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Li_2NiO_2 as a Novel Cathode Additive for Overdischarge Protection of Li-Ion Batteries

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It is widely agreed that lithium-ion batteries (LIBs) are the most promising energy storage devices in a variety of applications from mobile communications to personal transportation. Safety concerns, however, have been raised for LIBs. Subsequently, a vast amount of work has been devoted to the overcharge (OC) protection of LIBs, with appreciable progress.[1] However, studies focusing on overdischarge (OD) of LIBs, which is equally crucial to OC in practical aspects, have been limited.[2–4] The greater the number of cells that are connected in a series, the more serious both the OD and OC issues become, as in the case of high-voltage-requiring systems such as hybrid electric vehicles (HEVs). Slight differences in the initial state of charge (SOC) between the cells connected in series is amplified by prolonged cycling because the cells with relatively higher SOC will continue to be overcharged, whereas the cells with lower SOC will be exposed to repetitive OD.[5] The electronic circuit is often employed to prevent the imbalance between the cells, although inherent resistance to OC and OD abuses is required to ensure ultimate reliability of LIBs.

Most LIBs in the present market are based on Li_xMO_2 (M = Co, Ni, Mn)/carbon chemistry. The first cycle efficiency of the Li_xMO_y cathode is usually higher (90–97%) than that of carbon anode (80–92%).[4] In addition, the overall charge capacity of the cathode in a unit cell is always designed to be lower than that of the anode in order to avoid possible Li deposition, which is harmful both to safety and performance.[4,6] Therefore, the irreversible capacity of the anode in the first cycle is bound to be greater than that of the cathode. In this anode-limiting configuration, the anode primarily drives the voltage change of the full cell at the end of discharge as shown in Figure 1a. When the anode voltage increases beyond 3.5 V (vs Li/Li^+), the copper current collector of the anode is subject to the anodic dissolution, which leads to various adverse effects.[3–5] First, the dissolved Cu ion will be redeposited on the anode surface to form an electric shunt. Second, the adhesion between the anode material and copper collector may be lost. Third, severe copper dissolution around the joint with the Ni lead-out tap may result in electronic isolation of the whole anode sheet, and eventually all the cells in the same series will be blocked-off. To circumvent the damages by the OD abuse, the cathode-limiting configuration is required, in which the overshooting of the anode voltage beyond the onset potential of copper dissolution is inherently absent, as depicted in Figure 1b. The cathode-limiting configuration can be achieved in two ways. The first method is to increase the first cycle efficiency of the anode up to the value comparable to that of the cathode, which seems practically impossible at the present time. The other method is to decrease the first cycle efficiency of the cathode. In this context, overlithiated manganese oxide ($Li_{1+x}Mn_2O_4$) spinel has been proposed as an extra lithium reservoir.[7] However, the commercial usage of $Li_{1+x}Mn_2O_4$ has been hampered by several obstacles in its stability and performance.[8]

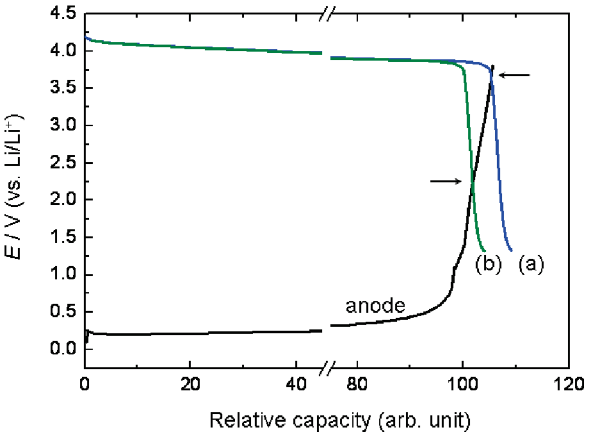

Figure 1. Discharge profiles of the anode and the cathode of the lithium-ion batteries with (a) anode-limiting configuration and (b) cathode-limiting configuration. Small arrows in the figure indicate the terminal voltages at the end of overdischarge to 0 V of full-cell voltage.

Here, we introduce a novel solution to tailor the first cycle efficiency of conventional cathode materials without deteriorating their characteristics by employing orthorhombic *Immm* Li_2NiO_2 as a cathode additive for the purpose of the OD protection of LIBs.

Orthorhombic *Immm* Li_2NiO_2 was prepared from a mixture of Li_2O (Aldrich, 97%) and NiO (Aldrich, 99%) in the stoichiometric composition of 1:1. The weighed powder was mixed and ground in an agate mortar and pestle, pressed into pellets, and then placed in an alumina crucible. It was first heated at 100 °C for 1 h, at 400 °C for 2 h, 600 °C for 10 h, and then cooled to room temperature under a flowing nitrogen atmosphere. The heating and cooling rates were 200 and 400 °C/h, respectively. The average particle size of

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(1) Balakrishnan, P. G.; Ramesh, R.; Kumar, T. P. *J. Power Source* **2006**, *155*, 401.

(2) Chen, J.; Buhrmester, C.; Dahn, J. R. *Electrochem. Solid-State Lett.* **2005**, *8*, A59.

(3) Maleki, H.; Howard, J. N. *J. Power Source* **2006**, *160*, 1395.

(4) Arora, P.; White, R. E.; Doyle, M. *J. Electrochem. Soc.* **1998**, *145*, 3647.

(5) Wu, M.-S.; Lin, C.-Y.; Wang, Y.-Y.; Wan, C-C.; Yang, C. R. *Electrochim. Acta* **2006**, *52*, 1349.

(6) Grate J., W., Frye, G. C. *Advances in Lithium-Ion Batteries*; Schalkwijk, W., Scrosati, B., Eds.; Kluwer Academic/Plenum Publishers: New York, 2002; pp 267–288.

(7) Tarascon, J. M.; Guymard, D.; Baker, G. L. *J. Power Source* **1993**, *43–44*, 689.

(8) Amatucci, G.; Tarascon, J. M. *J. Electrochem. Soc.* **2002**, *149*, K31.

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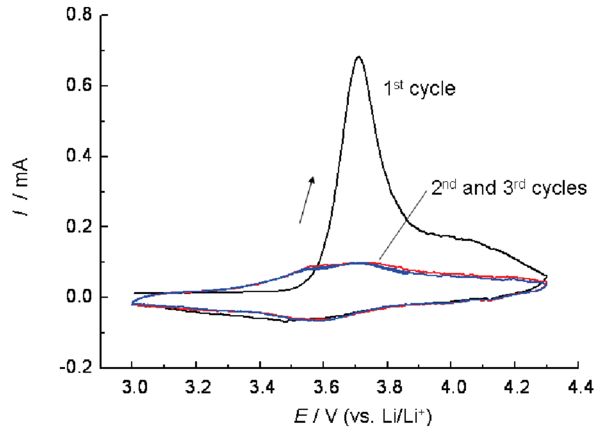

Figure 2. Three consecutive cyclic voltammograms of Li_2NiO_2 in 1 M $LiPF_6$ EC/EMC (1/2, v/v) solution. Scan rate = 0.05 mV s^{-1}.

synthesized Li_2NiO_2 was 20 ± 2 μm. Cyclic voltammetry for Li_2NiO_2 was obtained by using Li_2NiO_2/Li coin-type cells. The cathode consists of Li_2NiO_2, conducting carbon, and PVdF binder with the ratio of 85:10:5 wt%. The electrolyte used was battery grade 1 M $LiPF_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1/2, v/v). The cells employed for the overdischarge tests were 383562-size pouch cells, which are frequently called Al-laminated cells, with a nominal capacity of 700 mA h. They used mesocarbon microbeads graphite (Osaka gas, Japan), $LiCoO_2$ (NCI, Japan), Li_2NiO_2 (prepared as described above), polyethylene separator (Tonen, Japan), and 1 M $LiPF_6$ in EC/EMC (1/2, v/v). Li_2NiO_2 powder was added into a $LiCoO_2$ slurry and mixed to prepare the composite cathode. Three electrode measurements were performed to monitor the cathode and anode voltages during the overdischarge. Li-metal foil (2 cm^2) pressed on Cu mesh was used as a reference electrode that was placed at one side of the pouch cells. Before the overdischarge test, the cells were cycled over a 3–4.2 V range several times. Overdischarge tests were performed by applying constant current of 300 mA to 3 V, 3 mA to 2.7, and finally 1 mA to 0 V. The damage by the overdischarge is estimated with the 1 C capacity ratio before and after three repeated overdischarge tests.

Recently, orthorhombic *Immm* Li_2NiO_2 has been reported to show a charge capacity of 320 mA h g^{-1} and a discharge capacity of 240 mA h g^{-1} at the first cycle over 1.5–4.6 V (vs Li/Li^+).[9] However, we have observed that Li_2NiO_2 exhibits the distinctive first-cycle behavior over the normal voltage span of practical LIBs. Figure 2 presents the first three consecutive cycles of the cyclic voltammogram of Li_2NiO_2 over 3–4.3 V. The voltammogram at the first cycle is quite different from subsequent cycles. The current response at the first cycle shows an oxidation (charging) peak around 3.7 V followed by a broad shoulder over 3.9–4.1 V and a reduction (discharging) peak around 3.6 V. The charge and discharge capacities of Li_2NiO_2 at the first cycle are about 370 and 120 mA h g^{-1}, respectively, and the resulting columbic efficiency is only 32%. The current responses at the following scans are greatly decreased and become repetitive, giving a discharge capacity of approximately 115 mA h g^{-1} with an efficiency higher than 99.8%. The distinguished first cycle behavior of Li_2NiO_2 has been ascribed to the phase transition into layered $LiNiO_2$ upon the first charging process.[9,10] As presented in Figure 3, the Ni^{2+} ion in orthorhombic Li_2NiO_2 has a square planar coordination,[11] whereas the Ni^{3+} ion in layered $LiNiO_2$ has an octahedral geometry.[12] The phase transformation is irreversible as confirmed in the X-ray diffraction (see the Supporting Information).

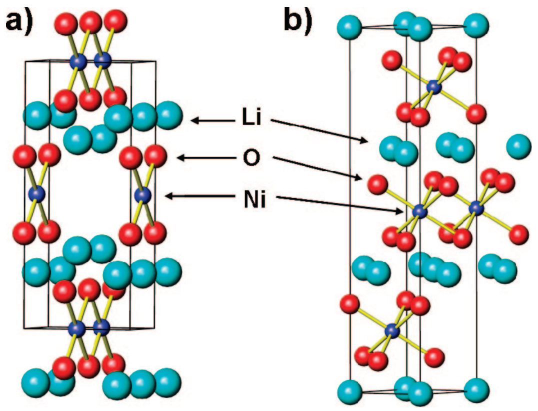

Figure 3. Unit-cell structure of (a) orthorhombic *Immm* Li_2NiO_2 and (b) trigonal $R\bar{3}m$ $LiNiO_2$.

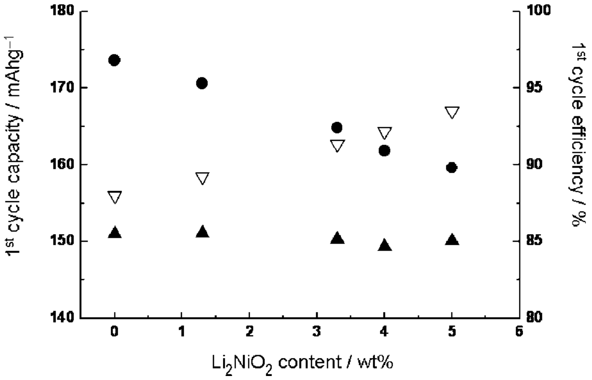

Figure 4. Charge capacity (∇), discharge capacity (▲), and columbic efficiency (•) of Li_2NiO_2:$LiCoO_2$ cathode at the first cycle over 3–4.3 V (vs Li/Li^+) as a function of Li_2NiO_2 content.

The large first-cycle irreversible capacity of Li_2NiO_2 can be used to tailor the first cycle columbic efficiency of the conventional cathode materials. Figure 4 shows that the charge and discharge capacities, and thus the columbic efficiency of Li_2NiO_2-added $LiCoO_2$ cathode (hereafter called Li_2NiO_2:$LiCoO_2$) can be varied with Li_2NiO_2 content. For example, Li_2NiO_2:$LiCoO_2$ (5:95, wt/wt) exhibits the first cycle efficiency of 89.8%, which is much smaller than pristine $LiCoO_2$ (96.8%), whereas its discharge capacity is only slightly decreased from 151 to 149 mA h g^{-1}. The first cycle efficiency of graphite anode used in this study is approximately 92% so that Li_2NiO_2:$LiCoO_2$ (5:95)/graphite cell exhibits a near-cathode-limiting configuration.

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(9) Kang, K.; Chen, C.-H.; Hwang, B.; Ceder, G. *Chem. Mater.* **2004**, *16*, 2685.

(10) Dahn, J. R.; von Sacken, U.; Michal, C. A. *Solid State Ionics* **1990**, *44*, 87.

(11) Rieck, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1972**, *392*, 193.

(12) Hirano, A.; Kanno, R.; Kawamoto, Y.; Takeda, Y.; Yamaura, K.; Takano, M.; Ohyama, K.; Ohashi, M.; Yamaguchi, Y. *Solid State Ionics* **1995**, *78*, 123.

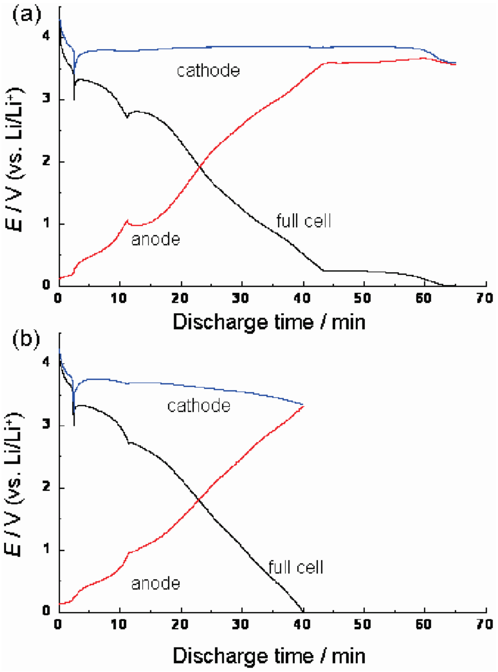

Figure 5. Voltage profiles of the cathode, the anode, and the full cell of (a) $LiCoO_2$/graphite and (b) Li_2NiO_2:$LiCoO_2$ (5:95)/graphite cell during the overdischarge tests. Overdischarge was performed by applying a constant current of 300 mA to 3 V, 3 mA to 2.7, and finally 1 mA to 0 V. The nominal capacity of the tested cells was 700 mA h.

The voltage profiles of the cathode, anode, and full cell during the OD event have been obtained by means of the three-electrode measurement. Figure 5a exhibits the voltage variations of $LiCoO_2$/graphite cell without Li_2NiO_2 addition (nominal capacity of 700 mA h, hereafter called pristine cell). The OD tests were performed by applying a constant current of 300 mA to 3 V, 3 mA to 2.7 V, and finally 1 mA to 0 V. During the slow 1 mA discharge period, the full-cell voltage initially decreases steadily and shows a plateau region around 0.25 V. The full-cell voltage is primarily determined by the anode voltage, whereas the cathode voltage remains nearly invariant, which is the typical feature of the anode-limiting configuration. As the fuel-cell voltage reaches the plateau region, the anode voltage is also saturated around 3.6 V (vs Li/Li^+) where the anodic copper dissolution is estimated to occur. Indeed, dark spots were observed near the joint between the copper sheet and the Ni tab at the postmortem observation, which is obviously caused by the severe copper corrosion. In contrast, the Li_2NiO_2:$LiCoO_2$ (5:95)/graphite cell (nominal capacity of 700 mA h, hereafter called Li_2NiO_2-added cell) shows no plateau region during the OD test (Figure 5b). The fuel-cell voltage of Li_2NiO_2-added cell monotonously decreases down to 0 V during the 1 mA discharge. The maximum anode voltage is limited to less than 3.4 V, which is sufficiently below the onset potential of copper oxidation. Note that the suppression of the anode voltage is attributed to the notable decrease in the cathode voltage at the latter part of the 1 mA discharge region. The cathode voltage gradually drops until it nears the anode voltage of 3.4 V. Thus, Li_2NiO_2-added cell exhibits the discharge behavior close to that of the cathode-limiting configuration, which is inherently immune to the damage by the OD abuse. Figure 6 summarizes the recovery ratio of the discharge capacity after three repeated OD tests. The control cell loses about 50% of its initial capacity, which is mainly due to the adverse effects of copper dissolution. On the other hand, the recovery ratio is increased with Li_2NiO_2 content so that more than 4 wt % Li_2NiO_2 addition secures a nearly 100% recovery rate.

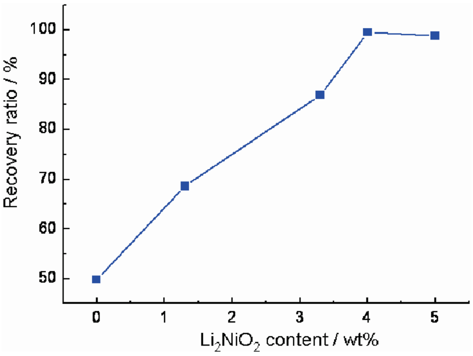

Figure 6. Recovery ratio of discharge capacity after three repeated overdischarge tests for $Li_2Ni_2O_2$:$LiCoO_2$/graphite cell as a function of $Li_2Ni_2O_2$ content. Discharge capacity was measured with 1 C current.

Regarding the effect of Li_2NiO_2 on the cyclability, it was found that there is no appreciable deterioration up to 9% addition of Li_2NiO_2 compared with that of the control cell (see the Supporting Information). Moreover, the rate capability was slightly better following Li_2NiO_2 addition (see the Supporting Information).

In summary, a novel overdischarge protection of present LIBs based on Li_xMO_2 (M = Co, Ni, Mn)/graphite has been reported. By employing orthorhombic *Immm* Li_2NiO_2 exhibiting the distinctively low coulombic efficiency at the first cycle as a cathode additive, we can tailor the first cycle columbic efficiency of the cathode so that the Li_2NiO_2-added cell exhibits a near-cathode-limiting configuration that is inherently immune to overdischarge abuse. This novel concept described herein offers a sophisticated way of overdischarge protection of present LIBs in the level of cell chemistry without compromising other performances, which is a significant breakthrough toward highly reliable LIBs.

Supporting Information Available: X-ray diffraction patterns for the Li_2NiO_2 electrode with respect to first charging and discharging and the effects of Li_2NiO_2on the cyclability and the rate capability (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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