

LiAl_xCo_{1-x}O₂ as 4 V cathodes for lithium ion batteries

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Abstract

Nominal LiAl_xCo_{1-x}O₂ with x ranging from 0.1 to 0.3 was prepared by heating mixture of Al(OH)₃, Co₃O₄ and LiOH at 750°C in air. The effect of substitution of non-transition metal, Al, in LiCoO₂ is investigated as a 4 V cathode for lithium ion. X-ray diffraction (XRD) indicates formation of a single phase (R $\bar{3}m$) within this range of substitution. When cycled between 4.5 and 2.5 V vs. Li/Li⁺ at a current density of 1 mA cm⁻², the LiAl_{0.15}Co_{0.85}O₂ cathode exhibits reversible capacity of 160 mA h g⁻¹ initially. XRD of the cathode made at the end of 10 cycles reveals no significant change on host structure. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

LiCoO₂ is a well established 4 V cathode material with respect to synthesis and performance, and has been used in commercial lithium ion batteries since 1990 [1,2]. However, due to the high costs of cobalt, it is now facing serious competition from other materials, such as LiMn₂O₄ [3–7], LiNiO₂ [8–13] and LiCo_{0.5}Ni_{0.5}O₂ (or more generally LiCo_xNi_{1-x}O₂, 0 ≤ x ≤ 1) [13–17]. These alternatives are considered to be attractive because of the fact that they are cheap and/or they provide higher capacity (Ni oxides). Obviously, partial replacement of Co in LiCoO₂ by other less expensive metals is of interest to yield a material which is cheaper than LiCoO₂, but with many of its advantages. In addition, substituted LiCoO₂ may possess high reversible capacity. LiNi_{0.5}Co_{0.5}O₂ is an example; its reversible capacity is over 150 mA h g⁻¹ [17], in excess of the value of 136 mA h g⁻¹ which corresponds to 0.5 Li per formula being involved on intercalation/deintercalation. This is of great significance because reversible lithium insertion/extraction in Li_yCoO₂ is limited to 0.5 ≤ y ≤ 1 [13,18,19]. Aluminium is a non-transition metal, and has been used as dopant to modify intercalation compounds such as LiNiO₂ [20–22]. However, large amount of aluminium substitution in LiCoO₂, to our knowledge, has been less investigated. Recently Ceder et al. [23] have explored Li(AlCo)O₂ as cathode material based on first-

principles calculation. In this paper, we investigate Al substituted LiCoO₂ by considering the facts that aluminium is a lighter element and its compounds are relatively cheap and less toxic.

Since α -LiAlO₂ is isostructural with LiCoO₂ (R $\bar{3}m$) [20] and the ionic radii of Al³⁺ and Co³⁺ are very close (0.54 and 0.55 Å, respectively, with coordination number of six), it is likely that a wide range of LiAl_xCo_{1-x}O₂ solid solutions exist. Sufficiently high Al content is essential so as to cut down the cost of the cobalt material. As an inactive element, however, the content of Al should be not too high to compromise capacity. Therefore, we focused on substitution of Co with Al from 10 to 30 at.%. The electrochemical performance of LiAl_xCo_{1-x}O₂ was evaluated using galvanostatic charge and discharge. X-ray diffraction (XRD) studies were carried out to monitor structural change during lithium extraction and on cycling so as to explore long cycling use in the view of structural stability.

2. Experimental

2.1. Synthesis

Starting materials for preparing LiAl_xCo_{1-x}O₂ were LiOH·H₂O (Fluka, > 99.5%), or Li₂CO₃ (Merck, > 99%), Co₃O₄ (Fluka, ≥ 71% Co) and Al(OH)₃ (Merck), or Al(NO₃)₃·6H₂O (Fluka, > 98%). Stoichiometric amounts of cobalt and aluminium compounds along with 3 at.% of

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lithium compound in excess, to compensate for any loss of lithium that may occur during the firing, were mixed using an agate mortar and pestle. The mixtures were heated in air, first at 550°C for 20 h and then at 750°C for 24 h, with two intermittent grindings.

2.2. Cells and electrodes

Composite cathodes (area: 0.6–0.5 cm²), containing 76 wt.% of active material, 12 wt.% of carbon (Super P, MMM, Sedema, Belgium) and 12 wt.% of PTFE (Aldrich) binder, were fabricated using dry mixing method and pressed on Al gauze under 2 tons. This type of cathodes was applied in three electrode cells for cycling test. Counter electrode and reference one were lithium metal. Another type of composite cathodes with an area of 2 cm² was prepared using wet coating method. Active material, carbon (Super P, MMM) and KYNAR polymer binder (ELF-Atochem America) were, in 80:10:10 by weight, well mixed in 1-methyl-2-pyrrolidinone solvent (Aldrich), and the resulting slurry was coated on Al foil. After drying under heating, half a ton was applied to press these composite cathodes. Two electrode cells consisting of the large size composite electrode and a lithium metal electrode were constructed. After electrochemical experiments, the cathodes were taken off for XRD measurements. Battery-grade electrolyte (Merck Germany), 1 molar LiPF₆ dissolved in mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 by volume), was used, and Celgard 2400 (polypropylene) was soaked with the electrolyte and used as separator between electrodes.

2.3. Measurements

XRD measurements were undertaken by Philips X-ray diffractometer with Cu K_α radiation. The cathodes after electrochemical tests were placed on a piece of glass and covered with Mylar film by tape sealing to exclude exposure to air during X-ray measurements. Solartron 1286 Electrochemical Interface (voltage resolution: 0.1 mV) was used to carry out electrochemical experiments. Specific capacities were based on the weight of LiAl_xCo_{1-x}O₂.

3. Results and discussion

3.1. Synthesis and structural characterisation of LiAl_xCo_{1-x}O₂

α-LiAlO₂, which has α-NaFeO₂ structure (R $\bar{3}$ m), was originally prepared by solid state reaction of α-Al₂O₃ (or Al(OH)) and Li₂CO₃ at 600°C [24]. Recently Ohzuku et al. [20] reported to prepare this phase by heating mixture of Al(OH)₃ and LiNO₃ (or Li₂CO₃) at 750°C in air. We

used LiOH instead of LiNO₃ and combined Al(OH)₃ with Al(NO₃)₃, and also obtained a single phase of α-LiAlO₂. Thus, LiOH, Co₃O₄ and Al(OH)₃ plus a small amount of Al(NO₃)₃ were mixed and heated in air first at 550°C for 20 h and then at 750°C for 24 h. Fig. 1 presents the XRD patterns of LiAl_xCo_{1-x}O₂ with *x* ranging from 0.1 to 0.3. Miller indexes are given assuming a hexagonal lattice. It is evident that a single phase of LiAl_xCo_{1-x}O₂ can be prepared by this method and the replacement of cobalt with aluminium up to 30 at.% does not change LiCoO₂ phase except for somewhat broadening in the peaks at high angles (> 50° in 2θ). The phenomenon of peak broadening is not so significant compared with the case of solid solution of LiAl_xNi_{1-x}O₂ [20]. By a least squares method, lattice parameters, *a* and *c*, are calculated and plotted against aluminium contents in Fig. 2, in which the values

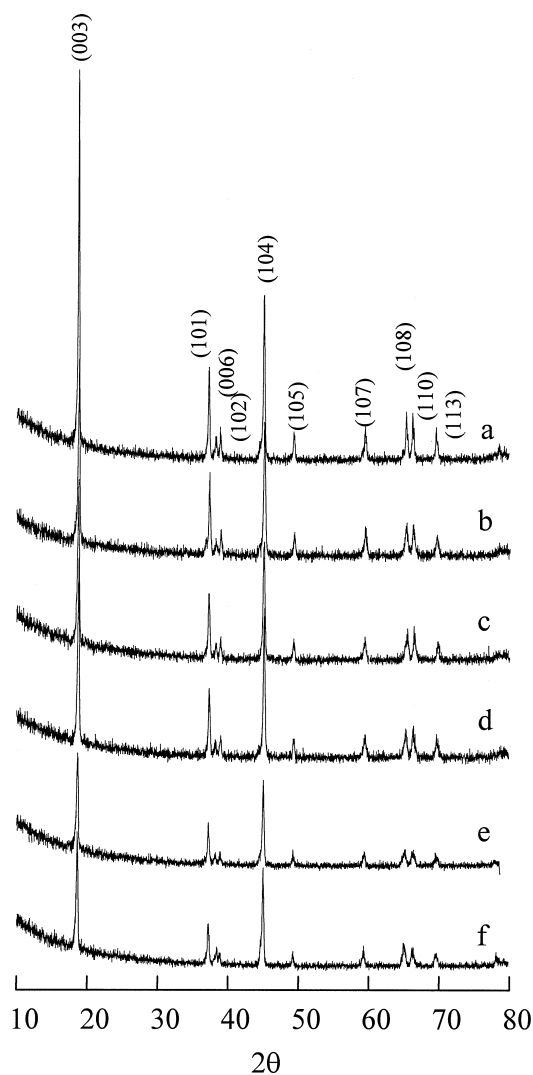


Fig. 1. XRD patterns for LiAl_xCo_{1-x}O₂: (a) *x* = 0, (b) *x* = 0.1, (c) *x* = 0.15, (d) *x* = 0.2, (e) *x* = 0.25 and (f) *x* = 0.3. LiAl_xCo_{1-x}O₂ were prepared by heating the mixture of LiOH·H₂O, Co₃O₄ and Al(OH)₃ at 750°C except for *x* = 0, which is commercial LiCoO₂ from Merck.

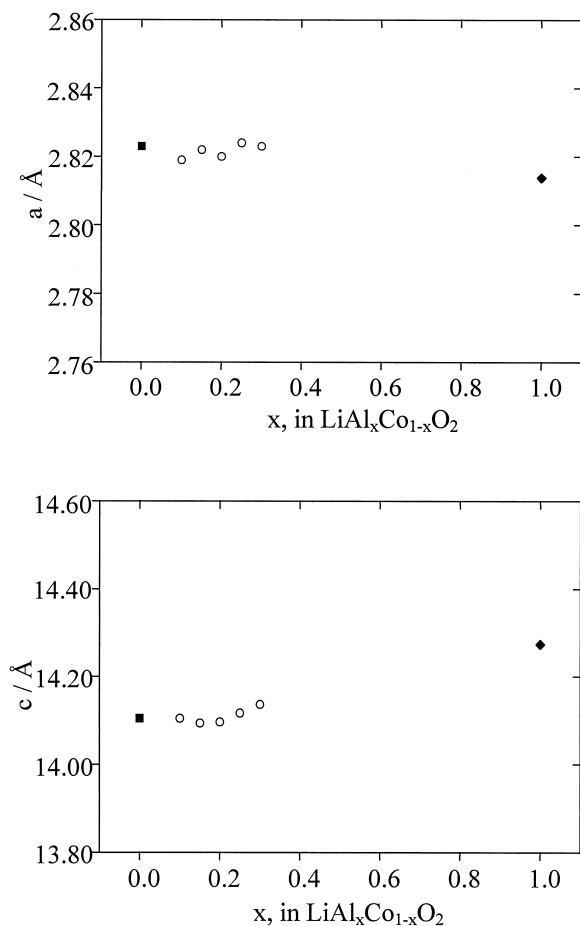


Fig. 2. Hexagonal unit cell parameters, a and c , as a function of x in $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$. The parameters were determined by a least squares method using the peaks in Fig. 1.

of lattice parameters for LiCoO_2 and LiAlO_2 are included for comparison. It can be seen from Fig. 2 that the values

of a -axis and c -axis of $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ with $0.1 \leq x \leq 0.3$ situate between those of LiCoO_2 and LiAlO_2 . This is characteristic feature of solid solution. The a -axis varies slightly with x , but the c -axis starts to increase more significantly at $x > 0.2$. It is worth pointing out that the 003 peak remains higher than the 104 peak for $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ with $0.1 \leq x \leq 0.3$. The ratio of 003/104, as has been acknowledged to be an indication of cation mixing, is around 1.25, except for the case at $x = 0.3$. This may suggest that the degree of cation mixing is negligible at least at $x < 0.3$.

3.2. Reversible capacity of $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$

Fig. 3 compares the first charge and discharge curves of $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ cathode with those of LiCoO_2 one, the former cycled between 4.3 and 2.5 V vs. Li/Li^+ and the latter between 4.2 and 2.5 V vs. Li/Li^+ . It is evident that Al substitution does not change the potential profiles of intercalation/deintercalation in LiCoO_2 significantly, but intercalation potential rises with the presence of Al in host, being consistent with the report by Ceder et al. [23]. As a result, capacity relatively decreases at a given charge voltage. To measure capacities, $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ cathodes were first cycled between 4.3 (or 4.2 V) and 2.5 V vs. Li/Li^+ for two times and then charge voltages raised to 4.5 V vs. Li/Li^+ in the subsequent cycles. The charge and discharge currents were 1 mA cm^{-2} . Fig. 4 presents the reversible capacity of $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ cathodes. For comparison, results from a cathode prepared from commercially available LiCoO_2 (Merck) are also included in Fig. 4. This LiCoO_2 cathode was first cycled between 4.2 and 2.5 V for two times and then between 4.4 and 2.5 V for further two times. By charging to 4.2 V, LiCoO_2 cathode gives nearly 120 mA h g^{-1} of discharge capacity, while

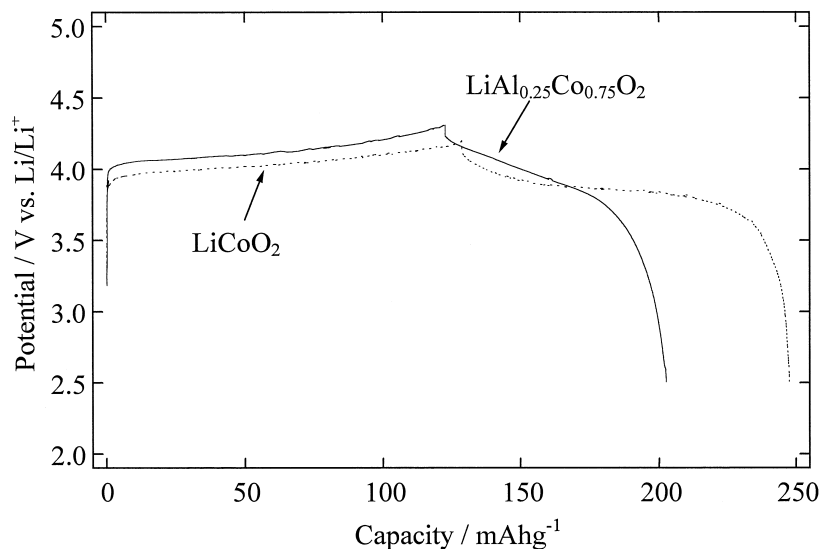


Fig. 3. The first charge and discharge curves of $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ (solid line) and LiCoO_2 (dash line) cathodes. Charge and discharge currents were 1 mA cm^{-2} .

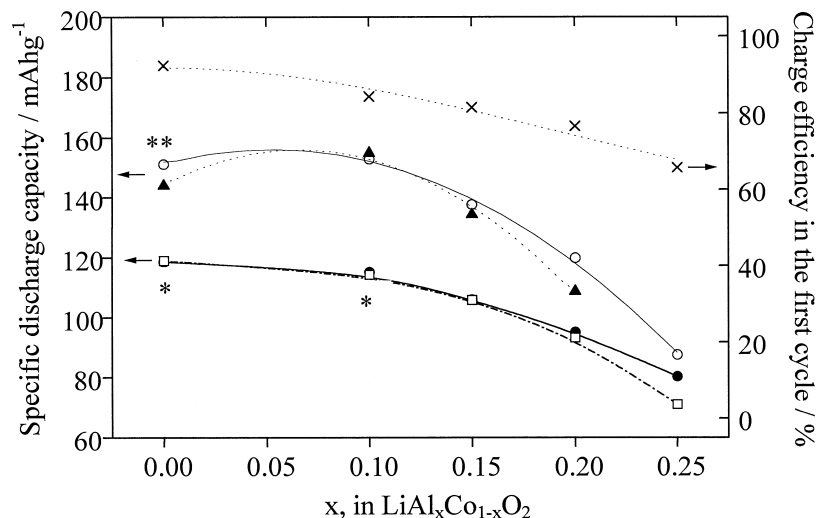


Fig. 4. Specific discharge capacities as a function of x in $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$: ● the first cycle, □ the second cycle, ○ the third cycle and ▲ the fourth cycle. Charge and discharge currents were 1 mA cm^{-2} . Cut-off voltages were 4.3 V (or 4.2 V with * marks) and 2.5 V in the first two cycles, and 4.5 V (or 4.4 V, with ** mark) and 2.5 V in the third and fourth cycles. The curve with × marks refers to charge efficiency in the first cycle.

the capacity of $\text{LiAl}_{0.1}\text{Co}_{0.9}\text{O}_2$ is 115 mA h g^{-1} . However, other $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ compositions have capacity less than 110 mA h g^{-1} even under charge voltages of 4.3 V. As a contrast, more capacities were obtained by charging to 4.5 V vs. Li/Li^+ in the third and fourth cycles. Even though the capacity of $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$ is still lower than 100 mA h g^{-1} , we noted that cathodes with $x = 0.1, 0.15$ and 0.2 in $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$, exhibit 153, 139 and 120 mA h g^{-1} of capacities, respectively, in comparison to 151 mA h g^{-1} of capacity obtained from LiCoO_2 (charge limit is 4.4 V).

Charge efficiencies in the first cycles for $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ and LiCoO_2 cathodes are also give in Fig. 4 (marked with

crosses). LiCoO_2 exhibits charge efficiency as high as 92% in the first cycle, while all $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ cathodes give values less than 90%. The charge capacities lose on the first discharge from 15% (at $x = 0.1$) to 34% (at $x = 0.25$). However, charge efficiencies do rise over 96% in subsequent cycles for all Al contents under test. The nature of the capacity loss in the first discharge is not clear at the present stage. It is worth pointing out that the potential profiles of charge and discharge curves vary less in the first cycle and subsequent ones. Hence, we expect that $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ should not have any major change in chemical composition and crystal structure after the first cycle. The X-ray data measured for $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ in-

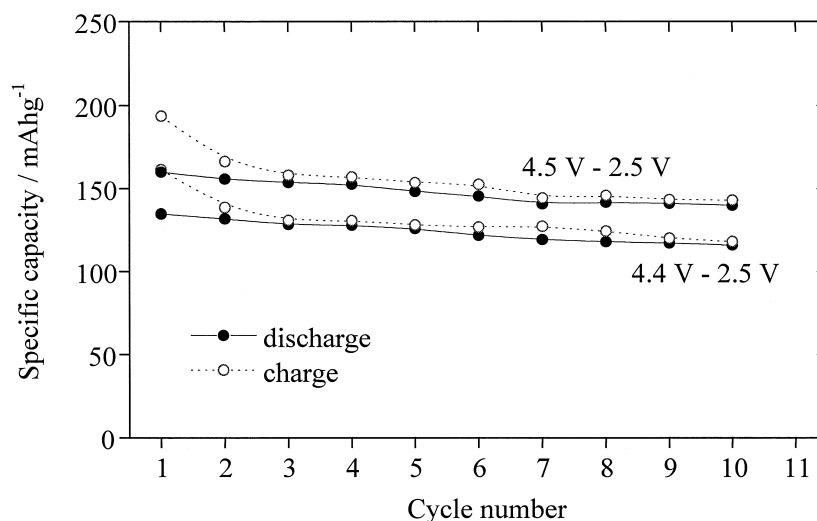


Fig. 5. Variation of specific capacity as a function of cycle number for $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ cathodes cycled between 4.5 and 2.5 V, and 4.4 and 2.5 V. Charge and discharge currents were 1 mA cm^{-2} .

deed do not show major structure change after one cycle, as will be discussed later.

3.3. $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$

As indicated in Fig. 4, the composition $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ is best from the point of a reasonable capacity associated with an essentially high Al content. Therefore, this composition was investigated further in the following. Under the same current density as the above (1 mA cm^{-2}), two cathodes of $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ were charged and discharged between 4.4 and 2.5 V, or 4.5 and 2.5 V, respectively, and the results are presented in Fig. 5. Again, it is evident that high reversible capacity is obtainable with high charge

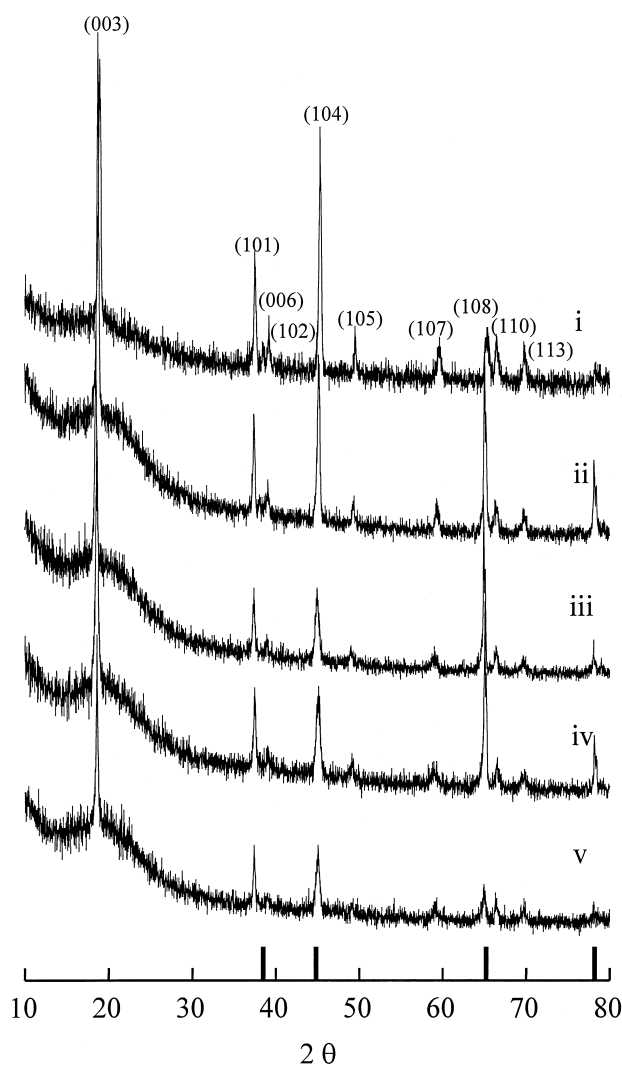


Fig. 6. XRD patterns of $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ after being charged by removing (i) 0, (ii) 35, (iii) 135, (iv) 175 and (v) 195 mA h g^{-1} of charge. Charge currents were $70 \mu\text{A cm}^{-2}$. The bars in the figure mark the positions of the peaks from Al substrate (of which the peak at 65.23° in 2θ is the most intensive). The very broad background peak at low angle ($<30^\circ$ in 2θ) arises from the tape used to seal the samples from atmosphere.

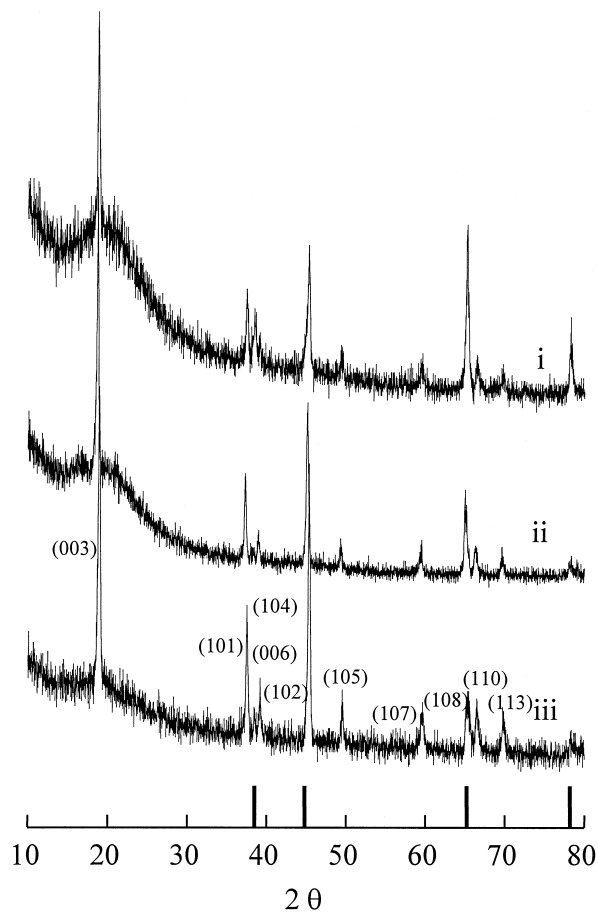


Fig. 7. XRD patterns of $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ measured at the end of discharge after (i) 10 cycles (hexagonal; $a = 2.81 \text{ \AA}$, $c = 14.08 \text{ \AA}$), and (ii) one cycle (hexagonal; $a = 2.82 \text{ \AA}$, $c = 14.11 \text{ \AA}$). The pattern in (iii) was from a fresh cathode (hexagonal; $a = 2.82 \text{ \AA}$, $c = 14.10 \text{ \AA}$). (See comments in caption to Fig. 6.)

voltage. And, no significant influence of charge voltage on capacity retention is observed within the first 10 cycles.

Corresponding to charge voltages of 4.3, 4.4 and 4.5 V vs. Li/Li^+ , the first charge capacities were 130, 162 and 194 mA h g^{-1} , while the charge efficiencies in the first cycle varies little, falling in the range of 82–83%. To monitor structure during deintercalation, several cathodes of $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ (with an area of 2 cm^2 , see Section 2 for more details) were charged at a current density of $70 \mu\text{A cm}^{-2}$ by removing 35, 135, 175 and 195 mA h g^{-1} of charge, respectively. These charges respectively correspond to the values of y in $\text{Li}_{1-y}\text{Al}_{0.15}\text{Co}_{0.85}\text{O}_2$ to be 0.12, 0.47, 0.61 and 0.68. After standing on open circuit for 10 h, these cathodes were taken out of cells and left for further equilibrium for at least three days before being subjected to XRD measurements. The resulting XRD patterns are presented in Fig. 6. It has been reported that LiCoO_2 structure changes from hexagonal to monoclinic phase over the range $0.44 \leq y \leq 0.49$ in $\text{Li}_{1-y}\text{CoO}_2$ (corresponding to the capacities from 120 to 135 mA h g^{-1})

[25–27]. In addition, there exist two hexagonal phases at the beginning of charging ($y < 0.25$, i.e., $< 70 \text{ mA h g}^{-1}$ of charge capacity) [14,25]. By contrast, the patterns in Fig. 6 remain unchanged during lithium extraction although the peaks from Al substrate exist, which overlap the 006, 104 and 108 peaks of $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$. There are no peaks splitting which are a sign of monoclinic deformation or two phase coexistence. For example, the 104 peak of hexagonal phase splits when monoclinic deformation appears [25]. Such a situation is very similar to the cases of Ni substituted in LiCoO_2 ($\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$) [14] and Al substituted in LiNiO_2 ($\text{LiAl}_{0.25}\text{Ni}_{0.75}\text{O}_2$) [20], which are reported to have no observation of monoclinic phase. In this point of no phase transformation, 15% of Al substitution may enhance LiCoO_2 structure stability.

To examine structure on cycling, two $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ cathodes (with an area of 2 cm^2) were charged and discharged at a current of $70 \mu\text{A cm}^{-2}$ in two electrode cells. One was charged by removing 175 mA h g^{-1} of charge and then discharged to 2.5 V vs. Li/Li^+ (giving 153 mA h g^{-1} of capacity). The other was subjected to 10 times of charge and discharge. In the first cycle, charge capacity was also limited to 175 mA h g^{-1} followed by discharging to 2.5 V. But in the subsequent cycles, the charge capacity was controlled to be same as that in the previous discharge process and discharge was always stopped at 2.5 V vs. Li/Li^+ . The discharge capacity was 153 mA h g^{-1} initially and 135 mA h g^{-1} at the end of 10 cycles. These two cycled-cathodes were subjected to XRD measurements, and the results are shown in Fig. 7 in which the result from an uncycled one is also included for comparison. It is clear that structure is highly recoverable. This is very encouraging for this Al-substituted material to be investigated for long term cycling use in future.

4. Conclusions

Solid solution $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ with $0.1 \leq x \leq 0.3$ can be prepared by heating the mixture of $\text{Al}(\text{OH})_3$ (or $\text{Al}(\text{NO}_3)_3$), Co_3O_4 and LiOH in air at 750°C . Intercalation potential increases as a result of the substitution of Al in LiCoO_2 , and so higher charge voltage, e.g., 4.5 V vs. Li/Li^+ , is of necessity to be applied. Initial capacity of 160 mA h g^{-1} can be obtained from the composition of $\text{LiAl}_{0.15}\text{Co}_{0.75}\text{O}_2$ when cycled at a current of 1 mA cm^{-2} and between 4.5 and 2.5 V vs. Li/Li^+ . XRD data do not show monoclinic phase as well as two phase co-existence which occur in LiCoO_2 . Structure of $\text{LiAl}_{0.15}\text{Co}_{0.85}\text{O}_2$ retains hexagonal symmetry after 10 cycles. These structural features are

very encouraging for this material to be investigated further for possible practical use.

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