

# Electrochemical evaluation of mixed oxide electrode for Li-ion secondary batteries: $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$

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## Abstract

In attempt to utilize spinel compound, a blend type of positive electrode,  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (1:1 in weight), was representatively investigated. Though spinel  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  is modified by Li replacement at Mn sites, its capacity fading was inevitable by HF attack into the electrolyte at 25 °C and especially at 60 °C. The specific discharge capacity of the mixed positive electrode,  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (1:1 in weight), had a sum average value of  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  electrodes. Interestingly, the mixed positive electrode had greatly improved capacity retention even at 60 °C. The capacity fading was only of about 8 mAh g<sup>-1</sup> by applying 1 C rate (150 mA g<sup>-1</sup>) during 100 cycles. In the full cell test utilizing graphite as the negative electrode, the retained capacity was about 96% of its initial capacity by applying 1 C current at 25 °C. It is suggested that the mixed electrode is considered to be a quite promising positive electrode material to be applied for lithium-ion batteries.

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**Keywords:** Spinel;  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ ;  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ; Positive electrode; Lithium; Battery

## 1. Introduction

Manganese spinel  $\text{LiMn}_2\text{O}_4$  and its derivatives are the most attractively studied cathode materials for lithium secondary batteries because of their three dimensional Li<sup>+</sup> diffusion, low cost, abundance, and nontoxicity [1–3]. Though  $\text{LiMn}_2\text{O}_4$  cycles well on the 4 V region, capacity fading occurs severely by cycling at elevated temperatures (>50 °C). A lot of efforts have been made to improve the capacity retention at higher temperature. Substitution for Mn sites was effective for high capacity retention such as Li, Al, Co, Ni, Fe, Cr, etc. [4–9]. Since the Li is one of the light elements, if the Li replaces the Mn sites the obtainable theoretical capacity is higher than other elements.

Though the structure of  $\text{LiMn}_2\text{O}_4$  is stabilized by Li replacement on Mn sites, however, the obtained specific discharge capacity is still smaller than that of layered compounds, such as  $\text{LiCoO}_2$  [10] and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  [11]. Layered  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  delivers a large specific discharge over

180 mAh g<sup>-1</sup>. Though the high capacity is pretty attractive, the critical drawback of this material is structural instability at highly oxidized state, as it was observed by differential scanning calorimetry (DSC) [12].

Recently, Numata et al. [13] reported interesting results that when the blended electrode of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders were stored at 80 °C for 10 days, the concentrations of both HF and Mn<sup>2+</sup> into the electrolytes were lower comparing to  $\text{LiMn}_2\text{O}_4$ . Therefore, it is thought that if both materials are mixed with a constant ratio, they would compensate for their disadvantages each other and could be comparable or beat the conventional  $\text{LiCoO}_2$  in respect to capacity, structural and thermal stability. Here, we report on the basic properties of the mixed oxide electrodes.

## 2. Experimental

$\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  oxides were prepared by a conventional solid-state reaction. The composite materials were prepared by mixing  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (1:1 in weight) oxides in a mixer.

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Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) measurement using Cu K $\alpha$  radiation was employed to identify the crystalline phase of the prepared materials and electrochemically cycled electrodes. XRD data were obtained  $2\theta = 10\text{--}80^\circ$ , with a step size of  $0.03^\circ$  and a count time of 5 s.

For fabrication of the cathode, the blended powders were mixed with acetylene black and polyvinylidene fluoride (95:3:2) in *N*-methylpyrrolidinon. The slurry thus obtained was pasted onto Al foil and dried at  $80^\circ\text{C}$  for 1 day for roll-pressing, and then dried again at  $120^\circ\text{C}$  for 4 days in vacuum state prior to use. A coin cell (CR2016) consisted of the cathode, lithium foil as the anode and 1 M LiPF $_6$  in ethylene carbonate – diethyl carbonate (1:1 in volume) as the electrolyte. The assembly of the cells was carried out in an Ar-filled glove box. The cells were firstly charged, and then discharged between 3.3 and 4.3 V with various current rates at 25 and  $60^\circ\text{C}$ . Long cycle-life tests were performed by employing a laminated type cell (size: T16W90L160). Graphite was used as the negative electrode. The cell was cycled between 3.0 and 4.2 V at  $25^\circ\text{C}$ .

### 3. Results and discussion

The initial discharge profiles of Li $_{1.1}$ Mn $_{1.9}$ O $_4$  and LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ , and the mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$ :LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  = 1:1 in weight) were cycled between 3.3 and 4.3 V with 0.2 C ( $30\text{ mA g}^{-1}$ ) at  $25^\circ\text{C}$ , as shown in Fig. 1. The initial discharge capacity of the spinel compound was about  $103\text{ mAh g}^{-1}$  and that of the layered LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  delivered approximate  $205\text{ mAh g}^{-1}$ . From these results, it is expected that the mixed electrode may show a discharge capacity of about  $150\text{ mAh g}^{-1}$ , based on their gravimetric capacity in Fig. 1. The initial discharge capacity of the mixed electrode obtained was about  $153\text{ mAh g}^{-1}$ , as anticipated. The capacity was comparable or a little higher than that of LiCoO $_2$ .

Fig. 2 exhibits continuous charge–discharge profiles of the mixed electrode during 100 cycles. Firstly, rate-capability

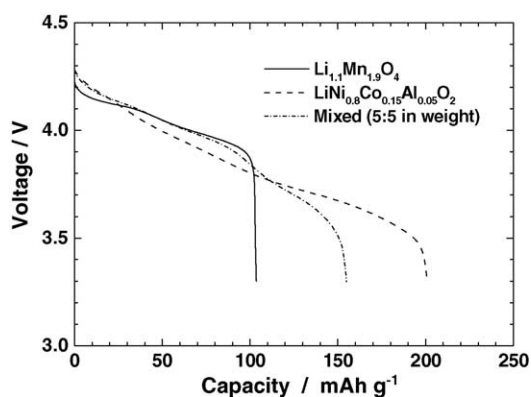


Fig. 1. Initial discharge curves of Li $_{1.1}$ Mn $_{1.9}$ O $_4$ , LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ , and mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$ :LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  = 1:1 in weight). The applied current density across the cathode was  $30\text{ mA g}^{-1}$  (0.2 C) at  $25^\circ\text{C}$ .

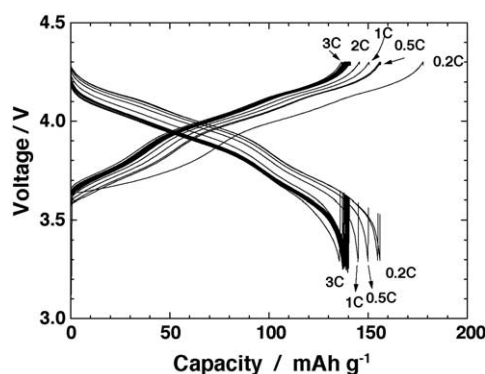


Fig. 2. Consecutive charge and discharge curves of mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$ :LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  = 1:1 in weight). Firstly, the sequence of the applied current densities are as follow;  $30\text{ mA g}^{-1}$  (0.2 C),  $75\text{ mA g}^{-1}$  (0.5 C),  $150\text{ mA g}^{-1}$  (1 C),  $300\text{ mA g}^{-1}$  (2 C), and  $450\text{ mA g}^{-1}$  (3 C) at  $25^\circ\text{C}$ . Then, the cell was continuously cycled 100 times by applying  $450\text{ mA g}^{-1}$  (3 C) at  $25^\circ\text{C}$ .

tests were done at various currents. Then, the cell was continuously cycled at 3 C ( $450\text{ mA g}^{-1}$ ). The rate capability was relatively good. In comparison with 0.5 C operation, the obtained discharge capacity was about  $140\text{ mAh g}^{-1}$  at 3 C rate, of which the capacity corresponds to 93.3% of that of 0.5 C. The higher capacity was maintained during 100 cycles in Fig. 2.

Fig. 3 shows continuous cycling results of Li $_{1.1}$ Mn $_{1.9}$ O $_4$ , LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ , and the mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$ :LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  = 1:1 in weight) by applying 1 C ( $150\text{ mA g}^{-1}$ ) at 25 and  $60^\circ\text{C}$ . Spinel Li $_{1.1}$ Mn $_{1.9}$ O $_4$  exhibited a gradual capacity fading during 100 cycles (about  $15\text{ mAh g}^{-1}$ ). Such a capacity fading is due to the disproportionation reactions at the particle surface of discharged Li $_x$ Mn $_2$ O $_4$  electrode, resulting in a soluble MnO component [14]. On contrary, the mixed electrodes showed less capacity fading at 25 and  $60^\circ\text{C}$  cycling. It is quite unusual that because the spinel Li $_{1.1}$ Mn $_{1.9}$ O $_4$  is only physically blended with LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  so that the mixed electrode should

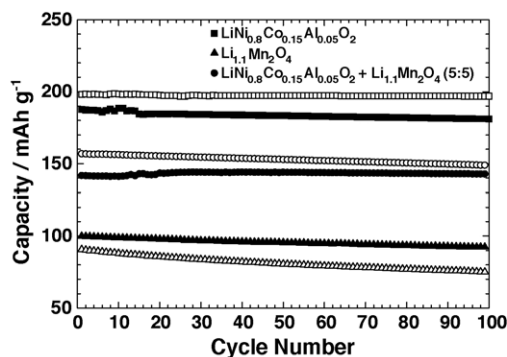


Fig. 3. Specific discharge capacities of Li $_{1.1}$ Mn $_{1.9}$ O $_4$ , LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ , and mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$ :LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$  = 1:1 in weight). The applied current density across the cathode was  $150\text{ mA g}^{-1}$  (1 C) at 25 and  $60^\circ\text{C}$ ; closed marks denotes  $25^\circ\text{C}$  cycling and open marks signifies  $60^\circ\text{C}$  cycling.

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