

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⁻¹ by applying 1 C rate (150 mA g⁻¹) 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 LiMn_2O_4 and its derivatives are the most attractively studied cathode materials for lithium secondary batteries because of their three dimensional Li⁺ diffusion, low cost, abundance, and nontoxicity [1–3]. Though LiMn_2O_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 LiMn_2O_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 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⁻¹. 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 LiMn_2O_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 Mn²⁺ into the electrolytes were lower comparing to LiMn_2O_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 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 α 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° 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°C for 1 day for roll-pressing, and then dried again at 120°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°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°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 mA g^{-1}) at 25°C , as shown in Fig. 1. The initial discharge capacity of the spinel compound was about 103 mAh g^{-1} and that of the layered LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ delivered approximate 205 mAh g^{-1} . From these results, it is expected that the mixed electrode may show a discharge capacity of about 150 mAh g^{-1} , based on their gravimetric capacity in Fig. 1. The initial discharge capacity of the mixed electrode obtained was about 153 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

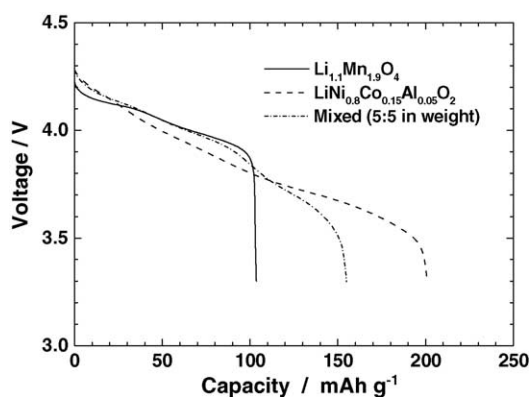


Fig. 1. Initial discharge curves of Li $_{1.1}$ Mn $_{1.9}$ O $_4$, LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$, and mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$:LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ = 1:1 in weight). The applied current density across the cathode was 30 mA g^{-1} (0.2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

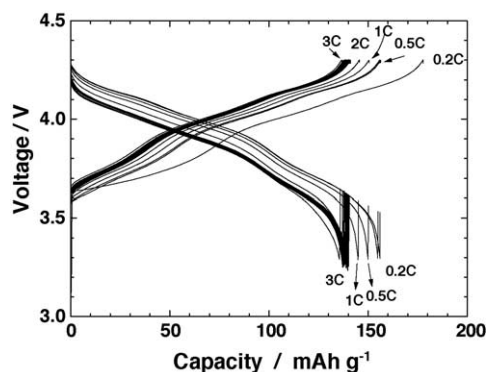


Fig. 2. Consecutive charge and discharge curves of mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$:LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ = 1:1 in weight). Firstly, the sequence of the applied current densities are as follow; 30 mA g^{-1} (0.2 C), 75 mA g^{-1} (0.5 C), 150 mA g^{-1} (1 C), 300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

tests were done at various currents. Then, the cell was continuously cycled at 3 C (450 mA g^{-1}). The rate capability was relatively good. In comparison with 0.5 C operation, the obtained discharge capacity was about 140 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 $_2$ 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 mA g^{-1}) at 25 and 60°C . Spinel Li $_{1.1}$ Mn $_2$ O $_4$ exhibited a gradual capacity fading during 100 cycles (about 15 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°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

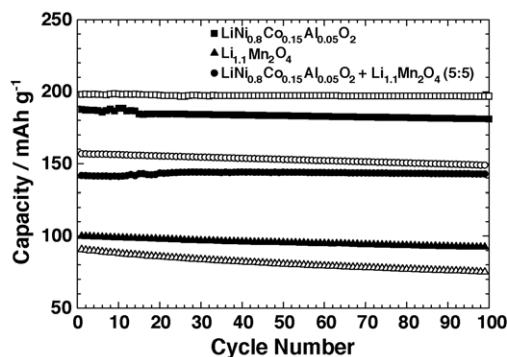


Fig. 3. Specific discharge capacities of Li $_{1.1}$ Mn $_{1.9}$ O $_4$, LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$, and mixed electrode (Li $_{1.1}$ Mn $_{1.9}$ O $_4$:LiNi $_{0.8}$ Co $_{0.15}$ Al $_{0.05}$ O $_2$ = 1:1 in weight). The applied current density across the cathode was 150 mA g^{-1}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

show the similar capacity fading by electrochemical cycling. The capacity loss was only about 8 mAh g^{-1} during 100 cycles for 60°C test. In fact, the use of electrolyte-flooded cells enables the amplification of capacity-fading problems because the relatively high solution volume increases the detrimental impact of contamination, for example, acidic species such as HF, and allows the dissolution of protective surface films. On the other hand, the use of such flooded cells employing the mixed electrode ($\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4:\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 = 1:1$ in weight) enables a clear demonstration of improvement on preventing capacity fading. Recently, Nohma et al. [15] also reported the similar phenomena in the blended electrode, $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and $\text{LiNi}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2$ (6:4 in weight).

Fig. 4 depicts powder XRD patterns of fresh $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and 100 times cycled mixed electrode ($\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4:\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 = 1:1$ in weight) by applying 1 C (150 mA g^{-1}) current at 25 and 60°C . It is common that extensive cycling of spinel electrode led to a broadening of diffraction peaks in XRD pattern, which is due to the degradation of the original structure. However, as can be seen in Fig. 4, the peak broadening is hardly observed in the XRD patterns of 25 and 60°C cycling results. No other secondary peaks were observed in the XRD pattern. Comparing to the XRD pattern of the fresh $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$, it is thought the original host structure is rather maintained even after cycling. The high capacity retention in Fig. 3 clearly supports that manganese dissolution into the electrolyte is not severe during cycling and is probably suppressed by the simple blending of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. As a result, the

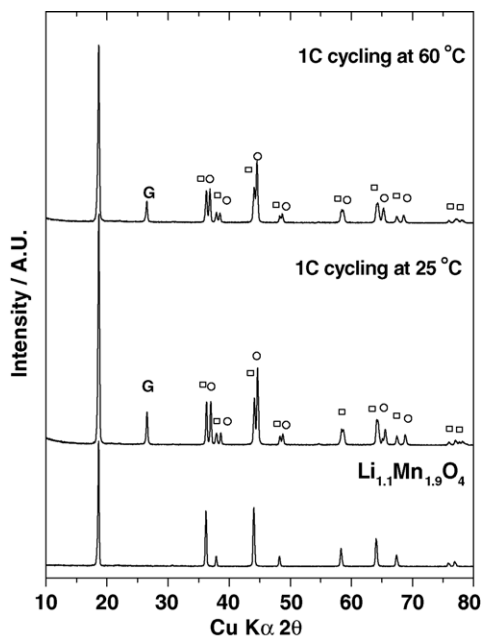


Fig. 4. XRD patterns of mixed electrode ($\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4:\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 = 1:1$ in weight) after 100 times cycling at 25 and 60°C . $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ was plotted as a reference material.

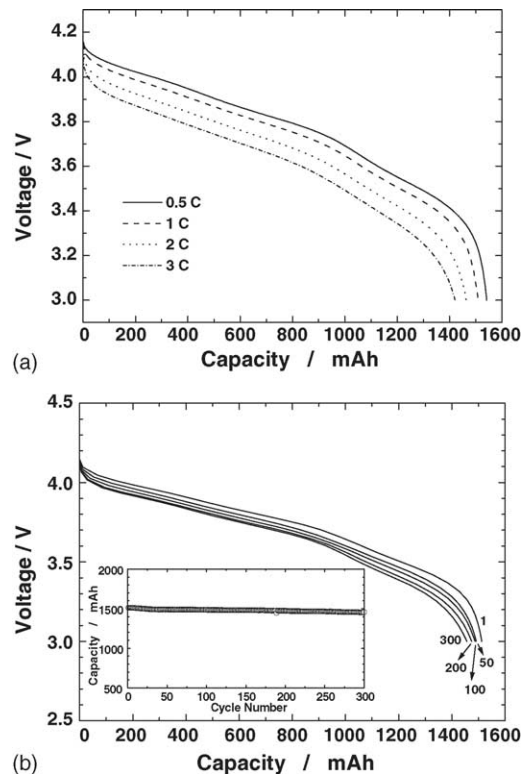


Fig. 5. (a) Rate capability of mixed electrode ($\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4:\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 = 1:1$ in weight)/carbon full cell and (b) selective discharge curves during 300 cycles. The inset means the corresponding cyclability. The cell was charged and discharged by applying 1 C current at 25°C .

higher capacity might be kept. Further studies are necessary to elucidate the origin of capacity retention of the mixed oxide electrode (Fig. 5).

A full cell adapting graphite as the negative electrode was fabricated. Rate capability of the full cell was comparable to that of coin cell shown in Fig. 2. To observe the cycling stability of the mixed electrode, continuous cycling was carried by applying 1 C rate at 25°C . The cell showed discharge capacity about 1510 mAh, as designed, and the capacity retention was satisfactory. Spinel LiMn_2O_4 electrode usually shows a severe capacity fading so that the capacity retention is difficult during cycling [1–9]. It is surprising that even though the positive electrode is composed of 50 wt.% of spinel oxide, over 96% of its initial capacity was maintained during 300 cycles. It is likely that if manganese dissolution occurred the higher capacity would not be kept during the extensive cycling. Therefore, we believe that the mixed electrode ($\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4:\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 = 1:1$ in weight) is considered to be a quite promising positive material for lithium-ion batteries.

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