# Electrochemical Properties of $LiNi_{1/2}M_{1/2}O_2$-$Li_2MO_3$(M=Ti, Mn) Solid Solution

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## . Introduction

High capacity cathode materials based on $Li_2MnO_3$ recently attract much attention because it can improve the capacity of Lithium Ion Batteries. Since its high capacity can not be explained by redox reaction of metal ions, several mechanisms have been proposed.[1.2] Recently Ohzuku et al have proposed possible two mechanism to explain its high capacity.[3] One is redox of Mn ion, the other that of $O^{2-}$ ion.

In this paper, we discuss which mechanism is suitable for $Li_2MnO_3$ based cathode materials to evaluate the capacities of $LiNi_{1/2}M_{1/2}O_2$-$Li_2MO_3$ (M=Ti, Mn) solid solution. Here, a ratio of $LiNi_{1/2}M_{1/2}O_2$ to $Li_2MO_3$ was fixed at 1/2, then chemical formula of the solid solution would be written as $Li_{5/3}Ni_{1/6}Mn_{5/6-x}Ti_xO_{8/3.}$

## Experimental

Precursors were prepared by spray drying method where pH of aqueous solution containing $Mn^{2+}$, $Ni^{2+}$, $Li^+$ and $Ti(C_2O_4)_3^{2-}$ and citric acid is adjusted at 5 – 6 by $NH_3$ solution. After precursors were decomposed in air at 400 $^oC$, they were fired at 900 $^oC$ for 12 h in air.

The electrochemical characterizations were performed using CR2032 coin type cells at 60 $^oC$. The electrolyte was 1M $LiPF_6$-EC/DMC (1:2 in volume). The current density is 0.2 mA/cm$^2$.

## Results and discussion

Figure 1 shows the XRD profiles of $Li_{5/3}Ni_{1/6}Mn_{5/6-x}Ti_xO_{8/3.}$($0 \leq x \leq 5/6$) prepared at 900 $^oC$. All peaks excepting for $2\theta$ =20 – 35 $^o$ were assigned to be common hexagonal structure and any impurity peaks are not observed. The differences of peak profiles between 20 $^o$ and 35 $^o$ would indicate that atomic arrangement in the layer would change from $C_{2/m}$($0 \leq x \leq 1/6$) to $C_{2/c}$($4.5/6 < x < 5/6$).[4] Lattice parameters, a and c, increase as an increase in x, on the other hand values of $I_{003}/I_{104}$ gradually from 1.54 to 0.9.

Figure 2 shows charge/discharge curves of $Li_{5/3}Ni_{1/6}Mn_{5/6-x}Ti_xO_{8/3}$ at 0.2 mA/cm$^2$. Initial charge curve is composed of sloped part(3.5 – 4.4 V) and flat part. Capacities of the former part are nearly same(60 – 80 mAh/g), however those of the latter depends on the x value(150 – 230 mAh/g). Its values decrease extremely beyond x = 4/6. Shapes of discharge curves are roughly divided into two group. Samples with low x value shows continuous voltage change, on the other hand those with high x value show two voltage plateau at more than 3.5 V and less than 2.5V. Initial discharge capacities of former samples exceed 250 mAh/g.

In this paper, we will discuss the possibility of Mn species where redox reaction of Ti ion would be neglected because of high voltage.

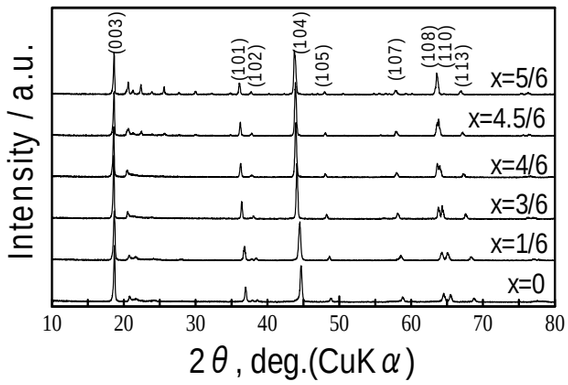


Fig. 1 XRD profiles of $Li_{5/3}Ni_{1/6}Mn_{5/6-x}Ti_xO_{8/3.}$

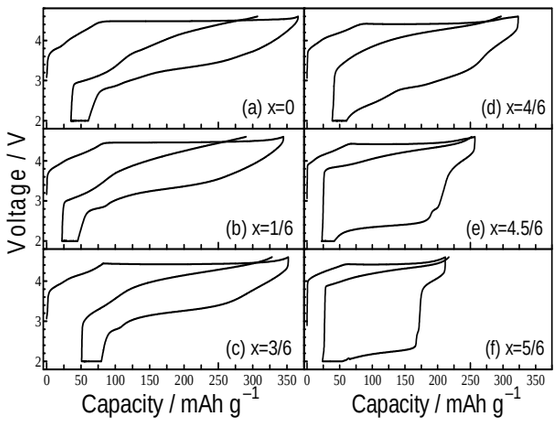


Fig. 2. Charge/discharge curves of $Li_{5/3}Ni_{1/6}Mn_{5/6-x}Ti_xO_{8/3}$ at 60 $^oC$.

## References

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