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Novel lithium insertion material of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for advanced lithium-ion batteries

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Abstract

A novel lithium insertion material of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was reported for advanced lithium-ion batteries. $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ ($R\bar{3}m$; $a = 2.862(2)$ Å and $c = 14.227(8)$ Å in hexagonal setting) shows about 200 mAh g^{-1} of rechargeable capacity with rate capability as high as 1.6 A g^{-1} between voltages of 2.5 and 4.6 V. Preliminary cycle tests of a $Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell were also carried out for 30 cycles and shows that loss of rechargeable capacity was negligible. Thermal behavior of fully charged $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was examined by differential scanning calorimetry and shown that the exothermic reaction of $\square_{0.88}Li_{0.12}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ with electrolyte is much milder than that of $\square NiO_2$ or $\square CoO_2$. From these results we have discussed whether or not this material can be used for advanced lithium-ion batteries.

Keywords: Lithium insertion material; Lithium-ion battery; Lithium cobalt nickel manganese oxides

1. Introduction

During the past 10 years, lithium-ion batteries with $LiCoO_2$ [1] and graphite [2] have been developed to a quite high level. Energy density based on weight or volume, however, will become saturated in the near future unless material innovations can be made. One of the strategies to advance lithium-ion batteries in terms of the energy density is to extend rechargeable capacity of the positive-electrode material to more than 200 mAh g^{-1}. Among candidate materials reported so far, such as $LiNiO_2$ [3], more generally $LiCo_xNi_{1-x}O_2$ [4], or $LiAl_{1/4}Ni_{3/4}O_2$ [5], etc. no material can store and deliver electricity more than 200 mAh g^{-1} in a useful voltage range. After several trials from both theory and practice [6,7], a series of lithium nickel manganese oxides with or without cobalt has been proposed [6–9] for advanced lithium-ion batteries. In this paper we report on the cycle behavior and rate capability of lithium cells with $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$.

2. Experimental

$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was prepared from $LiOH{\cdot}H_2O$ and a triple hydroxide of cobalt, nickel, and manganese (MX-016, Co:Ni:Mn = 0.98:1.02:0.98, Tanaka Chemical Corp. Ltd.). Starting materials were well mixed and pressed into pellets (23 mm diameter and ca. 5 mm thickness). The pellets were predried at 150 °C in air for 1 h and then heated at 1000 °C for 14 h in air. The reaction product was ground into powder using a mortar and pestle and stored in a desiccator over blue silica-gel before use. The samples were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (XD-3A, Shimadzu Corp., Japan) with copper Kα radiation. The system was equipped with a diffracted graphite monochromator.

In preparing the electrodes, polyvinylidene fluoride (PVdF) dissolved in *N*-methyl-2-pyrrolidone (NMP) solution was used as a binder. The black viscous slurry consisting of 88 wt.% $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, 6 wt.% acetylene black, and 6 wt.% PVdF was cast on an aluminum foil (15 mm × 20 mm) with blade. Then, NMP was evaporated at 120 °C for 30 min, and finally the electrodes were dried under vacuum at 150 °C for 15 h. A lithium electrode was prepared by pressing a lithium metal onto a stainless steel sheet (15 mm × 20 mm). Two sheets of porous polypropylene membrane (Celgard 2500) were used as a separator. The electrolyte used was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3/7 v/v) solution.

For differential scanning calorimetry (DSC), charged sample of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, $LiNiO_2$, or $LiCoO_2$ was electrochemically prepared using a compressed pellet of the samples without adding any conductive or organic binder (forming pressure: 10^3 kg cm^{-2}; 11.3 mm diameter

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and ca. 0.6 mm thickness). The electrochemical oxidation of the pellets was performed galvanostatically at 0.3 mA cm^{-2} while monitoring the cell voltage. The samples (11–13 mg) containing electrolyte was sealed in an aluminum cell (5.5 mm diameter and ca. 1 mm thickness). Twelve milligrams of α-Al_2O_3 in the aluminum cell was used as a reference. All procedures for handling and fabricating the electrochemical cells were performed in an argon-filled glove box.

The electrochemical cells and the data acquisition system used in this study are the same as described in a previous paper [10]. Other sets of experimental conditions are given in Section 3.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LiNiO_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and $LiCoO_2$. The XRD pattern of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is quite similar to that of $LiCoO_2$ [11] or $LiNiO_2$ [3]. The lattice parameters of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for the nine identical samples reported here are calculated to be $a = 2.862(2)$ Å and $c = 14.227(8)$ Å in a hexagonal setting. The values are averages for nine samples. The parameters for each sample were obtained by a least squares method using 11 diffraction lines. Among $LiNiO_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and $LiCoO_2$ in Fig. 1, $LiCoO_2$ has the smallest lattice constant and unit cell volume, i.e. $a = 2.819(2)$ Å, $c = 14.069(4)$ Å and 96.8 $Å^3$, and $LiNiO_2$ has the largest unit cell volume of 102.3 $Å^3$. The unit cell volume

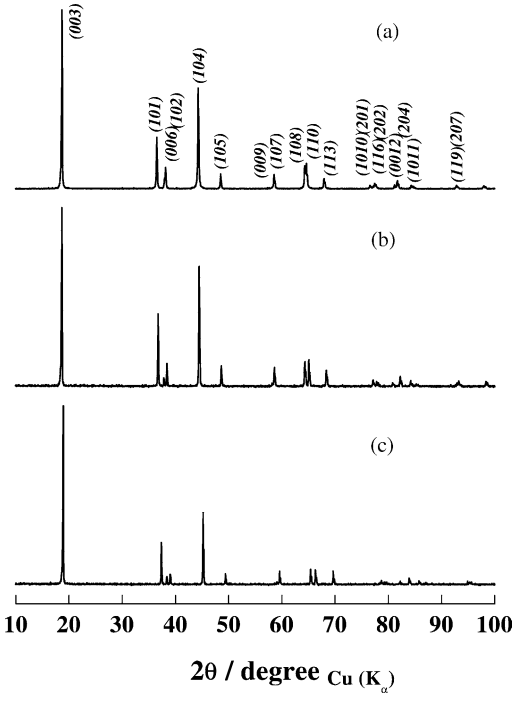

Fig. 1. X-ray diffraction patterns of (a) $LiNiO_2$, (b) $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and (c) $LiCoO_2$.

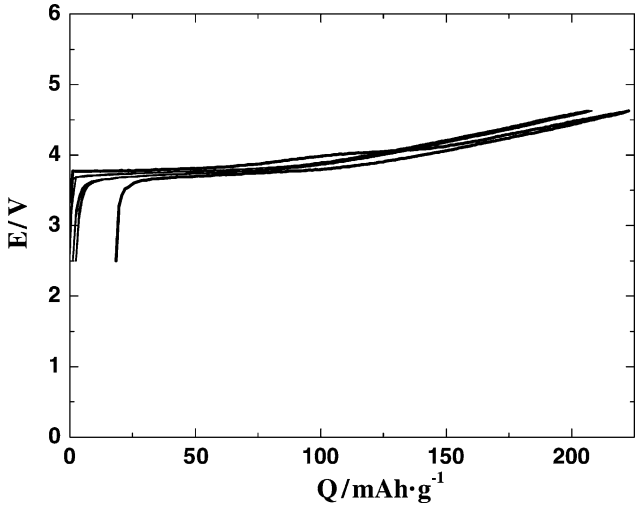

Fig. 2. Charge and discharge curves of a Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell operated at 0.17 mA cm^{-2} in voltages of 2.5–4.6 V at 30 °C. The sample weight loaded was 0.0341 g. The first charge and discharge curves are deviated from the subsequent charge and discharge curves which converge to a steady curve.

of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is 100.6 $Å^3$, which is midway between $LiCoO_2$ and $LiNiO_2$.

Fig. 2 shows the charge and discharge curves of a Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell operated at 0.17 mA cm^{-2} between 2.5 and 4.6 V at 30 °C. As seen in Fig. 2, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ shows 200 mAh g^{-1} of rechargeable capacity. On charging at 0.17 mA cm^{-2}, the voltage rapidly increased to about 3.7 V and then stayed along an almost horizontal line at 3.75 V, that is ca. 0.2 V lower operating voltage than that of $LiCoO_2$, until the charge capacity reaches 90–95 mAh g^{-1}. The slope in the E versus Q curves increased at 90–95 mAh g^{-1} and voltage curves linearly increased until voltage reaches 4.6 V. The irreversible capacity usually observed in the first cycle was about 20 mAh g^{-1}.

In order to examine whether or not a kinetic limitation of lithium-ion transfer in the solid state was important in the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode, the rate-capability tests were carried out. The results are shown in Fig. 3. To measure the rate capability the cell was charged at 0.17 mA cm^{-2} until the voltage reached 4.6 V and then discharged at 0.17–14.7 mA cm^{-2} corresponding to 18.3–1600 mA g^{-1} based on $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ weight. The discharge capacity observed is 200 mAh g^{-1} at 0.17 mA cm^{-2} or 18.3 mA g^{-1}. When the cell is discharged at 14.7 mA cm^{-2} or 1600 mA g^{-1} based on $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ weight, 73% capacity is observed. In other words, if we define C-rate with respect to the 200 mAh g^{-1} observed at the low rate discharge of 18.3 mA g^{-1}, 8C-rate (1600 mA g^{-1}) discharge are possible for this sample.

Change in the charge and discharge capacities is shown in Fig. 4 as a function of cycle number for a cell operated at 0.17 mA cm^{-2} between 2.5 and 4.6 V. We selected 4.6 V, because this voltage is a critical upper limit for $LiCoO_2$ [11],

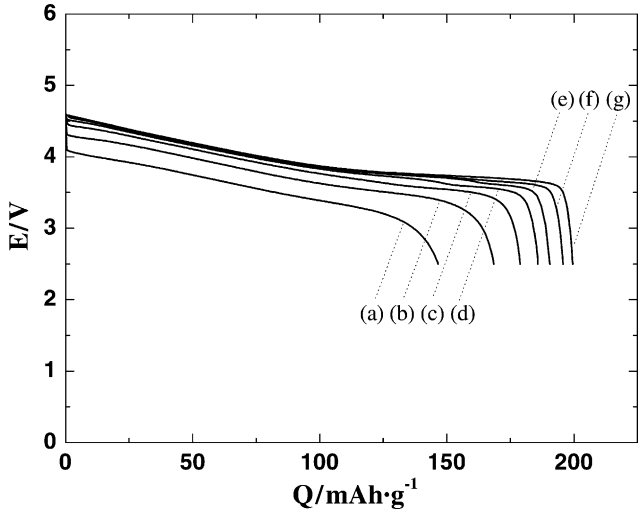

Fig. 3. Rate-capability tests on a Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell. The cell was charged at 0.17 mA cm^{-2} up to 4.6 V and then discharged to 2.5 V at (a) 14.7 mA cm^{-2} (1600 mA g^{-1} based on $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ sample weight), (b) 7.3 (800), (c) 3.7 (400), (d) 1.8 (200), (e) 0.92 (100), (f) 0.46 (50.0), or (g) 0.17 (18.3). The sample weight loaded was 0.0272 g. The electrode thickness was 90 μm.

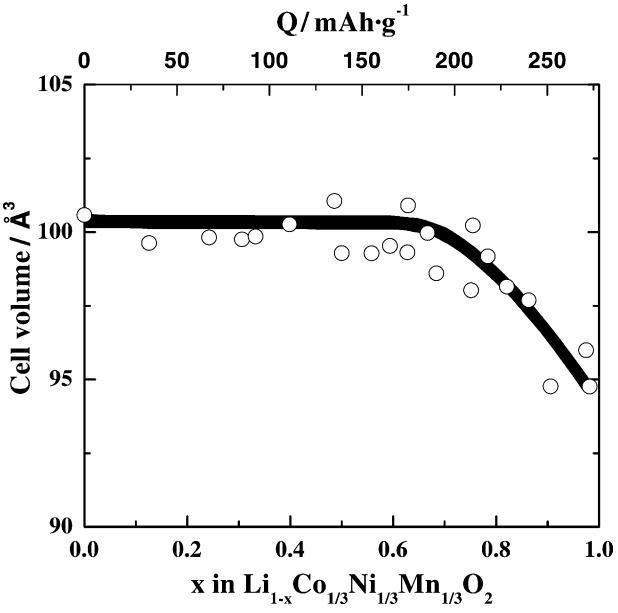

Fig. 5. Change in the unit cell volume as a function of x in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$. Zero-volume change can be seen in $x = 0$ to 0.67.

$LiNiO_2$ [3] or $Li[Li_xMn_{2-x}]O_4$. As was reported previously [3], when a Li/$LiNiO_2$ cell was operated below 4.2 V, it cycles without any noticeable loss of rechargeable capacity. However, it deteriorates rapidly at voltages above 4.2 V due mainly to the formation of nickel dioxide. For the Li/$LiCoO_2$ cell, $LiCoO_2$ can be cycled over the composition range of $0 < x < 0.5$ in $Li_{1-x}CoO_2$ with a rechargeable capacity of 135–150 mAh g^{-1}. The upper limit of charge-end voltage is about 4.3 V for many reasons, such as cycle life, safety, gassing, and so forth. As can clearly be seen in Figs. 2 and 4, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ showed a rechargeable capacity of more than 200 mAh g^{-1} with excellent capacity retention. The charge and discharge coulombic efficiencies are approximately 99% in this case. Constant current charge followed by constant voltage charge (so-called CCCV) at 4.3–4.6 V is possible, although a better selection of electrolyte must be done to improve coulombic efficiency.

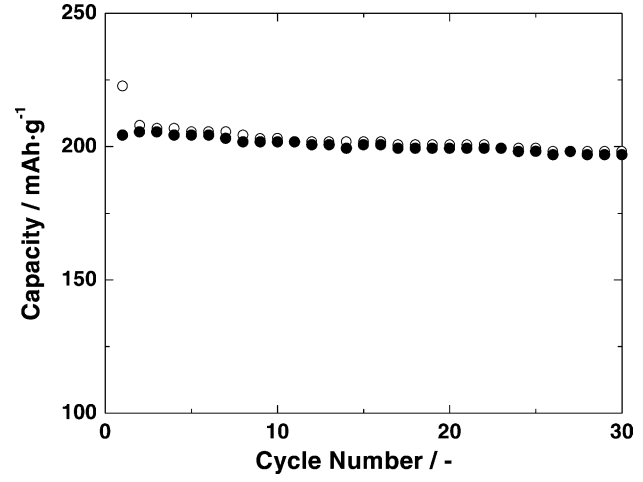

Fig. 4. Charge and discharge capacities as a function of cycle number for a cell operated at 0.17 mA cm^{-2} in voltages of 2.5–4.6 V at 30 °C. Open and closed circles indicate charge and discharge capacities, respectively.

Fig. 5 shows the change in unit cell volume determined by ex situ XRD. For $0 \leq x \leq 0.67$ in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$, the c-axis dimension elongated from 14.23 to 14.50 Å while the a-axis shortened from 2.86 to 2.82 Å (not shown). Consequently, the unit cell volume remains almost constant, i.e. zero-volume change until $x = 0.67$ in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$. This is similar to the zero-volume change for $LiCo_{1/2}Ni_{1/2}O_2$ [12]. In the case of $LiCoO_2$ [11], the unit cell volume expands from 97 $Å^3$ to a maximum value of 100 $Å^3$ on charge, so that the unit cell volume of the charged state of $LiCoO_2$ is almost the same as that of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$. Therefore, a lithium-ion cell with $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is expected to be equivalent to or superior to that with $LiCoO_2$ in terms of both gravimetric and volumetric energy densities.

The thermal behavior in the charged states of lithium insertion materials with electrolyte solution is key to considering suitability the positive electrodes for lithium-ion batteries. Fig. 6 shows the results on the DSC measurements for $\square_{0.88}Li_{0.12}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$, $\square_{0.88}Li_{0.12}NiO_2$ and $\square_{0.89}Li_{0.11}CoO_2$. The DSC samples were prepared electrochemically. After a constant-current charge at 0.3 mA cm^{-2} up to 5.0 V the electrode was taken out of the cell, and excess electrolyte (1 M $LiPF_6$ EC/DMC = 3/7) was wiped off with filter paper. A piece of the crushed pellet was mechanically sealed in an aluminum cell. The weight of the sample in the aluminum cells was calculated by measuring the cell weight with and without the sample. DSC signals were measured at a heating and cooling rate of 5 °C min^{-1}.

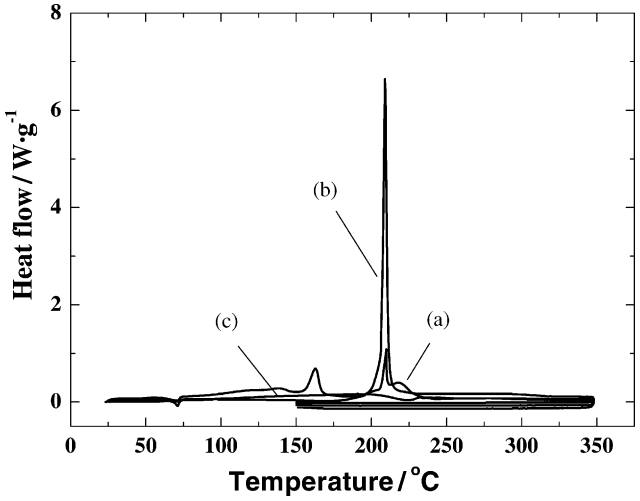

Fig. 6. DSC curves for (a) $\square_{0.88}Li_{0.12}NiO_2$, (b) $\square_{0.89}Li_{0.11}CoO_2$, and (c) $\square_{0.88}Li_{0.12}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ containing electrolyte of 1 M $LiPF_6$ EC/DMC (3/7 v/v). The samples were prepared electrochemically using compressed pellets. Heating and cooling rates were 5 °C min^{-1}.

The degree of oxidation x in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$, $Li_{1-x}NiO_2$ or $Li_{1-x}CoO_2$ was calculated from the charge capacity and the theoretical capacity based on a one-electron transfer per $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (278 mAh g^{-1}), $LiNiO_2$ (275 mAh g^{-1}) or $LiCoO_2$ (274 mAh g^{-1}). As seen in Fig. 6, two exothermic spikes were observed at ca. 160 and 210 °C for charged $LiCoO_2$ and a spike at ca. 210 °C for the charged $LiNiO_2$. Although some exothermic and endothermic reactions are involved in DSC signals on $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, the thermal behavior of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is milder than that of $LiCoO_2$ or $LiNiO_2$.

As was described above, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is equivalent to or better than $LiCoO_2$, $LiNiO_2$, or $Li[Li_xMn_{2-x}]O_4$ for lithium-ion batteries. We believe that $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is a possible alternative to $LiCoO_2$ for advanced lithium-ion batteries.

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