Structure and Electrochemical Properties of Li[Ni_{3/10}Co_{2/10}Mn_{1/10}]O_{2} and Li[Li_{1/10}Ni_{x/10}Co_{3/10}Mn_{3-x/10}]O_{2} (x= 0 and 1) Prepared by Solid State Reaction

Hoon Taek Chung, Jung Min Kim, and Soo Kwan Jang
Department of Ceramic Engineering, Faculty of Engineering, Dong-shin University, Naju, South Korea

Recently, layered Li[Ni_{2/3}Co_{1/3}Mn]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 Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]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 Li[Ni_{x}Co_{1/3}Mn_{2/3}]O_{2} (x = 1/4 and 3/8) by the “mixed hydroxide” method and these compounds showed good electrochemical properties. Moreover, they also prepared Li[Ni_{x}Li_{1/3}Co_{2/3}Mn_{3/10}]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 Li[Ni_{x}Co_{1/3}Mn_{2/3}]O_{2} and Li[Li_{1/10}Ni_{x/10}Co_{3/10}Mn_{3-x/10}]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 Li[Li_{1/10}Ni_{x/10}Co_{3/10}Mn_{3-x/10}]O_{2} (x= 0 and 1) have less cation mixing than Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]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 Rietveld results that Li[Li_{1/10}Ni_{1/10}Co_{3/10}Mn_{1/10}]O_{2} (x= 0 and 1) shows better electrochemical properties than Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]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 Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2} and Li[Li_{1/10}Ni_{1/10}Co_{3/10}Mn_{1/0}]O_{2}. Whereas Ni ingredient in Li[Li_{1/10}Ni_{1/10}Co_{3/10}Mn_{1/2}]O_{2} exists nearly as Ni^{3+} to compensate oxidation state. As expected, Li[Li_{1/10}Ni_{1/10}Co_{3/10}Mn_{1/2}]O_{2} (x= 0 and 1) shows better electrochemical properties than Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]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

Figure 1. XRD patterns of (a) Li[Ni_{3/10}Co_{2/10}Mn_{1/10}]O_{2}, (b) Li[Li_{1/10}Ni_{x/10}Co_{3/10}Mn_{3-x/10}]O_{2}, and (c) Li[Li_{1/10}Ni_{2/10}Co_{3/10}Mn_{1/10}]O_{2} calcined at 950°C in Air.

Figure 2. XANES spectra of (a) Li[Ni_{3/10}Co_{2/10}Mn_{1/10}]O_{2}, (b) Li[Li_{1/10}Ni_{x/10}Co_{3/10}Mn_{3-x/10}]O_{2}, and (c) Li[Li_{1/10}Ni_{2/10}Co_{3/10}Mn_{1/10}]O_{2}. 

3/10