

Flat plate prismatic Li-ion cells using advanced cathode materials

G.M. Ehrlich^{*}, F.J. Puglia, R. Gitzendanner, B. Hellen, C. Marsh

Yardney Technical Products, USA

Abstract

Recent advances in $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ mixed metal oxide based cathode materials for Li-ion batteries have resulted in an improved generation of Li-ion cells for high capacity, long life batteries. Candidate cathode materials have been characterized and evaluated in prototype 3.5 Ah flat plate prismatic Li-ion cells. For comparison, 3.5 Ah prismatic Li-ion cells which used a LiCoO_2 based cathode material were also evaluated. All cells in this study utilized a graphitic carbon based anode material. The most energy dense material evaluated, $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($x = 0.82$), offered 206 mAh/g on the first charge and was cycled at the C/2 rate at 157 mAh/g in prototype 3 Ah cells with rate capability comparable to similar cells which used a LiCoO_2 material. Prototype cells using this material offer 130 Wh/kg and 340 Wh/l. This cell design has been scaled to 20 Ah. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the commercialization of Li-ion technologies which used a lithium cobalt oxide (LiCoO_2) based positive electrode material and a coke based negative electrode material, continued innovation has produced new materials permitting improvement of Li-ion technologies. For applications which are weight, volume or cost sensitive, materials which offer improved specific capacity, higher energy density or lower cost are attractive. Towards improved cell capacity lower cost materials related to LiCoO_2 ($\text{LiM}_x\text{Co}_{1-x}\text{O}_2$) [1,2] have been developed and are now commercially available.

Li_xCoO_2 is a layered material iso-structural to $\alpha\text{-NaFeO}_2$. Commercially available Li_xCoO_2 offers 150 mAh/g ($0.5 < x < 1.1$), further, recent work has shown $\text{Li}_{1.05}\text{CoO}_2$ can be fully de-intercalated electrochemically [3] to yield 274 mAh/g. Li-ion battery technologies based on related iso-structural phases, such as LiNiO_2 [4], have also been developed. Nickel oxides offer the potential of lower cost and high capacity, commercially available materials offer 160–210 mAh/g [5], but LiNiO_2 has received

less commercial interest since LiNiO_2 was shown to be less stable than cobalt based materials, reduction to form NiO has been described [6]. More recently, $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ materials have been developed. These materials have the potential to offer characteristics of LiNiO_2 and LiCoO_2 , thus the possibility of a material with higher capacity and lower cost than LiCoO_2 and stability superior to LiNiO_2 .

This evaluation of cathode materials was performed as part of a program which is developing a Li-ion technology as an alternative to the zinc–silver oxide battery presently used in NASA's extra-vehicular man unit (EMU). In this application, energy density is paramount and cycle life in excess of 100 cycles is required. In the target application, the materials must offer stability comparable to LiCoO_2 and exceptional specific capacity.

2. Experimental

Four $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ and three LiCoO_2 materials were evaluated in 3 Ah prismatic prototype cells. All materials were obtained commercially. Particle size analysis was performed on a Horiba LA-900 instrument by light scattering and specific surface area determined using the BET technique. In electrochemical studies, electrode materials were prepared using a PVDF binder, microporous polypropylene separator and carbonate based electrolyte.

^{*} Corresponding author. 82 Mechanic St., Pawcatuck, CT 06379, USA. Tel.: +1-860-599-1100 ext. 227; Fax: +1-860-599-3903; E-mail: ehrlich@yardney.com

The positive electrode material incorporated a coating of the oxide of interest on aluminum foil and the negative electrode material utilized a coating of graphitic carbon on copper foil. The negative electrode material in all cells was identical and, unless otherwise stated, incorporated excess material such that the graphite was intercalated to a level no greater than 232 mAh/g. Unless otherwise stated, all testing was performed at 25°C and cells were cycled between 4.1 and 3.0 V.

3. Results

3.1. Physical characterization

In the SEM micrographs of the most energy dense materials evaluated, crystal edges and faces could be identified suggesting similar degrees of crystallinity with var-

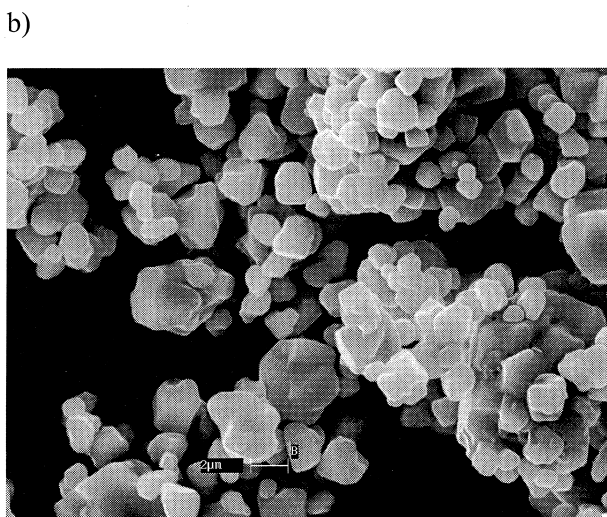
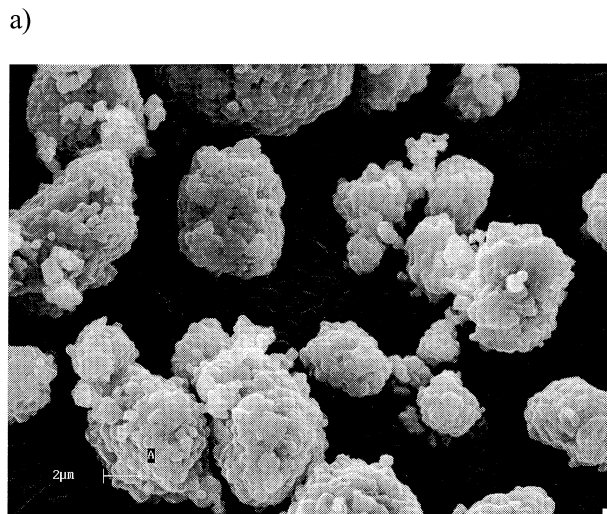


Fig. 1. SEM micrographs of (a) $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 and (b) $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #2.

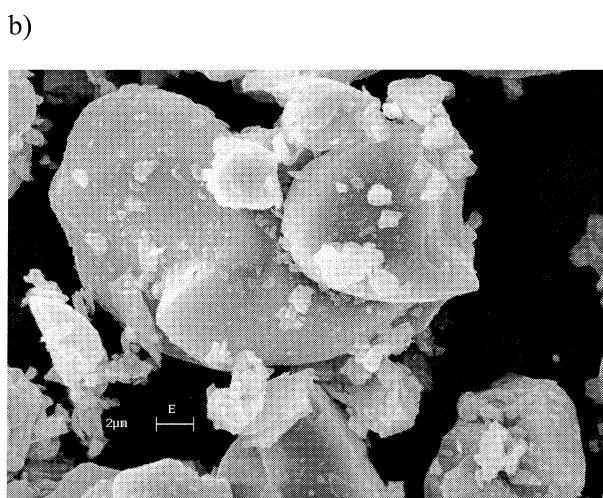
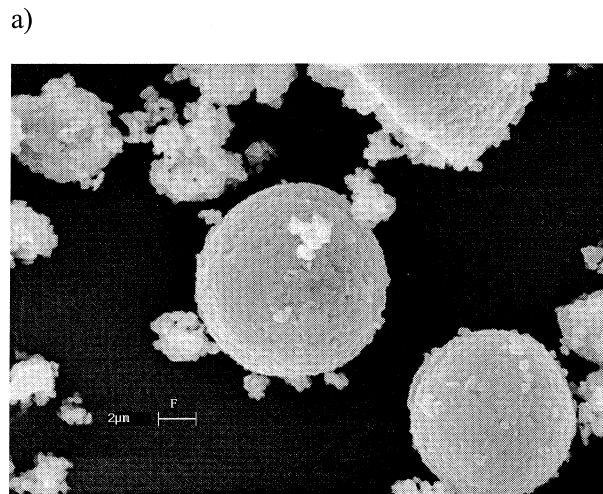


Fig. 2. SEM micrographs of (a) $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #3 and (b) LiCoO_2 #2.

ied degrees of agglomeration. In lower capacity materials, crystal faces or edges were not observed suggesting a lower degree of crystallinity. This is illustrated in Fig. 1, a micrograph of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 and $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #2, the most energy dense materials evaluated, and Fig. 2, a micrograph of two lower capacity materials, $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #3 and LiCoO_2 #2. $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 is highly agglomerated and appears as 2–6 μm particles composed of agglomerated 0.5–1 μm crystallites. $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #2 is less agglomerated and composed of larger crystallites, 1–4 μm in diameter. In less energy dense materials, such as LiCoO_2 #2, crystal edges or faces could not be identified and larger particles were observed. All the materials had similar and low ($< 1 \text{ m}^2/\text{g}$) specific surface area as shown in Table 1. The median particle size is also tabulated in Table 1. The particle size data was consistent with SEM observations. The most energy dense materials had a small median particle size ($< 10 \text{ μm}$) and a particle size distribution smaller than the average material.

Table 1

Specific capacity of the candidate materials on the first charge (de-intercalation), discharge (intercalation), the 30th discharge, their median particle size and specific surface area

Material	Charge #1 (mAh/g)	Discharge #1 (mAh/g)	Cycle 1 loss (%)	Discharge #30 (mAh/g)	PSA (μm)	BET (m^2/g)
$\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1	206	168	18.0	156	9.3	0.68
$\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #2	182	153	15.6	121	6.9	0.50
$\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #3	171	145	15.0	129	10.6	0.89
$\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #4	185	145	21.4	113	8.8	0.49
LiCoO_2 #1	131	115	12.6	105	12.0	0.26
LiCoO_2 #2	140	112	20.0	101	13.0	0.50
LiCoO_2 #3	156	133	14.7	120	N/A	N/A

3.2. Electrochemical characterization

The specific capacity for the positive electrode material in the prototype cells for the first and 30th cycles is shown in Table 1. The first cycle for all materials was at the C/20 rate whereas the 30th cycle was at the C/2 rate for cells with $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ and the C rate for cells with LiCoO_2 . In both the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ materials and the LiCoO_2 materials a range of performance is observed, 171 to 206 mAh/g and 131 to 156 mAh/g, respectively, but the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ materials consistently offered higher capacity (30% on average) than the LiCoO_2 materials. Cells with higher capacity materials also had higher irreversible capacity on the first cycle. Aside from differences related to the specific capacity, cells with materials of a given type had similar discharge curves. Cells with the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ material offered higher capacity but at slightly lower average voltage than cells with the LiCoO_2 material, 3.68 V vs. 3.85 V on average. For clarity, only the discharge curves for the highest capacity materials are shown in Fig. 3, one for a cell which utilized $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 and one for cell which utilized LiCoO_2 #3.

To evaluate the capacity fade, cells with either the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 or LiCoO_2 #3 materials were cycled at the C/2 and C rate, respectively. At the C/2 rate, the cell

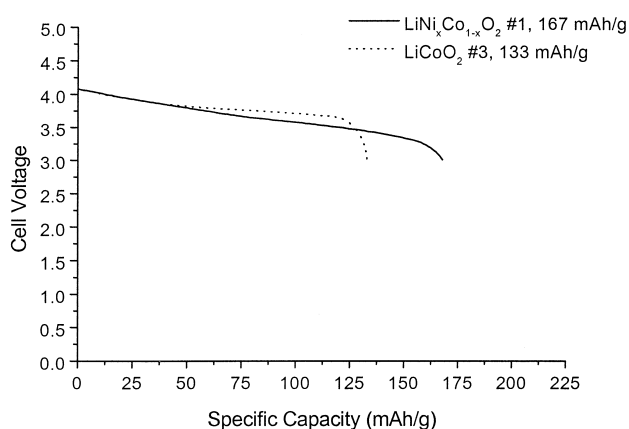


Fig. 3. Discharge curves for two cells, one of which used $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 and the other LiCoO_2 #3.

with the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ material offered stable capacity of 157 mAh/g. When the upper cutoff voltage was 4.1 V, the fade rate was 0.037%/cycle. When the upper cutoff voltage was lowered to 4.0 V the fade rate was reduced to 0.0185%/cycle although the capacity was 9.4% less. Changing the lower cutoff voltage from 3.0 to 2.5 did not have a significant effect on the fade rate although the capacity was increased by 11% with the lower voltage limit. The cell which utilized the LiCoO_2 material offered high capacity, 140 mAh/g initially, but when cycled at the C rate faded at a rate of 0.3%/cycle.

Cells with the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ or LiCoO_2 materials offered comparable rate capability, as shown in Fig. 4. Again we observe the improved specific capacity possible with the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ material but as the slope of the curves is comparable, the rate capability of the materials is similar. At the C rate, or 2.4 mA/cm², the discharge capacity of the cell with $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ was 89% of the capacity at C/10 compared to 76% for the cell which used LiCoO_2 . All cells contained excess graphite anode material. Cells with $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 were fabricated with less excess graphite anode material. In these cells the cathode utilization was 174 mAh/g at the 1 A rate due to less irreversible loss at the carbon anode. These prototype

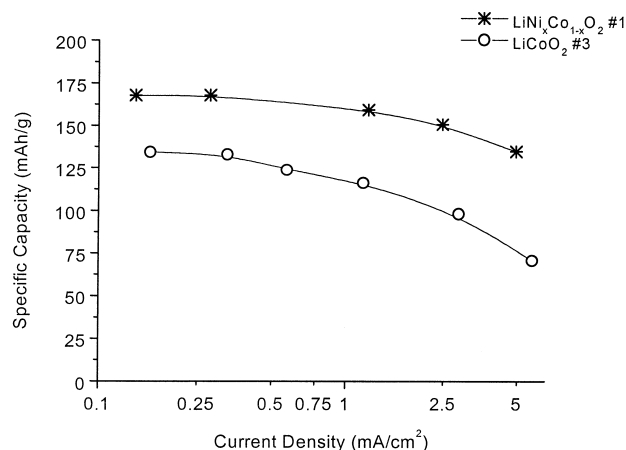


Fig. 4. Rate capability of two cells, one of which used $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ #1 and the other LiCoO_2 #3.

Table 2
The specific energy and energy density of the prototype '3 Ah' cells

Rate	Cell specific energy (Wh/kg)	Cell energy density (Wh/l)
1 A (0.2 C)	130	340
2 A (0.4 C)	125	326
5 A (C)	115	302
10 A (2 C)	100	262

'3 Ah' cells offered the specific energy and energy density described in Table 2.

4. Conclusions

A series of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ and LiCoO_2 have been characterized and evaluated. The $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ materials offer reversible specific capacity over 157 mAh/g, capacity fade as low as 0.014%/cycle and cells with the $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ materials offer rate capability comparable to cells with LiCoO_2 . The most energy dense materials

consisted of agglomerated small ($< 10 \mu\text{m}$) particles of small (0.5–1 μm) crystallites. Prismatic cells fabricated with the most energy dense $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ material evaluated offer 130 Wh/kg and 340 Wh/l.

Acknowledgements

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