co., purity 99%) and ZnO (Aldrich Co., purity 99%) were used for 1, 2, or 5 wt% additions. TiO_2 or ZnO was mixed with $LiNiO_2$ for 24 h in a magnetic stirrer.

The samples were characterized by X-ray diffraction analysis (Rigaku III/A diffractometer) using Cu Kα radiation. The scanning rate was $6° \min^{-1}$ and the scanning range of diffraction angle (2θ) was $10° \leq 2\theta \leq 80°$.

The electrochemical cells consisted of $LiNiO_2$ or TiO_2 or ZnO-added $LiNiO_2$ as a cathode, Li foil as a anode, and electrolyte (Purelyte (Samsung General Chemicals Co., Ltd.)) prepared by solving 1 M $LiPF_6$ in an 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cathode consisted of 85 wt% synthesized materials, 10 wt% acetylene black, and 5 wt% polyvinylidene fluoride (PVDF) binder solved in N-Methyl-2-pyrrolidinone (NMP), which were pasted on Al foil and dried at 353 K for 24 h. A Whatman glass-filer was used as a separator. The cells were assembled in an argon-filled dry box and the coin-type (2016) cell was employed. All the electrochemical tests were galvanostatically cycled in the voltage range 2.7–4.2 V at 0.1 C-rate.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LiNiO_2$, 2 wt% TiO_2-added $LiNiO_2$ after 5 charge–discharge cycles, and 2 wt% ZnO-added $LiNiO_2$ after 5 charge–discharge cycles. All the samples exhibit peaks of the $LiNiO_2$ phase, which has a α-$NaFeO_2$ structure with a space group of $R\bar{3}m$. The XRD patterns of 2 wt% TiO_2-added $LiNiO_2$ after 5 charge–discharge cycles and 2 wt% ZnO-added $LiNiO_2$ after 5 charge–discharge cycles show C peaks from acetylene black at the diffraction angles of 26.4° and 54.5°, Al peaks from aluminum foil at the diffraction angles of 38.5°, 44.7°, 65.1°, and 78.2°, and TiO_2 or ZnO peaks.

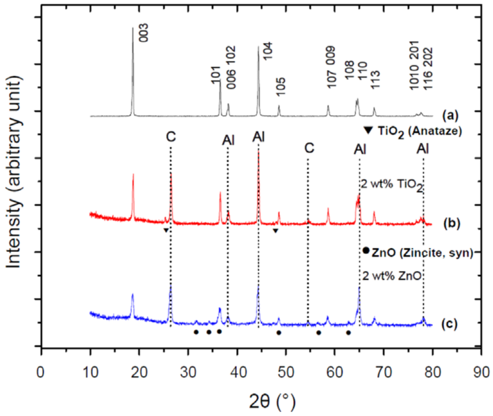

Fig. 1. XRD patterns of (a) $LiNiO_2$, (b) 2 wt% TiO_2-added $LiNiO_2$ after 5 cycles, and (c) 2 wt% ZnO-added $LiNiO_2$ after 5 cycles.

The SEM micrographs of $LiNiO_2$, 2 wt% TiO_2-added $LiNiO_2$, and 2 wt% TiO_2-added $LiNiO_2$ after 5 cycles are shown in Fig. 2. The particles of $LiNiO_2$ in the $LiNiO_2$ sample are polyhedral while those in the samples of 2 wt% TiO_2-added $LiNiO_2$ and 2 wt% TiO_2-added $LiNiO_2$ after 5 cycles are large and thin. TiO_2 exists in the form of fine particles. The 2 wt% TiO_2-added $LiNiO_2$ before charge–discharge cycling and 2 wt% TiO_2-added $LiNiO_2$ after 5 cycles have similar microstructures.

Fig. 3 shows the SEM micrographs of 2 wt% ZnO_2-added $LiNiO_2$ and 2 wt% ZnO_2-added $LiNiO_2$ after 5 cycles. The microstructures of these two samples are very similar. No large difference is observed between the microstructures of these two samples and those of the 2 wt% TiO_2-added $LiNiO_2$ before charge–discharge cycling and the 2 wt% TiO_2-added $LiNiO_2$ after 5 cycles.

The voltage vs. capacity curves for charge and discharge at different numbers of cycles for $LiNiO_2$, 2 wt% TiO_2-added $LiNiO_2$, and 2 wt% ZnO_2-added $LiNiO_2$ are shown in Fig. 4. All the samples showed much smaller charge capacity at the second cycle than at the first cycle, and the charge capacities at the 5th cycle are slightly smaller than those at the second cycle. In all the samples, the first discharge capacity is much smaller than the first charge capacity. It is believed that this is because at the first charging, the Li ions that entered the Ni sites deintercalate.

Fig. 5 shows the variations of discharge capacity at 0.1 C-rate with the number of cycles for $LiNiO_2$, 2 wt% TiO_2-added $LiNiO_2$, and 2 wt% ZnO-added $LiNiO_2$. $LiNiO_2$ has the largest first discharge capacity of 164.7 mA h/g, followed in order by 2 wt% TiO_2-added $LiNiO_2$ (135.8 mA h/g) and 2 wt% ZnO-added $LiNiO_2$ (112.5 mA h/g). The TiO_2 or ZnO-added $LiNiO_2$ sample has smaller discharge capacities than the $LiNiO_2$