New Phases and Phase Transitions Observed in Over-Charged States of LiCoO₂ Based Cathode Materials

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Introduction: LiCoO₂ is the most widely used cathode material in commercial lithium battery cells. LiNiO₂ has the same theoretical capacity as LiCoO₂, but is less expensive. However, its application in lithium batteries has not been realized due to serious safety concerns. Substituting a portion of Ni in LiNiO₂ with other cations has been pursued as a way to improve its safety characteristics. It was reported that Co-doped LiNi₀.₈Co₀.₂O₂ showed better thermal stability than pure LiNiO₂. New materials, such as LiNi₀.₇₅Mg₀.₁₂₅Ti₀.₁₂₅O₂ and LiNi₀.₆₅Co₀.₂₅Mg₀.₀₅Ti₀.₀₅O₂, have been developed. These materials exhibit even superior thermal stability to LiNi₀.₈Co₀.₂O₂. Using an ex situ XRD technique, Ohzuku has performed interesting studies on some of the Li₁₋ₓCoO₂ based materials. However, the charging voltage limit was set below 4.8 V in these studies. Dahn and co-workers have also published their results on the structural changes of Li₁₋ₓCoO₂ during charge using in situ XRD. The charging voltage used in that study was below 4.3 V. Amatucci and coworkers claimed a new phase transition, from a monoclinic phase M2 to a CdI₂ type single-layered hexagonal phase O1 for 0.9<x<1 in Li₁₋ₓCoO₂. Using the state of art synchrotron based in situ x-ray diffraction, we have reported new findings on phase transitions for both Li₁₋ₓCoO₂ and Li₁₋ₓNiO₂ systems. In this work, we have performed systematic studies on the structural changes of LiCoO₂, LiCo₀.₈Ni₀.₂O₂, LiCo₀.₇₅Ni₀.₁₂₅Ti₀.₁₂₅O₂, and LiCo₀.₆₅Ni₀.₂₅Co₀.₂₅Mg₀.₀₅O₂ cathode materials during charge in the voltage range from 3.5 V to 5.2 V.

Methods and Materials: LiCoO₂ and LiCo₀.₈Ni₀.₂O₂ were provided by FMC. LiCo₀.₇₅Ni₀.₁₂₅Ti₀.₁₂₅O₂ and LiCo₀.₆₅Ni₀.₂₅Mg₀.₀₅O₂ were synthesized by solid state reaction in our Lab. Cathodes were prepared by slurring the active material powder with 10% PVDF (KynarFlex 2801, Atochem), and 10% acetylene black (w/w) in a fugitive solvent, then coating the mixture onto Al foil. 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.). Mylar windows were used in these in situ cells. In situ XRD spectra were collected on beam line X18A at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory operated at an energy of 10375 eV (λ=1.195 Å).

Results: It was reported that a monoclinic phase M2 is located in the region of 0.75<x<0.85 for Li₁₋ₓCoO₂ in the over-charged state. However, in our in situ XRD data, no signature for the presence of a monoclinic phase M2 was observed. In the same composition region, we did observed more diffraction peaks. However, these new peaks can be indexed as two sets of O1 type structures. In other words, the formation of O1 structure takes two steps. An intermediate structure O1a is formed before the cathode totally converts to the final O1 structure. In the in situ XRD spectra of a LiCo₀.₇₅Ni₀.₁₂₅Ti₀.₁₂₅O₂ cathode, the formation of the O1 type structure was also observed when the cell was over-charged to 5.2 V. However, at the end of charge at 5.2 V, the system is a mixture of two phases. Only a small portion is in the O1 type structure, while the majority of the material has a CdCl₂ type structure. Similar phenomena were also observed in LiCo₀.₅Ni₀.₅O₂, and LiCo₀.₅Ni₀.₅O₂ samples. In these samples, at the end of charge at 5.2 V, the percentage of the O1 type structure increases with increasing Co content.

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References: