Effect of the Crystal Chemistry of $LiNi_{1/2}Mn_{3/2}O_4$ Spinels on its Electrochemical Properties

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$LiNi_{1/2}Mn_{3/2}O_4$ with the spinel structure is one of the promising candidates as a high power electrode material due to its facile Li-ion diffusion and high operating voltage by the virtue of its high redox potential (~4.7 V vs. Li^+/Li^0) [1]. This compound can crystallize into two polymorphs depending on the ordered state of Ni and Mn in the octahedral sites, disordered ($Fd\bar{3}m$) and ordered ($P4_332$) [2,3]. Such ordering has been controlled by temperature of synthesis at ~700°C [4,5]. Seggregation of a rocksalt phase that is richer in Ni than Mn with respect to the spinel also generates Mn^{3+} defects [6]. Although many previous studies reported that ordering and Mn^{3+} contents significantly affect the electrochemical properties, these two parameters always appear tangled with each other, so that their specific role has not completely been uncovered [7]. By a systematically controlled synthetic route, samples with different ordered states, amount of Mn^{3+}, and compositions were obtained while their particle sizes were kept virtually constant. We used this series of samples to try to ascertain their separate role on electrochemical properties.

$LiNi_{0.5}Mn_{1.5}O_4$ spinel samples were synthesized by a coprecipication method [6]. Using a controlled procedure of post-synthesis annealing at lower temperatures and O_2 partial pressures, a series of samples were prepared with the goal of decoupling the crystal chemical parameters, i.e., structure and composition,. The microstructural analyses of the samples were carried out by scanning electron microscope (SEM) and BET as shown in Fig 1. Crystal phases of the samples were determined using X-ray diffraction (XRD) (Fig. 2), which revealed spinel structures (JCPDS 32-0581) with very minor rock salt impurity phases. ^{6}Li MAS NMR and neutron diffraction data were acquired to define the degree of crystallographic ordering in the framework.

The resulting samples were tested in Li half cells using constant current with different cut-off voltage and rate capability experiments to study the effect of Ni/Mn ordering and Mn^{3+} content. In-situ and ex-situ high resolution XRD were also measured to provide in-depth observation for the origin of the different phase transformation behavior with ordering. The results of these studies will be discussed.

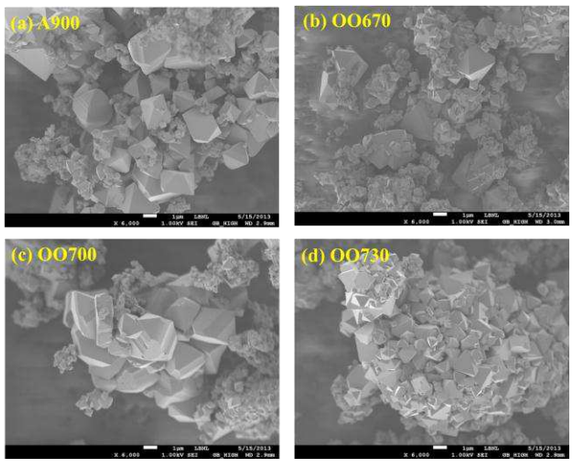

Fig. 1. (a), (b), (c), and (d) SEM images of $LiNi_{1/2}Mn_{3/2}O_4$ spinels. SEM images show that a series of $LiNi_{1/2}Mn_{3/2}O_4$ is well controlled to ascertain crystal chemistry effect without any variation in particle morphologies.

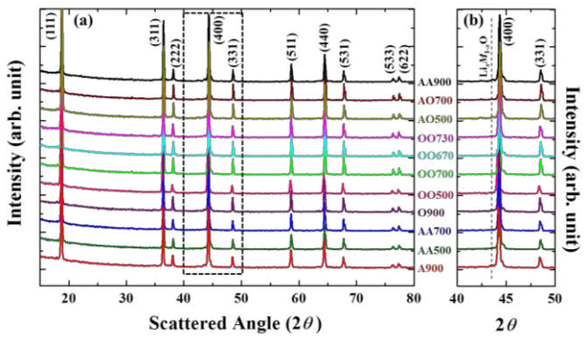

Fig. 2 (a) XRD patterns of all samples. (b) Zoom-in of the 40°-50° region of the patterns, highlighting the presence of a rocksalt impurity in some samples (see broken line).

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