Effect of Li Content on the Cycling Performance of High Voltage, High Capacity $Li_xMn_{1.5}Ni_{0.5}O_y$ Cathodes

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Recently, extensive research has been done to optimize lithium-ion rechargeable batteries (LIBs) for vehicle, military and grid applications. LIBs are preferred when compared to other secondary batteries due to their high voltage and high energy density. However, the capacity of current cathode materials used for LIBs is limited. Improvements in rate capability and capacity can insure a longer cycle life and enhance LIBs. Lithium manganese nickel oxide, $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) is a promising candidate because of high voltage operation.[1-6] However, dissolution of manganese due to reaction with electrolytes and lower capacity is still a concern. Recently, several groups have reported an integrated layered-spinel composite cathodes using LMNO and $Li_2Mn_{0.6}Ni_{0.2}O_3$ to form $Li_xMn_{1.5}Ni_{0.5}O_y$ (x=1.0~3.0).[1-6] These composite cathodes have shown better performances than the layered or spinel cathodes with respect to specific capacity and cyclability. One strategy is to study the effect of Li content in LMNO and investigate its structural characteristics and cycling performances. The $Li_xMn_{1.5}Ni_{0.5}O_y$ sample show high capacity only when the Li content is above 2.0. We will report in detail about the synthesis of $Li_xMn_{1.5}Ni_{0.5}O_y$ (x=2.0-3.0) cathodes and its electrochemical performances for lithium ion batteries.

The lithium free manganese-nickel oxides were prepared by a co-precipitation technique using nickel acetate and manganese acetate. The aqueous metal acetate solution was added to a solution of potassium hydroxide drop by drop. Precipitates were collected by filtration with fine filter paper and placed in an oven to dry for 18 h at 110 °C. The powder was collected and ground for 30 min. Netzsch STA 409 PC Thermal gravimetric analysis (TGA) was used to determine the exact metal oxide mass as 86% mass recovery. The addition of different concentrations of lithium to precursor powders was done by grinding the manganese-nickel oxides with lithium hydroxide in a mortar for 30 min. The powder was then fired in a tube furnace at 800 °C for 10 h at a rate of 4 °C/min.

X-ray diffraction (XRD) of the cathode materials were collected on a Scintag X-ray diffractometer with a Cu-kα between 2θ values of 5-80° at the scan rate of 1.00°/min. Electrochemical studies were done by preparing CR2032 coin cells. The cathode was prepared by casting slurry of 80% active material, 10 wt.% super carbon and 10 wt.% polyvinylidene difluoride (PVDF) binder in n-methyl-2-pyrrolidone (NMP) solvent on aluminum foil. Charge-discharge profiles of the coin cells were measured between 2 to 5 V at 25mA/g (c/10 rate assuming a capacity of ~ 200 mAh/g) by using Arbin Batter Test Equipment.

The Li content was determined by Inductively coupled plasma (ICP). The presence of both layered and spinel structures and the ratio in the cathode materials were confirmed from the XRD patterns and refinement results. From the cycling performances of $LixMn_{1.5}Ni_{0.5}O_y$ (x=2.0-3.0) cathodes, the following conclusions were made. The Li content was correlated with the ratio of layered phase and spinel phase. As shown in Fig. 1, during cycling between 2-5 V, all of the samples displayed capacities above 200 mAh/g, but high Li content sample produced the best cycle stability. During cycling between 2-4.6 V, all the samples showed better cycle performances, but much lower capacity. At high Li content, the highest capacities achieved are near 170 mAh/g. Detailed studies that elucidate the effect of the spinel-to-layered phase ratio on the electrochemical performances and stability of lithium ion batteries will be presented.

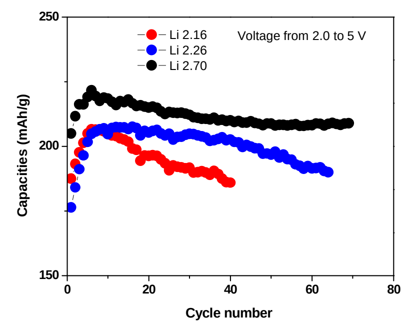

Figure 1. Cyclability data of the $Li_xMn_{1.5}Ni_{0.5}O_y$ (x=2.0-3.0) composite cathodes.

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