Cation Substitution Strategies for 5 V LiNi$_x$Mn$_{1-x}$O$_4$ Spinel Electrodes in Lithium Batteries

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The compound LiNi$_{0.5}$Mn$_{0.5}$O$_4$ with a cubic spinel structure has been investigated as a high-voltage (~5 V vs. Li metal) cathode (positive electrode) for lithium batteries [1-4]. During battery cycling at high voltages, the charge stored is due to a Ni$^{2+}$/Ni$^{3+}$ redox couple that occurs at the nickel metal center [5-7]. Negligible or very little charge is compensated at the tetravalent manganese metal center. Because the nickel in this system can undergo multi-electron transfer reactions, it provides a high charge storage or theoretical capacity of ca. 147 mAh/g. The combination of this property with a high 4.7 V (vs. Li metal) reaction voltage ($E_R$) results in a corresponding high theoretical specific energy of approximately 690 Wh/kg, which is greater than a 4 V Li/LiNi$_{0.5}$O$_4$ spinel cell at about 590 Wh/kg. Challenges for a practical 5 V spinel system, however, include high-temperature storage and operation limitations and electrolyte stability issues [8].

In this work, the role of substituted cations on the electrochemical performance of 5 V LiNi$_x$Mn$_{1-x}$O$_4$ spinel cathodes in lithium batteries was studied. Prior references discuss the addition of a third metal into the spinel LiNi$_x$Mn$_{1-x}$O$_4$ with some beneficial results. Specifically, these include the additions of Mg [9], Cu [10], Co [11], or Cr [12]. In this study, we survey the galvanostatic cycling performance of a series of X-substituted Li[Li$_{0.5}$Ni$_{0.5}$Mn$_{1-x}$]O$_4$ spinel electrodes in lithium cells cycled at high-voltages. The substitutions we report are exhaustively and include X=Mg, Al, Zn, Cu, Ga, Cr, Co, V, and Fe. In particular, these types of X were chosen in order to highlight the various roles that the substitution may have on affecting the cycling ability, including spinel tetrahedral (8a) or octahedral site (16d) occupancies, charge preferences, and/or redox capabilities.

Appropriate mole ratios of Li, Mn, and Ni nitrate or acetate salts were dissolved and mixed in pure water with the various corresponding acetate or nitrate of the substituted cation(s). Mixtures were heated to dryness, isolated, ground and then calcined at 450°C in air. Powders were subsequently ground and sintered at 900°C in air. Examples of electrode compositions are presented in Fig. 1. Figs. 1a-c show typical XRD patterns for three different mono-substituted 5 V spinels, while that in Fig. 1d is that of the unsubstituted LiNi$_{0.5}$Mn$_{0.5}$O$_4$. Single phase cubic spinel compounds were formed in all cases, and the lattice parameters were systematically affected by the substituted cation charge.

In addition we have synthesized and characterized related, but more complex 5 V spinel compounds which have a special combination of multiple metal cation substitutions. In such materials, the substitutions were chosen so that the final spinel composition would retain an overall net divalent Ni$^{2+}$ and tetravalent Mn$^{4+}$ redox character. The strategy and rationale follows the structural stability trend that Ni$^{2+}$ and Mn$^{4+}$ provides for layered LiNi$_x$Mn$_{1-x}$O$_4$ oxide electrode materials [13, 14]. An example (Fig. 1e) of such a multi-substituted material is Li[Li$_{0.25}$Ag$_{0.25}$Ni$_{0.5}$Mn$_{1.5}$O$_4$], which still affords a high theoretical capacity of 132 mAh/g with this composition. These 5 V spinel compounds and their related structures and electrochemistry in lithium cells will be discussed in this presentation.

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References


Fig. 1. XRD patterns of 5 V substituted spinels; (a) Li[Li$_{0.25}$Ni$_{0.5}$Mn$_{1.5}$]O$_4$, (b) Li[Fe$_{0.25}$Ni$_{0.5}$Mn$_{1.5}$]O$_4$, (c) Li[Zn$_{0.25}$Ni$_{0.5}$Mn$_{1.5}$]O$_4$, (d) standard Li[Ni$_{0.5}$Mn$_{0.5}$]O$_4$, (e) Li[Li$_{0.25}$Ag$_{0.25}$Ni$_{0.5}$Mn$_{1.5}$]O$_4$.  

Intensity (cps)  

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