Crystal structures and electrochemical properties of LiAl$_y$Ni$_{1-y}$O$_2$ solid solution

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Abstract

We describe the synthesis, structure and electrochemical properties of LiAl$_y$Ni$_{1-y}$O$_2$ solid solutions. LiNiO$_2$ charged to 4.1 V versus lithium metal can de-intercalate lithium to $x=0.7$ in Li$_{1-x}$NiO$_2$. Additional lithium can be removed above 4.1 V, but this degrades cell performance because the cathode structure is destabilized beyond $x=0.7$. In an overcharged Li$_{1-x}$NiO$_2$ cathode most of the nickel atoms are in the unstable Ni^{4+} state. Since LiAlO$_2$ is isostructural with LiNiO$_2$, we reasoned that substituting trivalent aluminium for nickel may limit the amount of lithium which can be withdrawn from the cathode. Single-phase LiAl$_y$Ni$_{1-y}$O$_2$ solid solutions were synthesized for $y \leq 0.3$. They were structurally characterized by X-ray diffraction and evaluated as the cathode in LiAl$_y$Ni$_{1-y}$O$_2$/Li coin cells. Although the substitution of aluminium for nickel had the desired effect of reducing the amount of lithium that can be removed on overcharge, it also reduced the reversible capacity of the cathode.

Keywords: Rechargeable lithium batteries; Crystal structure; Nickel oxide

1. Introduction

LiNiO$_2$ is one of the preferred cathode materials for lithium-ion batteries. One advantage is that LiNiO$_2$ is less expensive than LiCoO$_2$. When charged/discharged between 3.0 and 4.1 V versus Li metal the LiNiO$_2$ cathode supplies 138 mAh/g reversible capacity and 52 mAh/g irreversible capacity [1,2]. The latter is useful for compensating the irreversible capacity loss associated with the carbon anode. This corresponds to cycling over the range $0.2 \leq x \leq 0.7$ in Li$_{1-x}$NiO$_2$. More Li can de-intercalate when the voltage versus Li is above 4.1 V but this destabilizes the Li$_{1-x}$NiO$_2$ crystal structure. In overcharged Li$_{1-x}$NiO$_2$ most of the Ni is in the unstable Ni^{4+} state which should be avoided [3]. In this work we studied the possibility of modifying the cycling behaviour of Li$_{1-x}$NiO$_2$ by substituting Al for Ni. Since LiAlO$_2$ is isostructural with LiNiO$_2$ [4], we expect the substitution to be possible. Ideally this would limit the amount of Li which can be de-intercalated because Al must remain in 3+ oxidation state.

Table 1
Structure parameters for LiNiO$_2$, LiAl$_y$Ni$_{1-y}$O$_2$ and LiAlO$_2$ [a]

Samples	a (Å)	c (Å)	Al in Ni site
LiNiO$_2$			
$y=0$	2.882	14.198	
$y=0.01$	2.876	14.196	0.011
$y=0.02$	2.876	14.193	0.018
$y=0.05$	2.876	14.194	0.04
$y=0.10$	2.876	14.208	0.1
$y=0.20$	2.876	14.208	0.205
LiAlO$_2$			
$y=1$	2.801	14.214	

[a] This data was quoted from Ref. [3].
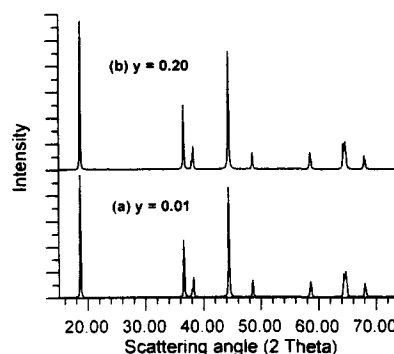
Fig. 1. Single-phase X-ray diffraction patterns for (a) LiAl$_{0.01}$Ni$_{0.99}$O$_2$ and (b) LiAl$_{0.2}$Ni$_{0.8}$O$_2$.

2. Experimental

LiAl$_y$Ni$_{1-y}$O$_2$ was synthesized by the solid-state reaction of a mixture of LiOH, NiO and Al compounds at 700 °C in air. Initial trials using Al$_2$O$_3$ or Al(OH)$_3$ as the source of Al were not successful, producing Al$_2$O$_3$ impurity. Single-phase LiAl$_y$Ni$_{1-y}$O$_2$ was prepared by reacting pure Al powder (300 mesh) with LiOH and NiO. A series of single-phase LiAl$_y$Ni$_{1-y}$O$_2$ solid solutions were made at 700 °C in air with $y \leq 0.2$ The structures of the LiAl$_y$Ni$_{1-y}$O$_2$ solutions were characterized by X-ray diffraction (Philips, Cu Kα radiation) and analysed using the Rietveld refinement program of Hill and Howard [5,6]. The amount of Al at the Ni site was obtained from the refinement LiAl$_y$Ni$_{1-y}$O$_2$/ Li coin cells as described in Ref. [7] were made to characterize the Li intercalation and de-intercalation. The electrolyte used in these tests was 1 M LiAsF$_6$ in propylene carbonate/dimethoxyethane (PC/DME). Cells were cycled at a constant current chosen such that 50 h would be required for $x = 1$ in Li$_{1-x}$Al$_y$Ni$_{1-y}$O$_2$.

3. Results and discussion

Table 1 shows the results of the refinement, which indicates that Al mainly occupies the Ni site. The X-ray data shows that the Al can substitute for Ni up to $y = 0.2$ in LiAl$_y$Ni$_{1-y}$O$_2$. Some additional unknown
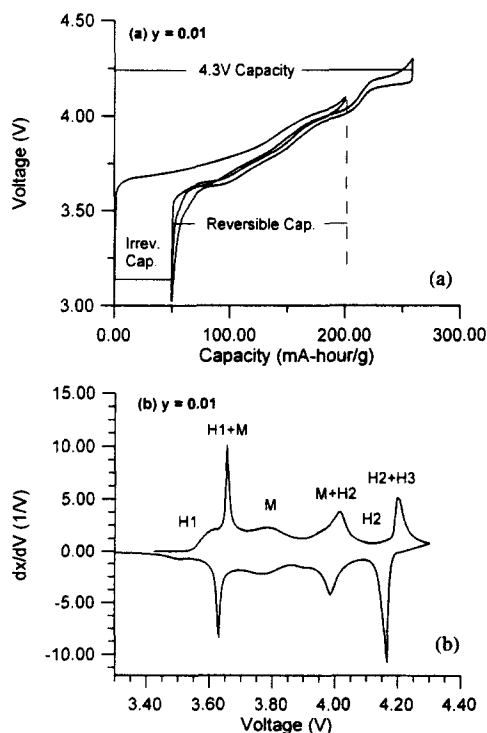

Fig. 2. (a) $V(x)$ and (b) dx/dV for LiAl$_y$Ni$_{1-y}$O$_2$ ($y = 0.01$). Single-phase (H1, M, H2, H3) and two-phase regions are identified according to Ref. [7].
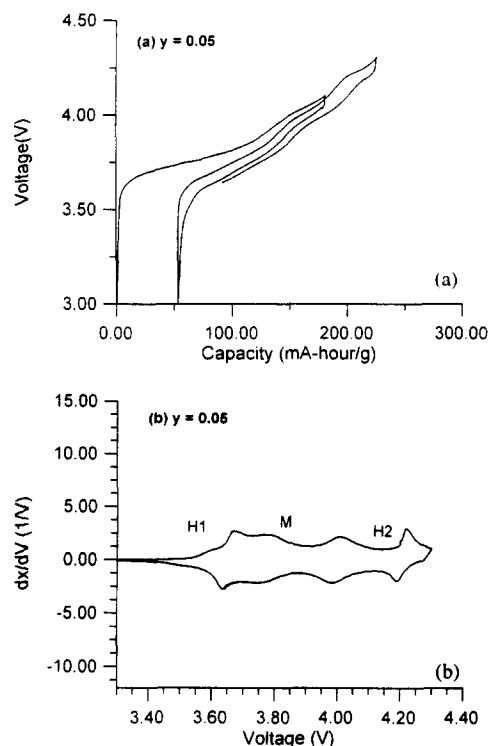

Fig. 3. (a) $V(x)$ and (b) dx/dV for LiAl$_y$Ni$_{1-y}$O$_2$ ($y = 0.05$).

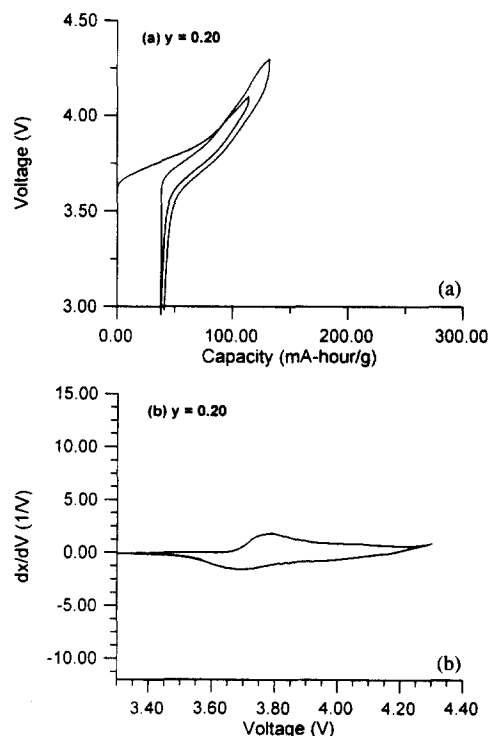Fig. 4. (a) $V(x)$ and (b) dx/dV for LiAl$_y$Ni$_{1-y}$O$_2$ ($y = 0.20$).

phase was observed when we attempted to synthesize LiAl$_{0.3}$Ni$_{0.7}$O$_2$. Fig. 1 shows the X-ray diffraction patterns for $y = 0.01$ and $y = 0.20$. The lattice constants of the LiAl$_y$Ni$_{1-y}$O$_2$ series are only slightly different from that of LiNiO$_2$. Only c changes when the amount of Al
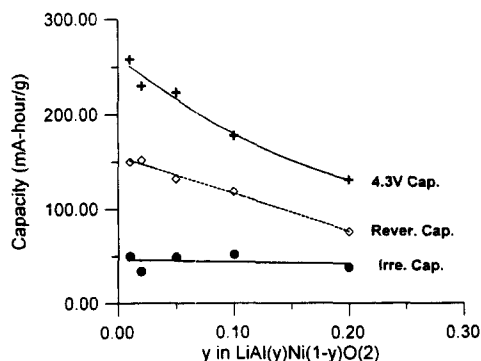
Fig. 5. (●) Irreversible capacity, (▲) reversible capacity, and (+) total capacity to 4.3 V for $LiAl_yNi_{1-y}O_2$ ($0 < y < 0.2$).

substituted varies. The lattice shrinks slightly in the c-direction until y approximates 0.02 and then expands beyond y is about 0.05.

To electrochemically characterize these materials, $LiAl_yNi_{1-y}O_2$/Li coin cells were initially charged to 4.1 V and then discharged to 3.0 V to obtain the irreversible and reversible capacity as indicated in Fig. 2(a). Thereafter, the cells were charged up to 4.3 V to get the total capacity to 4.3 V which we want to control by substituting Al. Fig. 2 shows the voltage (Fig. 2(a)) and dx/dV (Fig. 2(b)) curves for an $Li_{1-x}Al_{0.01}Ni_{0.99}O_2$/Li cell. With a small amount of substituted Al we obtain the same behaviour as for pure $LiNiO_2$ [7]. $Li_{1-x}Al_{0.01}Ni_{0.99}O_2$ has 50 mAh/g irreversible capacity and 148 mAh/g reversible capacity between 3.0 and 4.1 V (see Fig. 2(a)). Another 104 mAh/g can be removed from $Li_{1-x}Al_{0.01}Ni_{0.99}O_2$ if the cell is charged to 4.3 V, corresponding to $x = 0.94$ in $Li_{1-x}Al_{0.01}Ni_{0.99}O_2$. With most Ni atoms in the Ni^{4+} state, $Li_{0.04}Al_{0.01}Ni_{0.99}O_2$ is an unstable material and a strong oxidizing agent.

Based on in situ X-ray data Li et al. [7] analysed the phase diagram for the $Li_{1-x}NiO_2$. They showed that $Li_{1-x}NiO_2$ actually consists of four separate phases

(one monoclinic, M, and three hexagonal, H1, H2 and H3, as indicated in Fig. 2(b)). These of peaks in dx/dV curve (see Fig. 2 (b)) correspond to first order transitions between these phases.

Fig. 3(a) and Fig. 4(a) show that the amount of Li which can be withdrawn from $LiAl_yNi_{1-y}O_2$ decreases as more Al is substituted for Ni. Fig. 5 summarizes the irreversible, reversible and total capacity to 4.3 V for all of the compositions we tested. As expected, the addition of Al reduces the overcharge capacity between 4.1 and 4.3 V. Unfortunately the reversible capacity is also reduced significantly. Only the irreversible capacity remains almost constant.

The substitution of Al also has a strong effect on the phase transitions that occur as Li is de-intercalated from the lattice. The dx/dV curve for $y = 0.01$ is almost identical to that of pure $LiNiO_2$, but when $y = 0.05$ the peaks at 3.65, 4.0 and 4.2 V corresponding to first order phase transitions become very broad and when $y = 0.2$ these features are absent. Only the broad peak at 3.8 V in dx/dV, within the monoclinic single phase region for $LiNiO_2$, seems to be uneffected by the substitution of Al.

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