

Structure and Electrochemical Properties of **$\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ and $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3-x/10}\text{Co}_{3/10}\text{Mn}_{3+x/10}]\text{O}_2$ ($x=0$ and 1) Prepared by Solid State Reaction**

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Recently, layered $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ solid solutions have been investigated by Ohzuku's¹ and Dahn's group². Ohzuku's group and coworkers confirmed by XANES study that the oxidation states of Ni, Co, and Mn are +2, +3, and +4 in $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, respectively. On the other hand, Dahn's group proposed that these compounds should satisfy two rules, as follows: First, the sum of the cation occupation on the 3b sites of space group R-3m(166) in the transition metal layers equals one. Second, the sum of the cation oxidation state must equal three. Base on the rules, they synthesized $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ ($x = 1/4$ and $3/8$) by the "mixed hydroxide" method and these compounds showed good electrochemical properties. Moreover, they also prepared $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$ compounds by the same method and these compounds seems to improve their electrochemical properties in that case³. However, the "mixed hydroxide" method is more complicate than conventional solid sate reaction method. Therefore, we simply prepared $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ and $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3-x/10}\text{Co}_{3/10}\text{Mn}_{3+x/10}]\text{O}_2$ ($x=0$ and 1) by solid state reaction method.

As shown in figure 1, we could prepare the powders which have layered structure R-3m by solid state reaction method. Powder X-ray and Neutron diffraction Rietveld results indicated that $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3-x/10}\text{Co}_{3/10}\text{Mn}_{3+x/10}]\text{O}_2$ ($x=0$ and 1) have less cation mixing than $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. This cation mixing may cause the capacity loss as the Ni^{+2} on 3a sites does in LiNiO_2 system. Therefore, it is expected from Reitveld results that $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3-x/10}\text{Co}_{3/10}\text{Mn}_{3+x/10}]\text{O}_2$ ($x=0$ and 1) shows better electrochemical properties than $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. XANES spectra for Ni K-edge of the prepared powders show in figure 2. XANES spectra indicate that Ni ingredient exists as Ni^{+2} in $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ and $\text{Li}[\text{Li}_{1/10}\text{Ni}_{2/10}\text{Co}_{3/10}\text{Mn}_{4/10}]\text{O}_2$. Whereas Ni ingredient in $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3/10}\text{Co}_{3/10}\text{Mn}_{3/10}]\text{O}_2$ exists nearly as Ni^{+3} to compensate oxidation state. As expected, $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3-x/10}\text{Co}_{3/10}\text{Mn}_{3+x/10}]\text{O}_2$ ($x=0$ and 1) shows better electrochemical properties than $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$.

Acknowledgements

X-ray Absorption Spectroscopic measurements at the Pohang Light Sources (PLS) were supported in part by MOST and POSCO and the authors are grateful to authorities at HANARO for the Neutron powder diffraction experiments.

References

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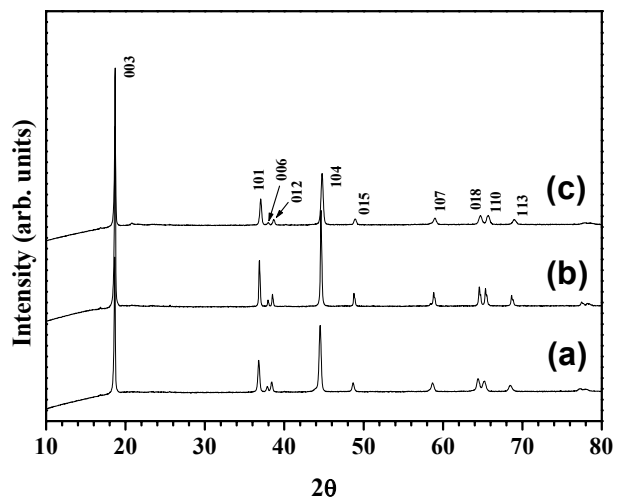


Figure 1. XRD patterns of (a) $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, (b) $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3/10}\text{Co}_{3/10}\text{Mn}_{3/10}]\text{O}_2$, and (c) $\text{Li}[\text{Li}_{1/10}\text{Ni}_{2/10}\text{Co}_{3/10}\text{Mn}_{4/10}]\text{O}_2$ calcined at 950°C in Air.

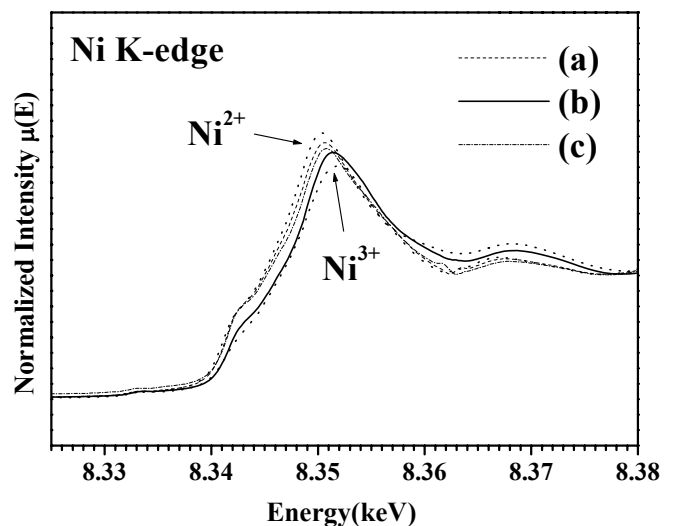


Figure 2. XANES spectra of (a) $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, (b) $\text{Li}[\text{Li}_{1/10}\text{Ni}_{3/10}\text{Co}_{3/10}\text{Mn}_{3/10}]\text{O}_2$, and (c) $\text{Li}[\text{Li}_{1/10}\text{Ni}_{2/10}\text{Co}_{3/10}\text{Mn}_{4/10}]\text{O}_2$.