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New phases and phase transitions observed in over-charged states of LiCoO₂-based cathode materials[☆]

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Abstract

Using synchrotron-based in situ X-ray diffraction, the structural changes of LiCoO₂, LiCo_{0.5}Ni_{0.5}O₂, and LiNi_{0.65}Co_{0.25}Mg_{0.05}Ti_{0.05}O₂ cathode materials during charge in the voltage range of 3.5 to 5.2 V have been studied. When a LiCoO₂ cathode was charged above 4.5 V, a new intermediate phase O1a was observed, before the terminal phase O1 was formed around 4.8 V. In the X-ray diffraction spectra for LiCo_{0.5}Ni_{0.5}O₂ and LiNi_{0.65}Co_{0.25}Mg_{0.05}Ti_{0.05}O₂ cathode materials, Bragg peaks representing the O1 structure were also observed. The amounts of O1 structure formed at the end of charge (5.2 V for LiNi_{0.65}Co_{0.25}Mg_{0.05}Ti_{0.05}O₂ and 5.0 V for LiCo_{0.5}Ni_{0.5}O₂) were increased with increasing Co content. © 2001 Elsevier Science B.V. All rights reserved.

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1. 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. Substitution for a portion of Ni in LiNiO₂ with other cations has been pursued as a way to improve its safety characteristics. It was reported that LiNi_{0.8}Co_{0.2}O₂ shows better thermal stability than pure LiNiO₂. New materials, such as LiNi_{0.75}Mg_{0.125}Ti_{0.125}O₂ and LiNi_{0.65}Co_{0.25}Mg_{0.05}Ti_{0.05}O₂, have also been developed. These materials exhibit thermal stability superior to LiNi_{0.8}Co_{0.2}O₂. Reimers and Dahn performed early studies on structural changes of Li_{1-x}CoO₂ during charge using in situ XRD [1]. The charging voltage was limited to <4.3 V due to corrosion of the beryllium window. Using an ex situ XRD technique, Ohzuku and Ueda [2] performed interesting studies on some of the Li_{1-x}CoO₂-based materials.

However, the charging voltage limit was set at 4.8 V. By raising the voltage limit to 5.2 V, Amatucci et al. [3] discovered a new phase transition, they described as being from a monoclinic phase M2 to a CdI₂-type single-layered hexagonal phase O1 for 0.9 < x < 1 in Li_{1-x}CoO₂. This is quite different from in the case of the LiNiO₂ system, where a phase transition from a hexagonal phase H2 to a same CdCl₂-type H3 phase was observed. Recently, Croguennec et al. in Delmas group [4] reported their new findings in a Li_{0.98}Ni_{1.02}O₂ sample, where a H4-type structure similar to the CoO₂ was observed when the sample was deintercalated close to Ni_{1.02}O₂. However, not much work has been published on the structure changes in LiNi_{1-x}Co_xO₂ and LiCo_{1-x}Ni_xO₂ systems during cycling, which we would like to discuss in this paper. The results presented here also provide further information about the relationship between the structural changes of these materials at over-charged state and their thermal stability. Using state-of-art synchrotron-based in situ X-ray diffraction, we have reported new findings on phase transitions for both Li_{1-x}NiO₂ and Li_{1-x}CoO₂ systems [5,6]. In this paper, we report our results on the structural changes of LiCoO₂, LiCo_{0.5}Ni_{0.5}O₂, and LiNi_{0.65}Co_{0.25}Mg_{0.05}Ti_{0.05}O₂ cathode materials during charge in the voltage range of 3.5–5.2 V. In this paper, we focus on the over-charged state. More detailed discussion,

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with systematic studies covering a series of samples of LiCoO_2 , $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$, and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mg}_{0.05}\text{Ti}_{0.05}\text{O}_2$ cathode materials will be published later.

2. Experimental

LiCoO_2 and $\text{LiNi}_{0.75}\text{Mg}_{0.125}\text{Ti}_{0.125}\text{O}_2$ were provided by FMC Corp. $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ was synthesized by solid-state reaction at Brookhaven National Lab. Due to the limited space in this proceeding paper, the effects of cation mixing in these samples are omitted, they will be discussed in the full-size paper. 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 LiPF_6 electrolyte in a 1:1 EC:DMC solvent (LP 30 from EM Industries Inc.). Mylar windows were used in these in situ cells. Most of the in situ XRD spectra were collected on beam line X18A at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using radiation wavelength of $\lambda = 1.195 \text{ \AA}$. Other in situ XRD spectra were collected at X7A using monochromated wavelength of $\lambda = 0.701 \text{ \AA}$. A high resolution position sensitive detector (PSD) used at X7A, significantly reduced the data collection time for each scan, giving us a great advantage in observing the phase transitions in real time with high resolution.

3. Results and discussion

It was reported that a monoclinic phase M2 appears in the region of $0.75 < x < 0.85$ for $\text{Li}_{1-x}\text{CoO}_2$ in the over-charged state [2,3]. The in situ XRD spectra covering $0.77 < x < 1.00$ of a FMC $\text{Li}_{1-x}\text{CoO}_2$ cathode during charge are plotted in Fig. 1. The phase transitions from CdCl_2 -type hexagonal phase H2 to CdI_2 -type O1a phase, and then to the final O1 phase are very clearly recorded. The Miller indices of H2, O1a, and O1 peaks are indicated accordingly. The origin of the formation of the intermediate phase O1a is not yet fully understood. We would like to point out that the detailed structure and space group of O1a have not been worked out yet. The Miller indices of O1a were assigned according to the O1 structure which may not be correct for O1a. Please note that the monoclinic phase M2, which was reported in the literature, was not observed in our data. Comparing the terminal phase H3 in $\text{Li}_{1-x}\text{NiO}_2$ and O1 in $\text{Li}_{1-x}\text{CoO}_2$, the main structural difference is the stacking of the oxygen octahedral slabs. These slabs are formed by a transition metal sandwiched in two oxygen layers. During the transition from H2 to O1, when most of the Li ions have been removed from lithium layers between these slabs, the neighboring slabs slide against each other to alter the stacking from ABCABC to AAAAAA. Therefore, the original O3 structure (three slabs with ABCABC stacking) transferred to an O1 structure (one slab with AAAAAA stacking). This is accompanied by a contraction of the “c”-axis. This implies that the integrity of the slabs in $\text{Li}_{1-x}\text{CoO}_2$ is intact even at the over-charged state. In contrast, during

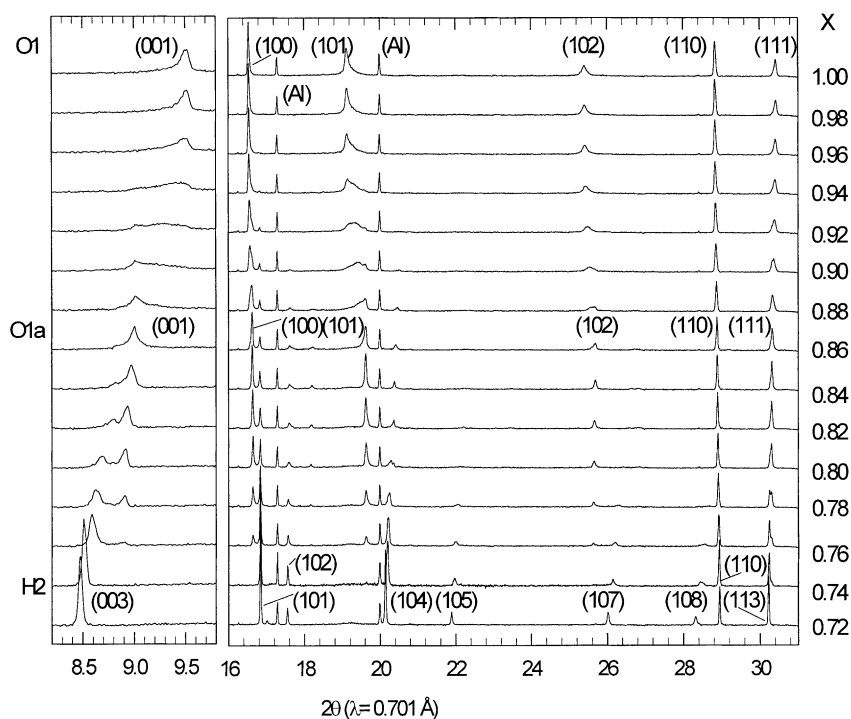


Fig. 1. Selected spectra from FMC $\text{Li}_{1-x}\text{CoO}_2$ first charge from 3.5 to 5.2 V at C/8 rate.

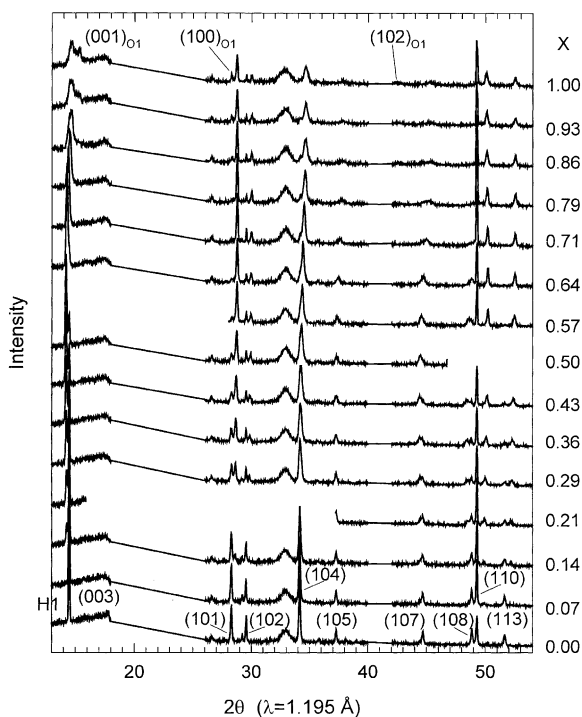


Fig. 2. FMC $\text{Li}_{1-x}\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mg}_{0.05}\text{Ti}_{0.05}\text{O}_2$ first charge from 3.5 to 5.2 V at $C/12$ rate.

the phase transition from H1 to H3 in $\text{Li}_{1-x}\text{NiO}_2$, the contraction of “ c ”-axis is observed, but no change in stacking occurs. This might be a result of cation mixing between Li^+ and Ni^{3+} (or Ni^{4+}), which will form pinning points against the sliding of the slabs, and damage the integrity of the slabs irreversibly. Part of this cation mixing might occur during lithium deintercalation, even when the degree of cation mixing of freshly made material was well controlled through synthesis procedure. The in situ XRD spectra of a cell containing $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mg}_{0.05}\text{Ti}_{0.05}\text{O}_2$ cathode charged from 3.5 to 5.2 V at $C/12$ rate are plotted in Fig. 2. For clarity, the indexes for the H2 phase are omitted. With 25% of Ni being replaced by Co, the formation of the O1-type structure can be clearly identified by the $(0\ 0\ 1)_{\text{O1}}$, $(1\ 0\ 0)_{\text{O1}}$, and $(1\ 0\ 2)_{\text{O1}}$ reflections. However, at the end of charge at 5.2 V, the system is a mixture of two phases. Only a minority is in the O1-type structure, with the majority of the material having CdCl_2 -type structure. In order to confirm the effects of Co doping on the formation of O1 phase, we have studied a series of samples with different levels of Co doping ($\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$, and $\text{LiCo}_{0.15}\text{Ni}_{0.85}\text{O}_2$). We have noticed that the percentage of O1 structure at the end of charge at 5.2 V is proportional to Co doping. Because we are only allowed to use three figures in this proceeding volume, we select the in situ XRD spectra of a cell containing $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cathode, charged from 3.5 to 5.0 V at $C/10$ rate and plotted in Fig. 3. The increase of O1 phase indicated by the intensity of $(1\ 0\ 0)_{\text{O1}}$ peak compared with the $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mg}_{0.05}\text{Ti}_{0.05}\text{O}_2$

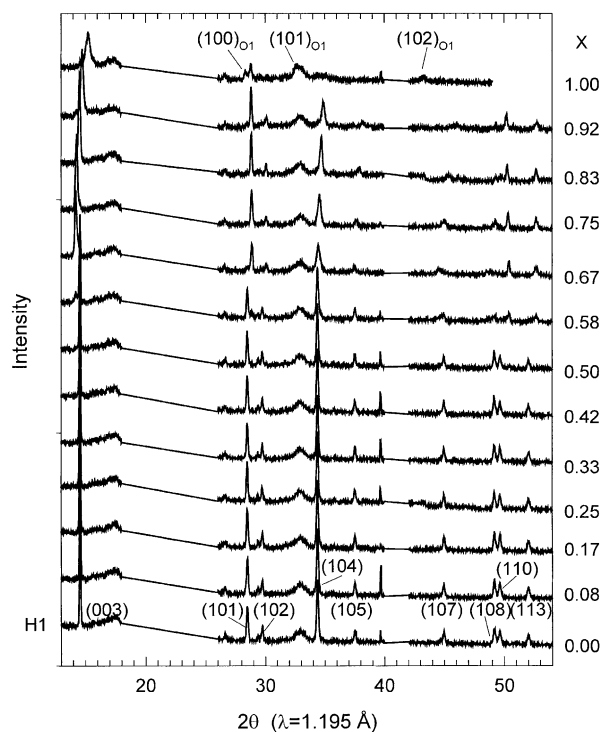


Fig. 3. BNL $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_2$ first charge from 3.5 to 5.0 V at $C/10$.

cathode at the end of charge is evident. The effects of this O1 phase formation on thermal stability and cyclability of the cathode materials will be further studied.

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