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Publication Date

2011-04-25

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Aliovalent Substitution in Mixed Ni-Mn-Co Oxide Cathodes

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We have recently observed improved electrochemical characteristics for some substituted NMC ($\text{Li}[\text{Ni}_x\text{Co}_{1-2x-y}\text{M}_y\text{Mn}_x]\text{O}_2$) cathode materials when $x=1/3$, $\text{M}=\text{Ti}$, and y is a low value ($<\sim 0.05$), compared to the baseline material. Some of these materials show an increase in discharge capacity of about 15% as well as improved cycling between 4.7 and 2.0 V, without the need for a high voltage activation step, and without compromising rate capability. Ti^{4+} substitution for Co^{3+} is more complex than other substitutions we have previously studied (most notably Al^{3+}) for the purpose of reducing Co content, because of the requirement for charge compensation in the as-made materials. In this paper, we discuss the effect of Ti substitution on the structure and electrochemical performance of NMCs, the mechanism of charge compensation and the possible origins of the performance enhancement we have observed.

Keywords: lithium batteries, cathode, transition metal oxides, aliovalent substitution

Acknowledgment

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.