

## Storage characteristics of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ in air as cathode material for lithium-ion batteries

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Much research effort has been directed towards the development of lithium-ion batteries due to the increased production and use of portable electronic devices. The performance of lithium-ion batteries is dependent on the insertion–deinsertion properties of the positive electrode material [1–6]. Among all cathode materials,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  has been considered as the most attractive substitute for the commercially used  $\text{LiCoO}_2$  [7–9]. Solid solution  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ), which has better cycleability and safety aspects, enjoys the advantage of both  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ . In the entire solid solution range, compounds with  $x = 0.1$ – $0.3$  have the most promising electrochemical characteristics. However, there is a problem of storage in air for  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ , especially with little or no cobalt content. As a potential cathode material for lithium-ion batteries, this problem is very important for industrial production, transportation, storage and the process of making batteries.

A significant amount of research has been focused on the synthesis, processing and electrochemical identification of cathode materials in lithium-ion batteries. Up to now, there have been few published reports regarding the storage behavior of  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  cathode materials in air. In the present paper, the storage property of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  in air was investigated by means of XRD, SEM and electrochemical tests.

A  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  sample was prepared by the solid-state method. Starting materials  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Ni}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3$  were reagent grade. The synthesizing process was as follows:  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Ni}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3$  were mixed in a molar ratio of  $\text{Li}:\text{Ni}:\text{Co} = 1.07:0.85:0.15$ . Excess lithium compensates for lithium vaporization at high temperature. The mixture was ground using an agate mortar and pestle, and then pressed into pellets at  $6 \times 10^7$  Pa. The obtained pellet was precalcined at  $600^\circ\text{C}$  for 6 hrs and ground and pelletized again. The final pellet was reacted at  $725^\circ\text{C}$  for 24 hrs under an oxygen flow in a tubular furnace (SR100-500/11, GERO Hochtemperaturöfen GmbH-D-75242 Neuhausen).

A powder sample was identified using a powder X-ray diffractometer (Rigaku, D/max-RB) with monochromatized  $\text{Cu K}\alpha$  radiation. Morphological observations were performed by scanning electron microscopy (SEM) (Jeol STM-5610LV).

The electrochemical performance of the sample was studied on assembling 2016-type coin cells with a lithium metal anode at room temperature, in which the cathode had a composition of 80 wt% active materials, 10 wt% acetylene black (as conducting agent) and 5 wt% polytetrafluorethylene (PTFE) binder. The electrolyte was 1 M  $\text{LiPF}_6$  in 1:1 (weight ratio) EC/DEC (Merck, Germany). A Celgard2300 membrane was used as cell separator. All manipulations were performed in a glove box filled with Ar under an oxygen level less than 5 ppm and water content less than 1 ppm. The galvanostatic charge–discharge experiments were undertaken at a current density of 18 mA/g in the voltage range of 3.0–4.3 V on a multichannel battery cycling unit (Arbin BT2000, USA).

$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  powder sample was stored in air at room temperature for different times. In order to compare the influence of storage time on the capacity of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ , electrochemical tests as well as XRD and SEM were carried out on the sample after different storage times in air.

The capacity change of the sample  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  during storage in air is shown in Fig. 1. For the initial, fresh sample, the initial charge–discharge capacities are 218.0 and 192.6 mAh/g, respectively, and its efficiency is 88.2%. After 15 days of storage in air, its initial charge and discharge capacities drop to 198.7 and 166.0 mAh/g, respectively, and its efficiency is 83.5%. As seen from Fig. 1, the charge voltage for the 15-day sample is higher and its discharge voltage is lower in comparison to those of the fresh sample. When the storage time increases the charge and discharge capacities decrease, and so does the efficiency. A surprising phenomenon is that the charge and discharge capacities of the 90-day sample are only 46.0 and 29.7 mAh/g, respectively, and its efficiency is only 64.6%. The curves of charge and discharge indicated that the polarization of the sample increase based on its high charge voltage and low discharge voltage.

In order to determine the properties of the sample during storage in air, the 90-day sample powder was selected for morphological study. Fig. 2 shows the SEM micrograph of the 90-day and fresh samples at magnification of 5.0 and 20.0 Kx. The particles of the fresh sample are generally in the form of smooth-edged polyhedra, indicating better crystallinity. After storing in air for 90 days the surface of the particles become

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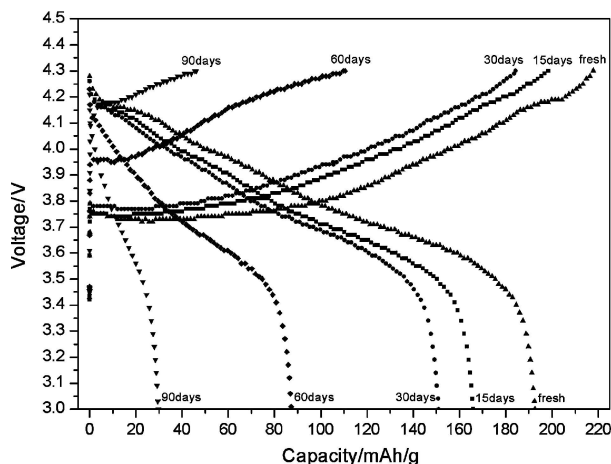


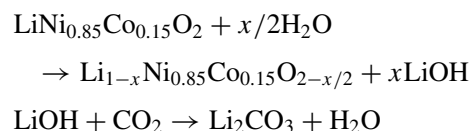
Figure 1 The initial charge-discharge curves of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  at different storage times.

coarse, and its particles seem to stick together. The phenomenon of agglomeration into clusters becomes serious. These results indicate that  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  is unstable during storage in air. It is reasonable to conclude that a reaction at the surface of the particles of the sample took place during storage in air.

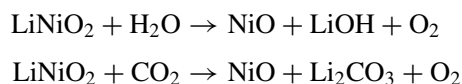
The phases occurring in the sample powder during storage were analyzed by X-ray diffractometry (XRD). Fig. 3 shows the XRD patterns of the fresh sample and 90-day samples. It can be observed from Fig. 3b that there are impurity peaks for the 90-day sample. In comparison to the standard XRD pattern, the impurity peaks indicate  $\text{Li}_2\text{CO}_3$ . As compared with the fresh sample

(Fig. 3a), the intensities of the (003) and (104) peaks in Fig. 3b decrease, and their intensity ratio  $I_{003}/I_{104}$  decreases as well, indicating that the layered characteristics of the crystallinity decrease and the cation mixing increases [10].

Based on the experimental results above, we believe that the reaction of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in air, took place during the storage. The reaction may be as follows [11–14]:



On the other hand,  $\text{Ni}^{3+}$  at the surface of the sample is unstable, and it easily transforms to become  $\text{Ni}^{2+}$  [15].



Therefore, the layer of “ $\text{Li}_2\text{CO}_3$ -NiO- $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ ” is formed on the surface of the sample during storage in air.

In conclusion,  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  exhibits a capacity decrease as the storage duration in air increases. XRD and SEM show that reaction with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in air took place. The performance of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  during storage in air became worse, which is not beneficial

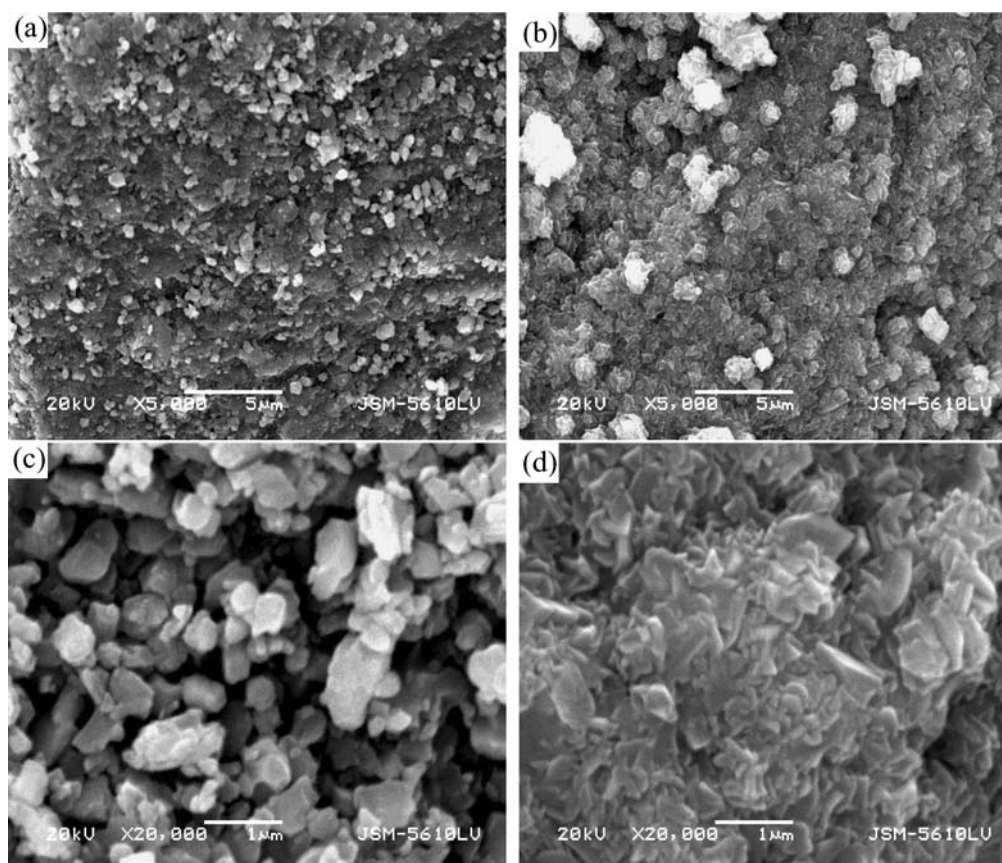


Figure 2 SEM morphology of (a), (c) fresh sample and (b), (d) 90-day sample.

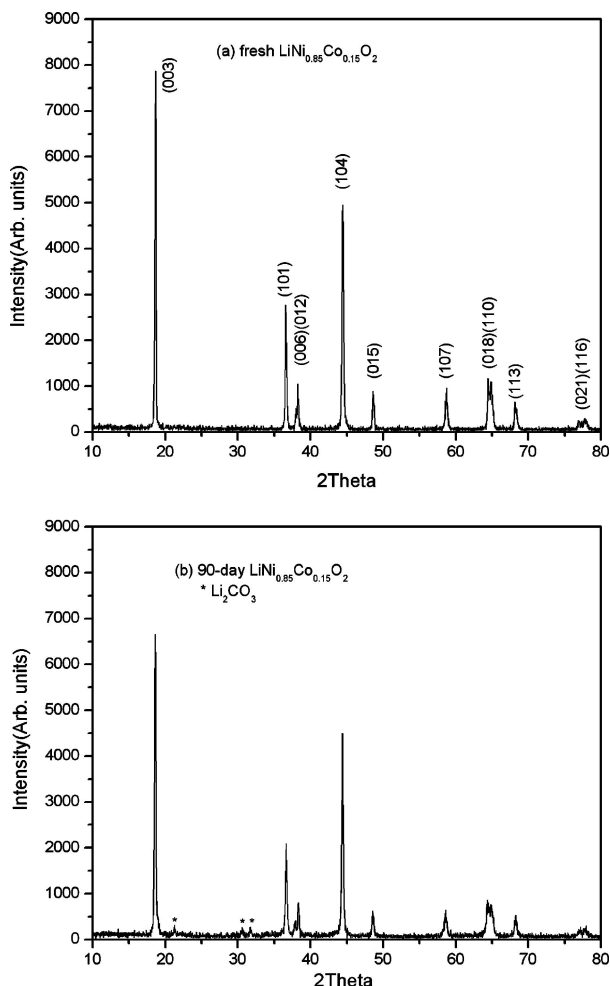


Figure 3 XRD patterns of (a) fresh sample, (b) 90-day sample.

for application as the cathode materials for lithium-ion batteries. In order to improve the storage performance of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ , it is necessary to be stored in atmosphere that has no  $\text{H}_2\text{O}$  or  $\text{CO}_2$ . Further studies are being carried out on  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  during storage in air.

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