

Studies of LiNiO_2 in lithium-ion batteries

S.P. Sheu^{a,*}, I.C. Shih^a, C.Y. Yao^a, J.M. Chen^b, W.M. Hurng^a

^a Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, ROC

^b Institute of Materials Science and Engineering, Tsing Hua University, Hsinchu, Taiwan, ROC

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Abstract

Lithium nickel oxide, LiNiO_2 , with different physical properties including crystalline phase, CV curve and particle-size distribution were characterized. LiNiO_2 with spherical agglomerates were constructed by $\sim 0.1 \mu\text{m}$ fine particles and their cycling stability showed to depend on the particle-size distribution when compared at different end-voltage and cycling rates. © 1997 Published by Elsevier Science S.A.

Keywords: Lithium-ion batteries; Nickel; Cycling behaviour

1. Introduction

Lithium-ion secondary batteries with lithium metal oxides and carbon as the cathodes and anodes are developed as high-energy/power, long cycle-life cells to replace the Ni–Cd cell [1]. Lithium metal oxides, LiMO_2 , with layered structures are the most promising cathode materials for secondary lithium batteries. Nowadays, LiMnO_2 is at the stage of evaluation while LiCoO_2 has been commercialized for years, and LiNiO_2 becomes a promising candidate for LiCoO_2 because it has the benefits of higher specific capacity and lower price [2]. In this study, the physical properties of two LiNiO_2 particle sizes were characterized, their performance at different charge end-voltage were compared by the charge and discharge recycling process, and the electrochemical behaviors are examined by cyclic voltammetry.

2. Experimental

Two particle sizes of LiNiO_2 , LN-A and LN-B (commercial products), were used as the cathode materials in this work. The compositions were determined to be both $\text{Li}_{1.00}\text{NiO}_2$ by inductively coupled plasma spectroscopy (ICP). Powder X-ray diffraction (XRD) diagrams were recorded with 2θ range from 15° to 80° with a step scan of 0.02° by using Cu $K\alpha$ radiation. The cathodes were prepared by mixing LiNiO_2 , acetylene black (AB), polyvinylidene fluoride (PVDF) and then spread onto an aluminum foil to

form the positive electrode. The LiNiO_2 electrochemical behavior was examined by a coin cell. The electrolyte was 1 M LiPF_6 in EC/DEC. The cyclic voltammetry (CV) measurements were carried out in the potential range from 3.0 to 4.5 V versus Li/Li^+ reference electrode under a scan rate of 0.1 mV/s.

3. Results and discussion

Particle-size distribution analyses characterized LN-A and LN-B as 5–10 μm and 10–20 μm , respectively. Scanning electron microscopy (SEM) graphs revealed that both the LN-A and the LN-B LiNiO_2 materials were spherical agglomerates which were constructed by $\sim 0.1 \mu\text{m}$ fine particles and also reported by Broussely et al. [3]. The XRD patterns of different particle sizes of LiNiO_2 are shown in Fig. 1. The diffraction pattern of LN-A (5–10 μm) LiNiO_2 resembled that of LN-B (10–20 μm) LiNiO_2 except that the integrated intensity ratio of $I(003)/I(104)$ of LN-A was larger than LN-B (LN-A: 1.13, LN-B: 0.99) indicating a better electrochemical reactivity [4].

The electrochemical performance of the two LiNiO_2 positive electrodes are compared by CV method in Fig. 2. In general, the CV curves are similar. However, an oxidation peak at 4.25 V and a reduction peak at 4.0 V were obviously more pronounced for LN-B LiNiO_2 (noted by arrows). According to literature, these CV peaks associated, most probably, with a third hexagonal phase, H_3 , or/and an irreversible phase when charge/discharge at voltage larger than 4.15 V [5].

* Corresponding author.

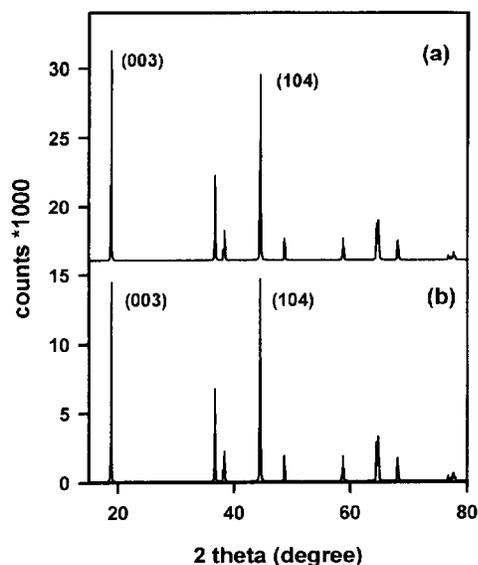


Fig. 1. XRD patterns of (a) 5 μm LN-A, and (b) 10 μm LN-B LiNiO_2 particles.

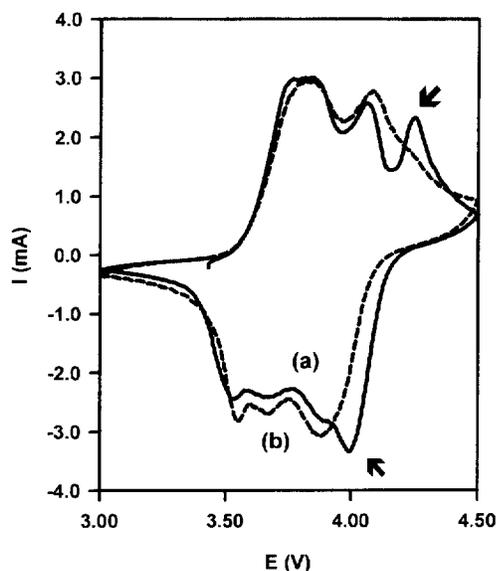


Fig. 2. CV curves of LiNiO_2 with particle size of (a) 10 μm LN-B, and (b) 5 μm LN-A.

The LiNiO_2 particle-size effect was examined by charge/discharge recycling process under two C rates as shown in Fig. 3 (upper). Concerning the initial specific capacity, it is reasonable that the two electrodes gave similar values (0.5 mA/cm^2 : 144 mAh/g , 2.5 mA/cm^2 : 127 mAh/g). At low current density (0.5 mA/cm^2), the cycle stability of the LN-A electrode (5–10 μm) was comparable with that of LN-B (10–20 μm). But at higher current density (2.5 mA/cm^2) the one with the 5–10 μm particle-size distribution (LN-A) behaved better as can be seen from Fig. 3 (upper). This might be interpreted by the better electrochemical reactivity of the

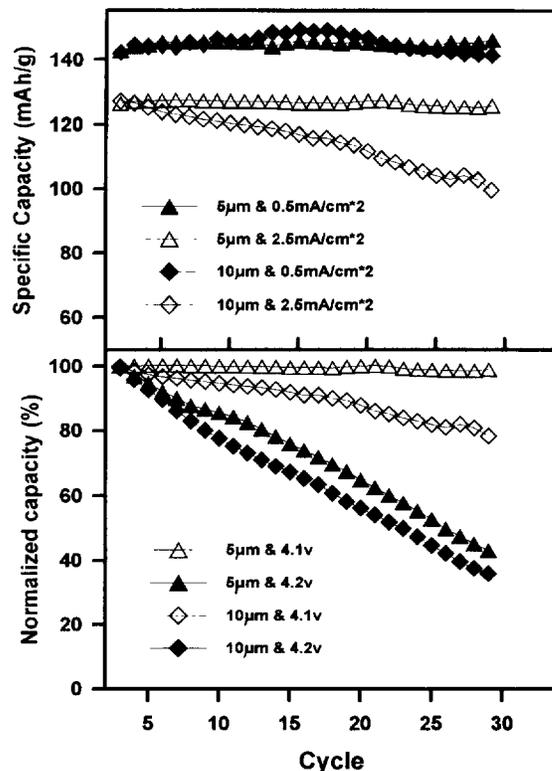


Fig. 3. (Upper) LiNiO_2 particle-size effect and (bottom) charge end-voltage effect which cycled at 2.5 mA/cm^2 current density on cycle stability.

5 μm LiNiO_2 (LN-A) as suggested by the X-ray results in the previous section.

The LN-A and LN-B LiNiO_2 were also tested by a recycling process at higher charge end-voltage, 4.2 V, which is almost the upper working voltage limit of LiNiO_2 cathodic material. Higher initial specific capacities of about 150 mAh/g could be obtained. Fig. 3 (bottom) shows the normalized cycle curves for the purpose of comparison. It is apparent that higher charge end-voltage led to dramatically poorer cycle stability of both particle sizes of LiNiO_2 though the 5 μm particle size still behaved better than the 10 μm particle size LiNiO_2 . The poorer cycle stability might be caused by the formation of the irreversible phase at higher voltage; further investigation is in progress.

4. Conclusions

LiNiO_2 materials of spherical agglomerates were constructed by $\sim 0.1 \mu\text{m}$ fine particles as characterized by SEM graphs. The cell performance of LiNiO_2 depends on the agglomerates size with smaller agglomerates giving better cycle-life stability when the 4.1 or 4.2 V end-voltage was used. The poorer cycle stability might be interpreted by the small portion of irreversible phase co-crystallized in the electroactive LiNiO_2 product.

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