Synthesis and electrochemical properties of molybdenum doped cathode materials prepared by ultrasonic spray pyrolysis

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Introduction
Layered lithium metal oxides, LiMO$_2$ (M = Co, Ni, Mn) and LiMnO$_4$ have been expanded in the last a few years in the application of rechargeable batteries as cathode materials for lithium secondary batteries. LiCoO$_2$ has been commercialized but has still some limits due to its high cost, low capacity, and environmental problems [1-3]. Recently, T. Ohzuku reported a new concept of one-to-one solid solution with atomic scale of LiNiO$_2$ and LiMnO$_2$, i.e., Li[Ni$_{1/2}$Mn$_{1/2}$]O$_2$ [4]. The Li[Ni$_{1/2}$Mn$_{1/2}$]O$_2$ delivered a reversible capacity of 150 mAh g$^{-1}$ in the voltage range of 2.5 to 4.3 V. Yoon et al. reported that Ni$^{2+}$ and Mn$^{4+}$ coexist in the layered Li[Ni$_{1/2}$Mn$_{1/2}$]O$_2$ structure and Ni$^{2+}$ ion is oxidized to Ni$^{4+}$, while Mn$^{4+}$ ions remain mostly unchanged as Li is de-intercalated from the material [5]. In this study, we have attempted to synthesize molybdenum doping on Li[Ni$_{0.5}$Mn$_{0.5}$]O$_2$ using MoO$_3$ precursor.

Experimental
M$\text{o}$ doped LiNi$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ (x in 0-0.05) powders were prepared by ultrasonic spray pyrolysis. Ni, Mn nitrate and molybdenum trioxide were used as starting materials for the synthesis of Ni$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ powder. The dissolved solution was added into a continuously agitated aqueous citric acid solution. The starting solution was atomized using an ultrasonic nebulizer with a resonant frequency of 1.7 MHz. The aerosol stream was introduced into the vertical quartz reactor heated at 500 °C. The as-prepared powder was thoroughly mixed with LiOH$\cdot$H$_2$O. After the mixture was softly ground, these were post-heated again at 900 °C in a box furnace.

Results and discussion
Figure 1 shows XRD spectra for Li[Ni$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ (x = 0-0.05) powders. All samples can be indexed based on a hexagonal $\alpha$-NaFeO$_2$ structure with a space group of R$ar{3}$m. The XRD pattern of the molybdenum doping Li[Ni$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ material shows a single phase of layered structure. This may be ascribed that this material derived from precursor has an atomic scale and homogeneously mixed to each other during calcinations process.

![X-ray diffraction patterns of LiNi$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ powders. x in (a) 0, (b) 0.01, (c) 0.02, and (d) 0.05.](image)

Figure 2 shows specific discharge capacity vs. number of cycle for Li/Li[Ni$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ (x = 0, 0.02) cell. Molybdenum 0.02 doped electrode delivered higher capacity (175 mAh g$^{-1}$) than un-doped electrodes, with good capacity retention.

![specific discharge capacity vs. number of cycle for Li/Li[Ni$_{0.5+x}$Mn$_{0.5-2x}$Mo$_x$O$_2$ (x = 0, 0.02) cell](image)

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References