

Electrochemical behaviors of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in lithium batteries at elevated temperatures

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Abstract

Electrochemical behaviors of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were examined in non-aqueous lithium cells and lithium-ion cells with $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ at 30, 55, 75, and 95 °C. $\text{Li}/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cells showed rechargeable capacity of 205 mAh g^{-1} at 30 °C, 210 mAh g^{-1} at 55 °C, and 225 mAh g^{-1} at 75 °C in voltages of 2.5–4.6 V. Results on rate-capability tests at 55 °C indicated that $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was capable to deliver 160 mAh g^{-1} of capacity even at 4000 mA g^{-1} while high-rate charge was very hard due to electrical shortage derived from lithium metal deposition. Lithium-ion cells of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ could operate with rechargeable capacity of 150 mAh g^{-1} at 1600 mA g^{-1} without any electrical shortage during charge and discharge at 55 °C. One-hundred cycle test of the lithium-ion cell with variation of temperature 55, 75, and 95 °C, in voltages of 1.00–3.05 V was also examined and shown that $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was the most promising positive-electrode material for advanced lithium-ion batteries.

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1. Introduction

In recent years, there has been a growing interest in lithium nickel manganese oxides with or without cobalt as positive-electrode materials for advanced lithium-ion batteries [1–6]. Among them, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ shows 200 mAh g^{-1} of rechargeable capacity in voltages of 2.5–4.6 V with excellent rate-capability [2]. The thermal behavior of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is milder than that of $\text{Li}_{1-x}\text{NiO}_2$ or $\text{Li}_{1-x}\text{CoO}_2$. $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ may be the most promising positive-electrode material for high-energy, high-power lithium-ion batteries [3]. For high-power application, electrochemical behaviors of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ at elevated temperatures have to be examined because batteries for such an application easily raise internal temperature.

In this paper, we report electrochemical behaviors of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in lithium non-aqueous cells and lithium-ion cells with $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ at 30, 55, 75, 95 °C

and discuss whether or not $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is a possible candidate material for high-power lithium-ion batteries.

2. Experimental

$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was prepared from $\text{LiOH}\cdot\text{H}_2\text{O}$ and a triple hydroxide of cobalt, nickel, and manganese (MX-034-1, Co:Ni:Mn = 1.00:1.00:1.00, Tanaka Chemical Co., Ltd.). Starting materials were well mixed and pressed into pellets (23 mm diameter and ca. 5 mm thick.). The pellets were heated at 1000 °C for 10 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. $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LT-855-17C, Ishihara Sangyo Co., Ltd., Japan) was used as received after identifying the sample with that reported [8].

In preparing electrodes, polyvinylidene fluoride (PVdF) dissolved in *N*-methyl-2-pyrrolidone (NMP) solution was used as a binder. Black viscous slurry consisting of 88 weight percent (wt.%) $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ or $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$, 6 wt.% acetylene black, and 6 wt.% PVdF was cast on an

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aluminum foil with blade. NMP was evaporated at 120 °C for 30 min, and finally the electrodes were dried under vacuum at 150 °C for 15 h. Then electrodes were punched out into a disk (16 mm of diameter). A lithium electrode was prepared by pressing lithium metal onto a stainless steel sheet. Two sheets of porous polypropylene membrane (Celgard 2500) were used as a separator. Electrolyte used was 1 M LiPF₆ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3/7 by volume) solution. Electrochemical cells used at 30 °C were the same as described previously [9]. For examinations at 55, 75 and 95 °C electrochemical cells (type TJ-A-01; Tomcell Japan Co., Ltd.) were used. Other sets of experimental conditions are given in Section 3.

3. Results and discussion

LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ prepared was identified by XRD to be the identical sample with that reported previously [1,2,4,6,7], i.e., LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ (P3₁₂; $a = 4.959(3)$ Å, $c = 14.254(8)$ Å) consisting of Co³⁺ (low spin state), Ni²⁺, and Mn⁴⁺ ions. Morphology of particles is spherical and its surface is smooth due to high-temperature synthesis [1].

Fig. 1 shows charge and discharge curves of Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ cells operated at 30, 55, and 75 °C. The cells were charged and discharged at 0.30 mA cm⁻² in the voltages of 2.5–4.6 V. According to our experience, charging curves usually scatter or fall down at certain voltage and voltage never reaches charge-end voltage above 4.5 V at elevated temperature. However, Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ cells cycle nicely at 4.6 V even at 75 °C. Increase in rechargeable capacity from ca. 205 to 225 mAh g⁻¹ is observed with increasing temperature from 30 to 75 °C. Since reversibility of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ have already been examined at 30 °C and the potentials as a function of x in Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O₂ were obtained, increase in rechargeable capacity is maybe due to the negative shift of reversible potential as a function of temperature, not kinetic effect. As seen in Fig. 1, charge and discharge coulombic efficiency decreased when temperature rises, suggesting side reactions associating with electrolyte. When the cell is cycled at 100 °C, steady-state charge and discharge curves were not observed due to increase in polarization cycle by cycle. After cell failure at 100 °C, when we renewed electrolyte and lithium, the cell can operate at 30 °C although some damage was seen in rechargeable capacity and voltage shape in charge and discharge curves.

Fig. 2 shows the results on rate-capability tests of a Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ cell examined at 55 °C. To measure rate-capability for discharge, a large lithium electrode (5.0 cm²) compared to the positive electrode (2.0 cm²) was used possibly to reduce polarization at a lithium electrode. The cells were charged at 0.50 mA cm⁻² un-

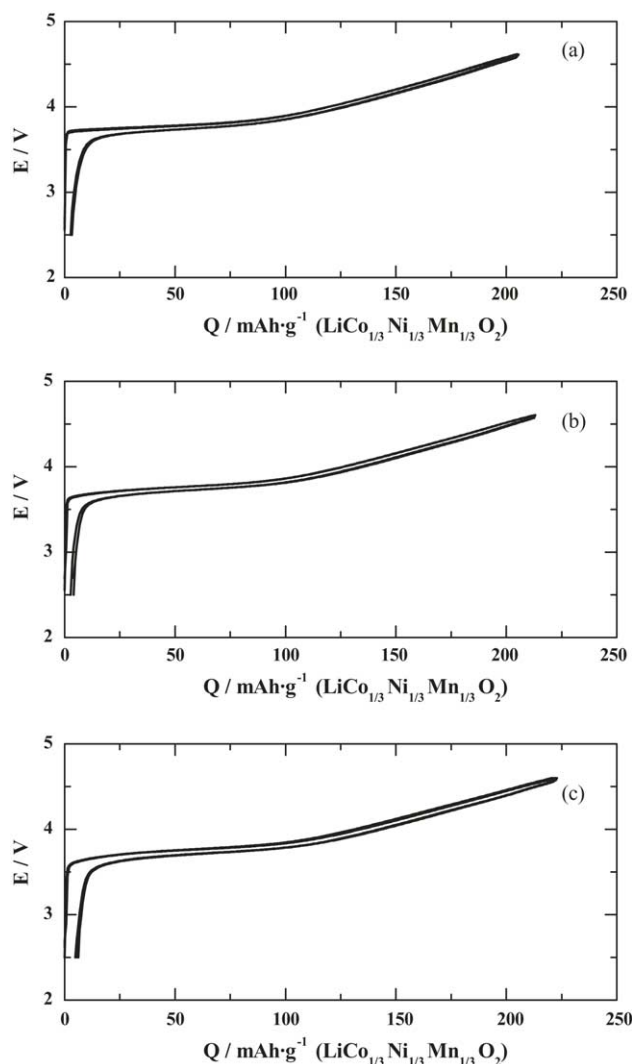


Fig. 1. Charge and discharge curves of a Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ cell operated at a rate of 0.30 mA cm⁻² in voltages of 2.5–4.6 V at (a) 30 °C, (b) 55 °C, or (c) 75 °C.

til voltage reaches 4.6 V and then held at 4.6 V totally for 5 h, which is so-called constant current and constant voltage charge (CCCV; 0.5 mA cm⁻², 4.6 V). The cell was discharged at 0.20–32.0 mA cm⁻² which corresponded to 25–4000 mA g⁻¹ based on LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ weight. The discharge capacity observed is 210 mAh g⁻¹ at 0.20 mA cm⁻² or 25 mA g⁻¹. When the cell is discharged at 32.0 mA cm⁻² or 4000 mA g⁻¹, discharge capacity is observed to be 160 mAh g⁻¹. If we define 200 mAh g⁻¹ is equivalent to nominal capacity, 4000 mA g⁻¹ of discharge current corresponds to 20 C-rate. As clearly seen in Fig. 2, LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ is capable to high-rate discharge as high as 20 C-rate. Recent power application of lithium-ion batteries is required not only for high-rate discharge but also for high-rate charge. The cell with a lithium-negative electrode cannot be used for high-rate charge because of electrical shortage due to irregular lithium deposition at high current.

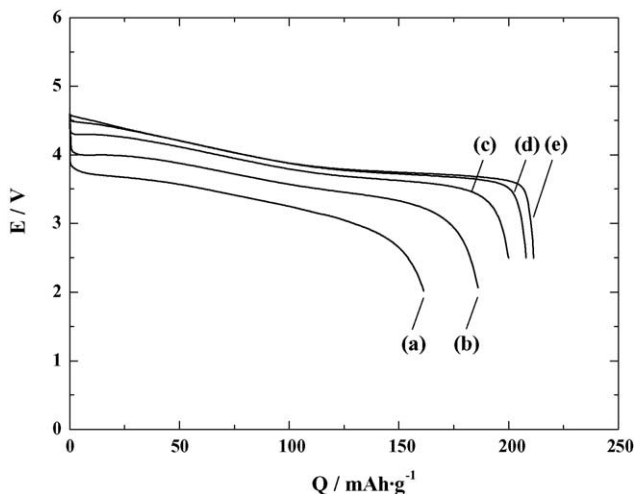


Fig. 2. Rate-capability tests on a $\text{Li}/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell operated at 55°C . The cell was charged at 0.50 mA cm^{-2} then held at 4.6 V totally for 4 h and discharged to 2.0 V at (a) 32.0 mA cm^{-2} (4000 mA g^{-1} based on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample weight, corresponding to 20 C-rate), (b) 19.2 mA cm^{-2} (2400 mA g^{-1}) and to 2.5 V at (c) 6.4 mA cm^{-2} (800 mA g^{-1}), (d) 1.6 mA cm^{-2} (200 mA g^{-1}), or (e) 0.2 mA cm^{-2} (25 mA g^{-1}). The electrode mix consisted of $88\text{ wt.}\%$ $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $6\text{ wt.}\%$ acetylene black, and $6\text{ wt.}\%$ PVdF. Electrolyte used was 1 M LiPF_6 dissolved in $\text{EC}/\text{DMC} = 3/7$ solution. Electrode thickness was ca. $60\text{ }\mu\text{m}$ in dry state.

In order to avoid the problem, lithium-ion cells with zero-strain insertion material of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$ were fabricated and examined for high-rate charge and discharge.

Fig. 3 shows the result on rate-capability tests of a lithium-ion cell of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$ and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The cell was operated at 55°C in voltages of $1.00\text{--}3.05\text{ V}$, which corresponded to voltages of $2.55\text{--}4.60\text{ V}$ against Li for $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode because $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$ showed flat operating voltage of 1.55 V versus Li [8]. The ratio of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$ to $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in weight was set to 1.64 , i.e., positive-electrode-limited capacity, in order to examine high-rate capability of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode for both charge and discharge. For charging tests, the cells were discharged at 0.15 mA cm^{-2} to 1.0 V and charged at several currents. For discharging tests, the cells were charged at CCCV (1.7 mA cm^{-2} , 3.05 V) for 1.5 h and discharged. Current applied for both charge and discharge was $0.43\text{--}13.6\text{ mA cm}^{-2}$ or $50\text{--}1600\text{ mA g}^{-1}$ based on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ weight. When the cell was charged and discharged at 0.43 mA cm^{-2} ($1/4\text{ C-rate}$), discharge capacity observed was more than 200 mAh g^{-1} . As clearly seen in Fig. 3(a), no cell damage due to electrical shortage is observed even at 13.6 mA cm^{-2} (8 C-rate). Capacity at 8 C-rate was ca. 150 mAh g^{-1} in this case.

Continuous cycles at high temperatures are not expected, but tolerance of high temperature is necessary and sufficient condition in applying lithium insertion materials to high-power application. In order to examine tolerance of high temperature for lithium-ion cells of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$

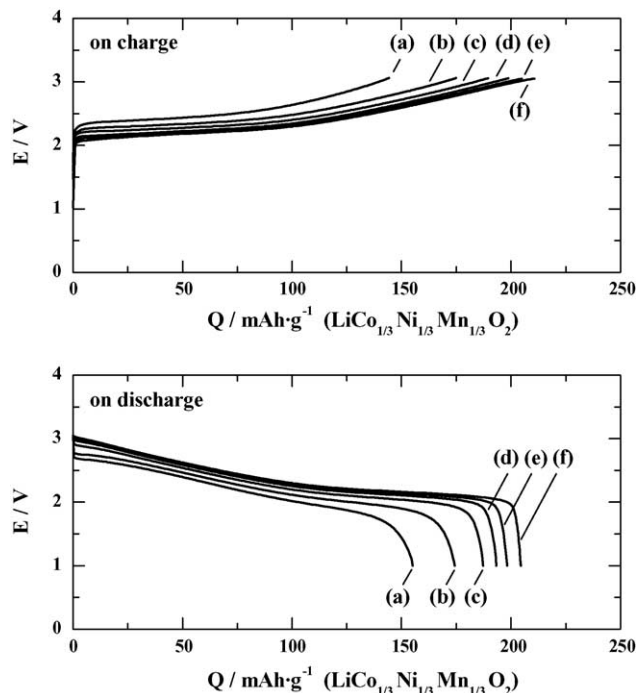


Fig. 3. Rate-capability tests on a lithium-ion cell consisting of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$ and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The cell was operated at 55°C at a rate of (a) 13.6 mA cm^{-2} (1600 mA g^{-1} based on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample weight, corresponding to 8 C-rate), (b) 10.2 mA cm^{-2} (1200 mA g^{-1}), (c) 6.8 mA cm^{-2} (800 mA g^{-1}), (d) 3.4 mA cm^{-2} (400 mA g^{-1}), (e) 1.7 mA cm^{-2} (200 mA g^{-1}) or (f) 0.43 mA cm^{-2} (50 mA g^{-1}). The ratio of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was 1.63 , i.e., positive-electrode-limited capacity.

and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, one-hundred-cycle test was performed with varying temperatures from 55 to 95 via 75°C in voltages of $1.00\text{--}3.05\text{ V}$. Fig. 4 shows charge and discharge curves of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell operated at 55 , 75 and 95°C , respectively. Discharge capacity as a function of cycle number is shown in Fig. 5. The cell was discharged at 1.4 mA cm^{-2} (1 C-rate) to 1.0 V after CCCV (2.1 mA cm^{-2} or 1.5 C-rate , 3.05 V)—charging for 1 h . CCCV at high voltage and high temperature is usually very hard to obtain steady charge and discharge curves. However, the cell can cycle nicely even at 75 or 95°C . Rechargeable capacities observed are 185 mAh g^{-1} at 75°C or 165 mAh g^{-1} at 95°C . Although LiPF_6 EC/DMC used in this study is not stable at temperatures above 60°C [10,11], fact is that lithium-ion cells with LiPF_6 EC/DMC can cycle even at $75\text{--}95^\circ\text{C}$ as seen in Fig. 4. After cycle tests at 95°C , electrolyte was changed from transparent to opaque or black in color. When the cell was operated at 120°C , the cell did not reach 3.05 V of charge-end voltage.

In examining lithium-ion cells of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, we used LiPF_6 EC/DMC as electrolyte in this study. However, we do not need EC-based or LiPF_6 -based electrolyte because of no graphite-negative electrode. Several option of selecting solute and solvent is possible in making lithium-ion cells of

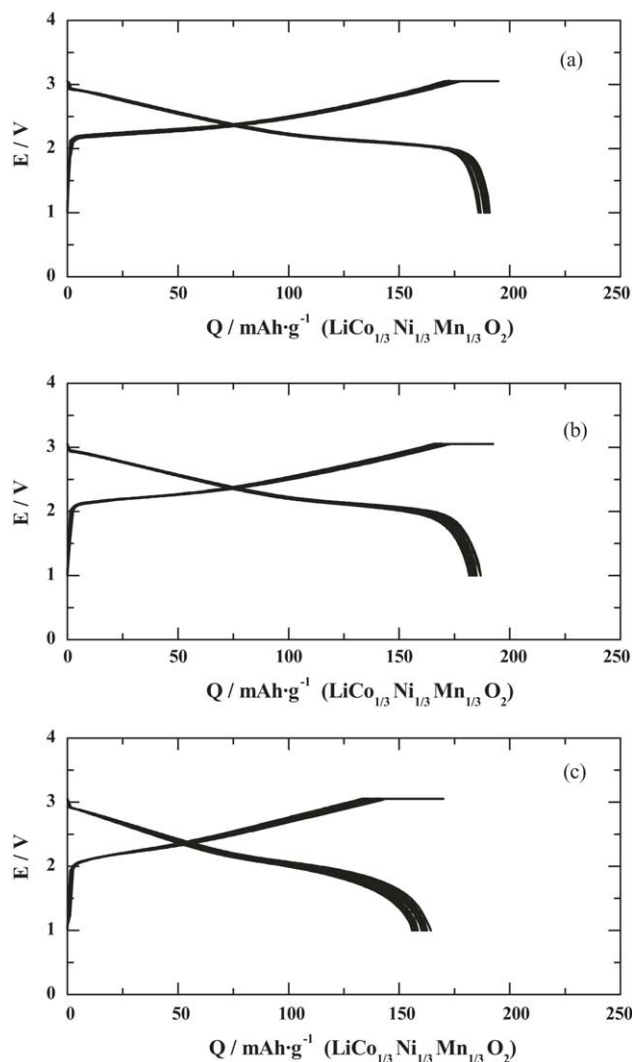


Fig. 4. Charge and discharge curves of a $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell operated at (a) 55 °C, (b) 75 °C, or (c) 95 °C in voltages of 1.0–3.05 V. Charge current applied was 2.1 mA cm^{-2} corresponding to 1.5 C-rate then held at 3.05 V totally for 1 h, and discharge current applied was 1.4 mA cm^{-2} (1 C-rate) to 1.0 V. The ratio of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was 1.63, i.e., positive-electrode-limited capacity. The curves were taken from (a) 11th to 20th, (b) 41st to 50th, and (c) 76th to 85th cycles in Fig. 5.

$\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. As were described in this paper, we have been collecting data on capacity failure under severe conditions, such as high-rate charge and discharge, high-temperature operation, and long-term tests. However, we have not seen that fatal damage is the structural destruction of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ yet.

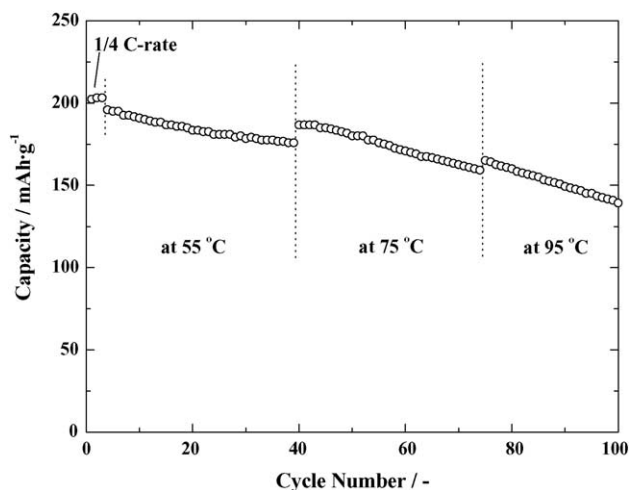


Fig. 5. Discharge capacities as a function of cycle number for the cell operated at 1.4 mA cm^{-2} (1 C-rate) at 55, 75, and 95 °C. Charge current applied was 2.1 mA cm^{-2} then held at 3.05 V totally for 1 h. The capacities for 1st–3rd cycles were obtained at 0.35 mA cm^{-2} (1/4 C-rate) at 55 °C. Charge and discharge curves were shown in Fig. 4.

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