Effects of Al Substitution for Mn on Structure and Performance of LiNi$_{0.5}$Mn$_1$O$_4$ Cathode Materials

Ying Luo$^{ab}$, Jingying Xie$^{ab}$, Yixiao Zhang$^b$, Lijun Yan$^a$ and Yi Feng$^a$

$^a$Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China
$^b$Shanghai Power & Energy Storage Battery System Engineering Tech. Co. Ltd., Shanghai 200240, China

Developing the cathode materials with high energy densities is one of the key challenges for lithium-ion batteries. High energy density can be obtained either by high voltage or high capacity. Due to the 4.7V high voltage platform, the spinel LiNi$_{0.5}$Mn$_1$O$_4$ material is a promising candidate for high energy lithium ion battery application. The spinel LiNi$_{0.5}$Mn$_1$O$_4$ material is developed on the basis of the spinel LiMn$_2$O$_4$ material with a three-dimensional diffusion channel of lithium ion. The theory capacity of the spinel LiNi$_{0.5}$Mn$_1$O$_4$ is 146.7mAh/g, which is similar with the spinel LiMn$_2$O$_4$, but the voltage platform of LiNi$_{0.5}$Mn$_1$O$_4$ around 4.7V is 15% higher than that around 4V voltage platform. Unfortunately, even this material still has a non-negligible capacity fading during cycling, especially at elevated temperatures, due to decomposition of electrolyte and Mn dissolution. So a number of groups have worked on improving the electrochemical performance of this cathode material, especially on its cycling stability, by means of surface coating and doping. In this study, we investigated structural and electrochemical performance of Al-doped LiNi$_{1.5-x}$Mn$_x$Al$_2$O$_4$ (x = 0, 0.03, 0.06 and 0.09) spinel material with various doping amount of Al.

The LiNi$_{1.5}$Mn$_1$Al$_2$O$_4$ with Al doping was synthesized by the co-precipitation method. Raman spectra were obtained by Renishaw inVia Reflex with a 532 nm wavelength. The charge-discharge performance was tested using the CR2016 type coin batteries. The electrolyte solution was a mixed solution of 1M LiPF$_6$ in ethylene carbonate and diethyl carbonate (3:7, v/v). In cycle test, charging was carried out constant current of 10C up to 4.9 V and constant voltage at 4.9V.

The Raman spectra of the LiNi$_{1.5}$Mn$_1$Al$_2$O$_4$ synthesized with various doping amount of Al are given in Fig. 1. The following observations can be made: (1) The 399 cm$^{-1}$ and 490 cm$^{-1}$ bands are associated with the Eg and F$_{2g}$ vibration modes of the Ni$^{2+}$-O bond; (2) the acronion at 588 cm$^{-1}$ band is associated with the symmetric Mn$^{4+}$-O stretching vibration; (3) the band at 632 cm$^{-1}$ can be unequivocally assigned to the A$_{1g}$ vibration mode. The intensity shift of vibration is attributed to the increase of the average valence state of Mn ions. For the sample synthesized without doping some new bands at 218 cm$^{-1}$ and 240 cm$^{-1}$ are detected, and the bands at 399 cm$^{-1}$ and 490 cm$^{-1}$ become strong, while the bond F$_{2g}$ splits in two components, which suggest that the Ni$^{2+}$/Mn$^{4+}$ disordering is decreased and the structure is in accordance with P4$_{3}$32 type. With increasing the Al content, the intensity of all these bands gradually lowers. When x $>$ 0.06, it is unobvious for the split of the F$_{2g}$ bond, and the bands at 218 cm$^{-1}$ and 240 cm$^{-1}$ disappear, which is a feature of Fe$^{3+}$ space group. These results indicate that the introduction of Al increases the disordering degree in the B-sites of the spinel.

Fig. 2 shows the cyclic performance of the samples synthesized with different Al content discharged at 10C. The discharge capacity is decreased with the Al doping, but the structure stability is improved. So the cyclic performance and the discharge voltage platform are effectively improved under the high rate discharge conditions. The discharge capacity of the LiNi$_{0.5}$Mn$_{1.5-x}$Al$_x$O$_4$ is 111mAh/g at 10C with the 4.49V voltage platform, and the capacity retention rate is about 100% after 100 cycles.

Fig. 1 Raman patterns of LiNi$_{1.5}$Mn$_1$Al$_2$O$_4$ doped with different amount of Al

Fig. 2 Cyclic performance of LiNi$_{1.5}$Mn$_1$Al$_2$O$_4$ at 10C

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References