

Electron microscopic characterization of electrochemically cycled LiCoO_2 and $\text{Li}(\text{Al},\text{Co})\text{O}_2$ battery cathodes

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Abstract

Electrochemical cycling of lithium battery cathodes introduces large absolute changes in lithium concentration that can result in microstructural damage and cation disorder. This damage can influence the long-term performance of battery systems, but has not to date been investigated in detail. We have conducted direct observations using transmission electron microscopy (TEM) of electrochemically cycled Li_xCoO_2 and $\text{Li}_x\text{Al}_y\text{Co}_{1-y}\text{O}_2$ cathodes. A rich variety of electrochemical cycling-induced damage is found. Intercalation oxide particles show widely varying degrees of damage suggesting differing depths of cycling on a local scale. Many particles exhibit severe strain, high dislocation densities, and localized fracture. Moreover, in particles that are severely strained, electron diffraction reveals two types of cation disorder brought about by electrochemical cycling. One is the Li and Co substitution/vacancies on their respective octahedral layers. The second is an evolution towards spinel ordering that is not detectable by bulk analytical methods such as X-ray diffraction (XRD). Unlike previously described ‘lithiated spinels,’ the observed spinel ordering is characterized by tetrahedral 8a site occupancy even at compositions near $x \sim 1$. Thus it is shown that even in LiCoO_2 , widely considered to be the most stable of the intercalation oxides in the layered $\alpha\text{-NaFeO}_2$ structure, electrochemical cycling results in a transformation towards spinel cation ordering. Similar results are seen in $\text{Li}_x\text{Al}_y\text{Co}_{1-y}\text{O}_2$. Cumulative damage of this kind may contribute to the degradation of LiCoO_2 cathodes after long-term cycling. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

An ideal cathode material for the lithium rechargeable battery should have an outstanding electrochemical performance, stable capacity upon extended cycling, and low cost. Of the lithium transition metal oxides (LiMO_2 , $M = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$), LiCoO_2 is considered to be amongst the most stable in the layered $\alpha\text{-NaFeO}_2$ structure. LiCoO_2 synthesized by firing at high temperatures has a highly ordered cation sublattice in which Li and Co ions occupy alternating $\{111\}$ layers of octahedral sites in a nearly cubic close-packed oxygen sublattice [1–4]. The structure is rhombohedral ($R\bar{3}m$ space group) with lattice parameters $a = 2.816 \text{ \AA}$ and $c = 14.051 \text{ \AA}$ in the hexagonal setting [1,3]. The remarkable electrochemical stability of layered LiCoO_2 upon extended cycling has largely been attributed to its structural stability, wherein the layered cation ordering is well preserved during repeated insertion and removal of Li^+ . It has been found that while Li_xCoO_2

undergoes a sequence of transformations from monoclinic through hexagonal phase during delithiation as $x \rightarrow 0$ [5–7], the cations are believed to remain octahedrally coordinated throughout. The typical reversible limit of delithiation for Li_xCoO_2 in commercial batteries is $x = 0.5$, which corresponds to a charge capacity of $\sim 140 \text{ mA h/g}$. Instability at higher delithiation is believed due to the mechanical failure associated with a large dimension change, rather than any change in cation ordering. However, few if any direct observations have been made to date of changes in the cathode oxide during repeated cycling.

In order to characterize the cathode materials on a microscopic scale, we used transmission electron microscopy (TEM) to directly examine cycling-induced damage to cathode particles in typical composite cathodes. Changes in cation ordering resulting from repeated cycling were observed using single crystal selected area electron diffraction (SAD) of individual particles. Both LiCoO_2 and $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ materials were studied, the latter being of interest due to the effect of Al doping on intercalation voltage [8] and cycling properties [9].

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2. Experimental

Powders of LiCoO_2 were synthesized by firing hydroxide precursors at 800°C for 2 h [11]. As-fired powders were characterized by X-ray diffraction (XRD) and SAD, as shown in Fig. 1. They showed that the starting materials had a well ordered $\alpha\text{-NaFeO}_2$ structure. As detailed in Ref. [12], cathodes were prepared by mixing the as-calcined oxide powders with carbon black (Cabot), graphite (TIM-CAL America) and poly(vinylidene fluoride) (PVDF; Aldrich). The test cells used two stainless steel electrodes with a teflon holder. Lithium ribbon was used as the anode and a 1-M solution of LiPF_6 in ethylene carbonate (EC) and diethylene carbonate (DEC) (EC:DEC = 1:1 by volume) as the electrolyte. The cells were electrochemically cycled 50 times between 2.5 and 4.35 V for LiCoO_2 and 20 times between 2.0 and 4.5 V for $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$, at the charging and discharging current density of $0.4 \text{ mA}/\text{cm}^2$ ($C/5$ rate), and terminated in the discharged state at 2.5 V. As shown in Fig. 2, after some initial fade, the discharge capacity in the LiCoO_2 is well maintained at

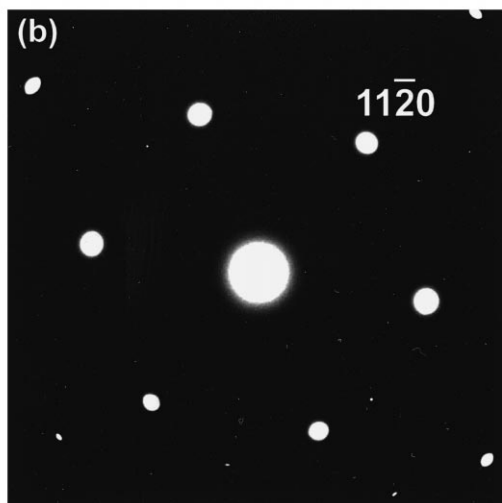
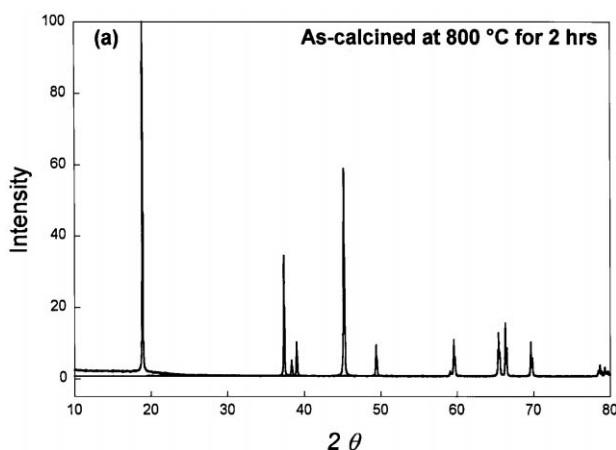


Fig. 1. Experimental (a) XRD and (b) single crystal SAD pattern (zone axis = $[0001]$) for as-calcined LiCoO_2 powders.

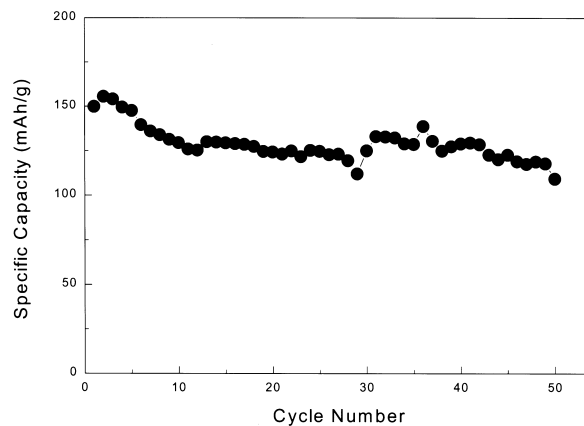


Fig. 2. Specific capacity vs. cycle number for LiCoO_2 cathode (Li anode) cycled between 2.5 and 4.35 V at $0.4 \text{ mA}/\text{cm}^2$ ($C/5$ rate).

approximately 130 mA h/g up to 50 cycles. In the $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$, greater cycling fade was observed as discussed in Ref. [9].

TEM samples were extracted from the cycled cathode pellets. Pieces of cathodes were ultrasonically de-agglomerated and dispersed on amorphous carbon film supported by a copper grid. Bright field imaging and SAD were conducted on clearly separated particles. Low index zone axes were found by tilting the sample around two axes. Oxide particles were stable during the observation under electron beam.

Single crystal SAD patterns, as well as XRD spectra were also computed for a large number of possible derivatives of the ideal layered structure, using commercial software [13], as presented in detail elsewhere [10]. The simulated results from model structures were compared with experimental results to identify the changes in cation ordering.

3. Cycling-induced microstructural damage

Fig. 3 shows the LiCoO_2 particles before and after electrochemical cycling. As-calcined particles, 300 to 500 nm in size, display little variation in contrast across the individual particle except for that due to thickness variation. It is consistent with the SAD result (Fig. 1) showing a high level of crystalline perfection. After repeated cycling, some particles exhibit non-uniform diffraction contrast within each particle, due to lattice strain, dislocations and defects, while the rest are lightly strained or remain unchanged. In particular, as shown in Fig. 4, some particles are severely strained with extensive internal defects and microcracks. Severely damaged particles represent about 20% of the total examined, while 50% of the total show some sign of damage. It is believed that damage can result from at least two possible mechanisms. One is differential lattice expansion and contraction due to local variation in Li concentration. Another is constrained deformation due

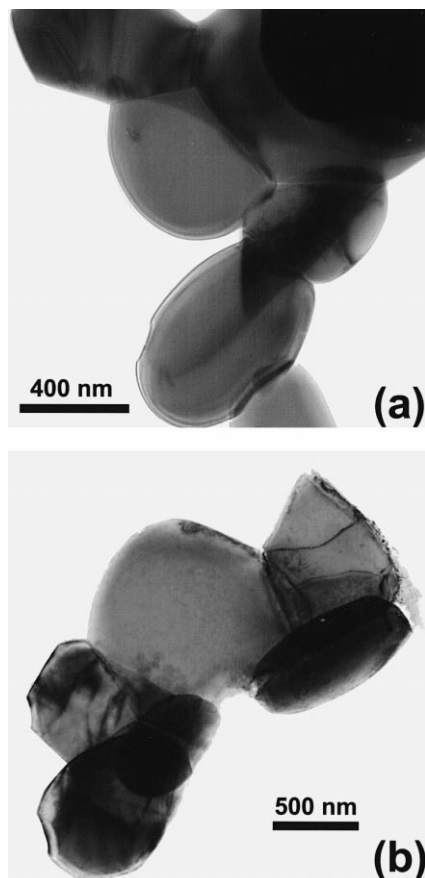


Fig. 3. TEM bright field image of (a) as-fired LiCoO_2 powders; (b) LiCoO_2 powders after 50 cycles between 2.5 and 4.35 V. Note diffraction contrast from internal strain and extended defects in the latter.

to the presence of sintered polycrystalline aggregates, upon charging/discharging-induced lattice expansion and contraction. These effects all can combine to result in the creation of localized irreversible crystallographic defects.

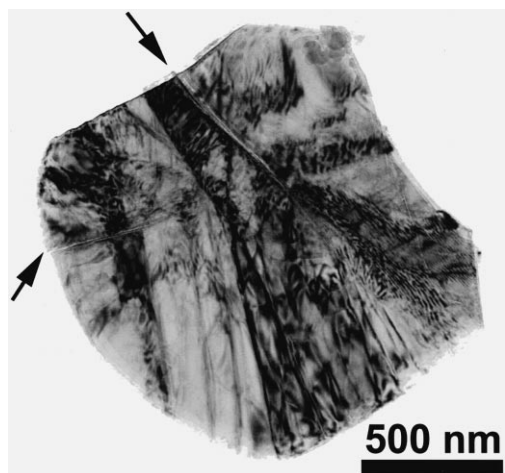


Fig. 4. Severely damaged LiCoO_2 particle from cycled cathode showing microcracks (arrows) and strong diffraction contrast from internal strain and extended defects.

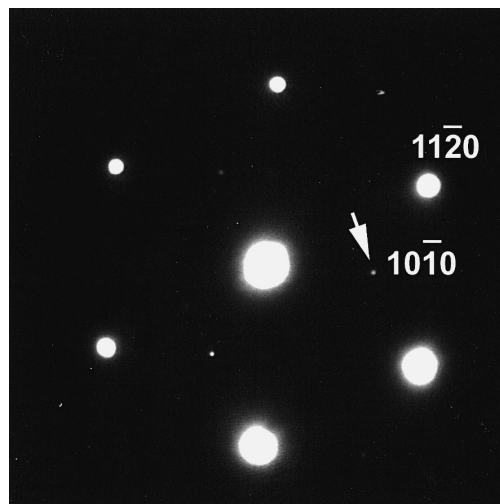


Fig. 5. Experimental SAD pattern of cycled LiCoO_2 particle with low strain, indexed according to the hexagonal setting, exhibits new $\{10\bar{1}0\}$ reflections indicating the Li/Co substitution/vacancy on octahedral site layers [10].

It is apparent that electrochemical cycling does not occur uniformly everywhere within the cathode. A wide variation in the depth of charge/discharge of active oxide particles is implied by the observations.

4. Cycling-induced cation disorder

Close investigation of single crystal SAD patterns of strained particles shows that two types of cation disorder occur in the cycled LiCoO_2 powders. One is cation mixing between Li and Co octahedral site layers. This is indicated by the appearance of $\{10\bar{1}0\}$ reflections, as shown in Fig. 5. These diffraction spots are very weak even when com-

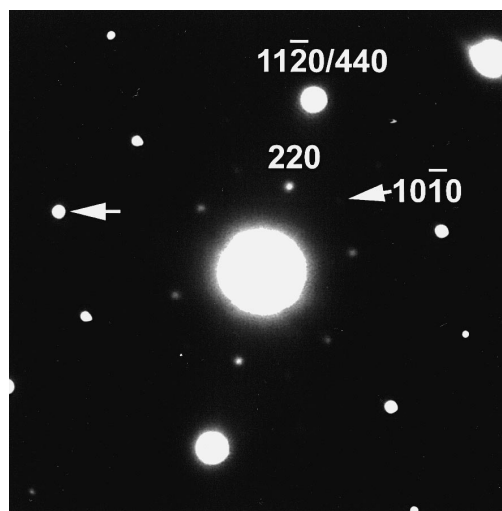


Fig. 6. Experimental SAD pattern from severely strained LiCoO_2 particles exhibits a new family of reflections $\{220\}$, indexed only in cubic setting, indicating cation occupancy on 8a tetrahedral sites [10].

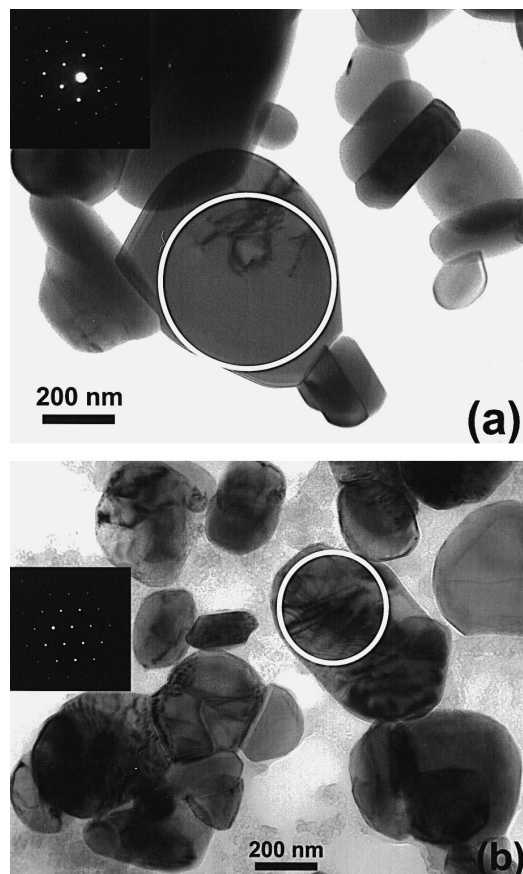


Fig. 7. TEM bright field images $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ particles and corresponding SAD patterns from circled particles. (a) Before electrochemical cycling. (b) After cycling, illustrating internal strain and extended defects created by repeated Li insertion/removal.

plete disorder between Li and Co layers is assumed (e.g., each layer has 50% Li and 50% Co) [10]. Another significant type of cation disorder is found only for severely strained particles (example shown in Fig. 4). New strong $\{220\}$ reflections (Fig. 6) are observed, which are characteristic of the cubic spinel structure with tetrahedral 8a occupancy of cations. This is the first observation of spinel disorder in LiCoO_2 due to electrochemical cycling, and suggests that the stable structure at intermediate Li concentration may be the spinel, as is also indicated by ab initio computations [14]. Continued development of spinel disorder may occur after longer cycling. Whether this mechanism alone, or disorder combined with microstructural damage, contributes to the long-term degradation of LiCoO_2 cathodes requires additional study.

In the $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ cathode, similar electrochemical cycling-induced strain damage was readily observed by TEM (Fig. 7). However, in contrast to the LiCoO_2 sample, we found fewer instances where the $\{220\}$ reflections characteristic of spinel disorder appeared. While more extensive studies are necessary, the results suggest that aluminum doping stabilizes LiCoO_2 against spinel disorder during electrochemical cycling. However, since the

$\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ cathode does show greater capacity fade [9], it appears that another mechanism of capacity loss apart from the spinel transformation may be active. It is notable that aluminum doping has been found to stabilize the layered rocksalt phases monoclinic LiMnO_2 [15] and rhombohedral LiNiO_2 [9] during synthesis. Aluminum substitution into the transition metal oxides of LiMO_2 stoichiometry may generally serve a role of stabilizing layered rocksalt ordering.

5. Conclusions

Direct TEM observation of cycled cathode materials LiCoO_2 and $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ shows that a wide variety of defects are created. Particles are extensively strained or microfractured, and often contain a high density of dislocations and extended defects. Single crystalline SAD patterns reveal two types of cation disorder resulting from the repeated insertion and removal of Li^+ . One is the cation substitution/vacancy of Li and Co on their respective octahedral site layers in the ordered $\alpha\text{-NaFeO}_2$ structure. The second, mainly observed in severely strained and fractured particles, is a partial structural transformation from octahedral cation ordering to spinel ordering with tetrahedral 8a site occupancy. These cycling effects are not detectable by bulk characterization methods such as XRD. The observed cation disorder provides the first direct experimental evidence for the stability of a spinel phase in Li_xCoO_2 .

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