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A Study of the Ti and Mg Doping for LiNiO₂ Cathode Materials and their Effects on Stabilizing the Structure of the Cathode Material in Overcharged State

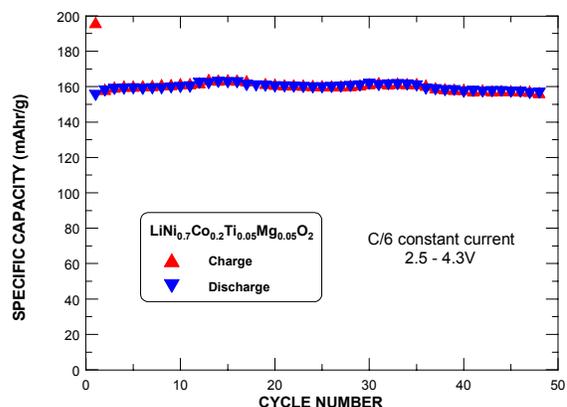
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Beamline(s): X18A

Introduction: Over 90% of today's commercial Li-ion batteries employ LiCoO₂ as the cathode material, while LiNiO₂, especially doped LiNiO₂ variations, are good candidates as the cathode material for the next generation Li-ion batteries. On the application side, the full theoretical capacity cannot be achieved from these materials, and only about 0.5-0.6 lithium can be utilized per formula unit. Further removal of lithium during charge causes exothermic decomposition of the oxide, releasing oxygen at elevated temperatures, which poses safety hazards.¹ We have earlier reported that the exotherm of the charged LiNiO₂ can be significantly reduced by doping with Ti and Mg,² and we also demonstrated excellent cycle performance and thermal stability with Ti and Mg doped LiNi_{1-x}Co_xO₂ (Lectro Plus 600TM).³

Methods and Materials: Samples are provided by FMC Corp. and the procedure of sample preparation was described elsewhere^{2,3}. The cathodes were incorporated into cells with a Li foil negative electrode, a Celgard separator and a 1 M LiPF₆ electrolyte in a 1:1 EC:DMC solvent (LP 30 from EM Industries Inc.). In situ XRD spectra were collected on beam line X18A (using $\lambda=1.195$ Å wavelength). The step size of 2 θ scan was 0.02 degrees. The XRD spectra were collected in transmission mode.

Results: It has been shown that when lithium is removed from LiCoO₂ during charge, significant electron density is depleted at the oxygen site.⁴ Indeed, when most of the lithium is removed from LiCoO₂ in an overcharged state,



the spacing in the c direction collapses, possibly due to the depletion of electrons from oxygen. Because Ni 3d has even larger binding energy than that of Co 3d, one can expect even more electron density should be depleted from oxygen when lithium is totally removed from LiNiO₂. The instability of the overcharged end members CoO₂ and NiO₂, which are highly covalent in nature, can therefore be expected especially in contact with combustible electrolyte solvents at elevated temperatures, with depleted electrons from oxygen.

Conclusions: Based on this, we argue that the stability and safety of LiNiO₂ or LiNi_{1-x}Co_xO₂ is improved with Ti and Mg doping, because a) a proportional amount of lithium becomes unremovable and that is completely ionized, and b) the highly ionized Ti⁴⁺ and Mg²⁺ together with the unremovable Li⁺ ions increase the ionic nature of the compound and thereby discourages the depletion of electron from the oxygen in the compound. This is confirmed by our in situ XRD data that shows minimum reduction of spacing in the c-direction compared to LiNiO₂, LiNi_{0.8}Co_{0.2}O₂, and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂.

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References:

1. J.R. Dahn, E.W. Fuller, M. Obrovac, & U. von Sacken, *Solid State Ionics* **69**, 265 (1994).
2. Y. Gao, M.V. Yakovleva, & W.B. Ebner, *Electrochem. & Solid-state letters* **1**, 117 (1998).
3. Y. Gao, and M.V. Yakovleva, US patent 6,277,521 B1.
4. M.K. Aydinol, A.F. Kohan, G. Ceder, K. Cho, & J. Joannopoulos, *Phys. Rev. B* **56**, 1354 (1997).