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Development of high energy density Li-ion batteries based on $LiNi_{1-x-y}Co_xAl_yO_2$

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Abstract

Electrochemical characterisation of $LiNi_{1-x-y}Co_xAl_yO_2$ cathode material was conducted and a high reversible capacity of 184 mAh g^{-1} was obtained with good capacity retention. Evaluation of $LiNi_{1-x-y}Co_xAl_yO_2$ performance with a graphitic carbon anode was undertaken in several alternative high energy density Li-ion cell configurations. These included a D-size (33,600) cell design, a flat, "soft-packaged" 10 Ah cell design and a high capacity 75 Ah metal case cell design. Energy densities of 160, 150 and 130 W h kg^{-1} were achieved, respectively, for these cell designs. Further optimisation of these designs is envisaged to lead to projected energy densities, respectively, of 175, 180 and 150 W h kg^{-1}.

Keywords: Li-ion batteries; Graphitic carbon anode; Maccor or Bitrode systems

1. Introduction

$LiNi_{1-x}Co_xO_2$ [1] is an attractive choice of cathode material in Li-ion cells due to its cost advantages and increased capacity compared with $LiCoO_2$. In comparison with $LiNiO_2$, $LiNi_{1-x}Co_xO_2$ offers improved safety benefits due to an enhanced structural stability at higher temperatures and voltages. Different strategies were attempted to further stabilise the structure of these materials. Among these, doping with electrochemically inactive ions (such as non-transitional metals ions) has been reported to enhance the chemical stability [2–4]. In fact, the introduction of small amounts of metal dopants, such as Al, into the $LiNi_{1-x}Co_xO_2$ lattice has been reported [5] to improve cycle behaviour. Moreover, on the basis of the ab initio calculation Ceder et al. [6] have suggested that the substitution of transition metal ions by non-transition metal ions may increase the operating voltage due to an increased participation of oxygen in the electron exchange. Based on these considerations, we selected an aluminium doped $LiNi_{1-x-y}Co_xAl_yO_2$ which should be chemically more stable than the $LiNi_{1-x}Co_xO_2$ at a given x and should exhibit good safety properties.

The aim of this work is to evaluate the performance of $LiNi_{1-x-y}Co_xAl_yO_2$ with a graphitic carbon anode in different cell-size configurations, such as a D-size (33,600) cell design, a prismatic "soft-packaged" cell design and a high capacity cell design, targeted for various applications such as military, medical, lap-top computers and electric vehicles.

2. Experimental

The graphitic carbon and the $LiNi_{1-x-y}Co_xAl_yO_2$ were of commercial grade. Composite carbon anodes and composite $LiNi_{1-x-y}Co_xAl_yO_2$ cathodes using a polymer binder were fabricated using a pilot scale coating plant. A three-electrode cell was used to evaluate the performance of both the composite anode and cathode. A lithium wire and a lithium metal disc were used respectively as the reference and counter electrode. Two polyethylene circular discs of 12.8 mm diameter were used to separate each individual electrode. For this electrochemical test, the composite circular electrodes had a diameter of 12.46 mm. $LiPF_6$ dissolved in a mixture of organic carbonates was used as the electrolyte.

Cylindrical D-size cells using a graphitic carbon anode and a $LiNi_{1-x-y}Co_xAl_yO_2$ cathode and prismatic Li-ion cells with a similar pair of composite electrodes and both using a

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polyethylene separator were fabricated and the latter were packaged in laminated aluminium foil bags. Metal case cells were assembled from prismatic graphitic carbon anode — $LiNi_{1-x-y}Co_xAl_yO_2$ cathode Li-ion cells. A vacuum filling method was used to introduce the liquid electrolyte. The liquid electrolyte phase was introduced via a fill tube after the cell case had been welded closed. In all cases the cells were allowed to soak overnight prior to testing. An initial cycle was performed as a capacity check after which the cells were charged and aged for a minimum of 2 weeks before cycling was resumed.

All the electrochemical tests on the high capacity cells were conducted on Maccor or Bitrode systems while the half-cell test was carried out on a Macpile system (Bio-Logic, Claix, France) operating both in a potentiostatic and galvanostatic mode. In this test, the potential was measured with respect to the Li/Li^+ couple. All the measurements were carried out at 20°C.

3. Results and discussion

Fig. 1 shows the voltage-capacity plot of a composite $LiNi_{1-x-y}Co_xAl_yO_2$ cathode for the first cycle. The cell was cycled at a current density of 0.246 mA cm^{-2} between voltage limits of 3.0 and 4.2 V. A discharge capacity of 184 mAh g^{-1} was obtained on the first cycle with good capacity retention over the subsequent cycles. The same test was carried out on the composite anode and a reversible capacity of 340 mAh g^{-1} with good capacity retention was obtained (not shown).

To ensure that the larger capacity cells (see below) were well balanced, a three-electrode cell comprising of a composite graphitic carbon counter electrode, a composite $LiNi_{1-x-y}Co_xAl_yO_2$ working electrode and a lithium reference electrode was fabricated. The cell was cycled at a current density of 0.246 mA cm^{-2}, corresponding approximately to a 15 h charge, between voltage limits of 2.5 and 4.2 V. The results are depicted in Fig. 2. When the battery voltage reached a cut-off voltage of 4.2 V, the voltage of the positive electrode was 4.23 V while the negative electrode reached a value of 0.0329 V. These findings showed that the cell was well balanced since a low voltage 0.0329 V for the anode with respect to the reference is indicative of a fully lithiated anode. Moreover, the voltage of the positive electrode on discharge was 3.2 V with respect to the reference, which is indicative of a lithiated cathode.

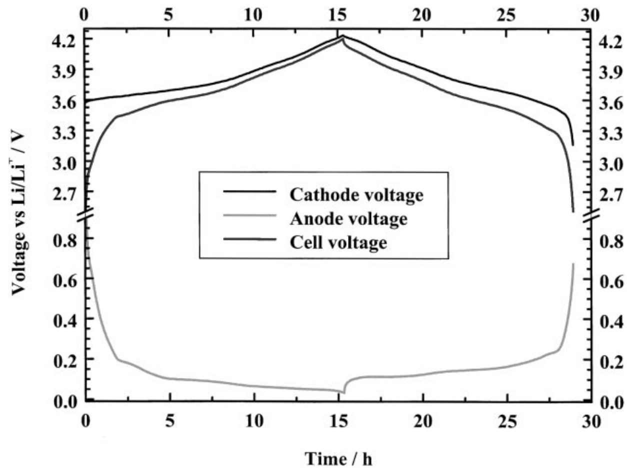

Fig. 2. Graphitic carbon — $LiNi_{1-x-y}Co_xAl_yO_2$ three-electrode cell showing voltage profile for each individual electrode; 20°C, cycle 1, 2.5–4.2 V, $I = 0.246$ mA cm^{-2} (15 h charge).

Different cell-size geometries using similar materials to those tested in the three-electrode cell were then fabricated and tested. Cells were cycled at *C*/5, with a lower voltage limit of 2.75 V and an upper voltage limit of 4.2 V. For instance, a 5 Ah D-size cell gave an energy density of 160 W h kg^{-1}. In addition, 100% of the rated capacity at *C* rate was obtained. Optimisation is in progress to further increase the energy density of the D-size cells and a

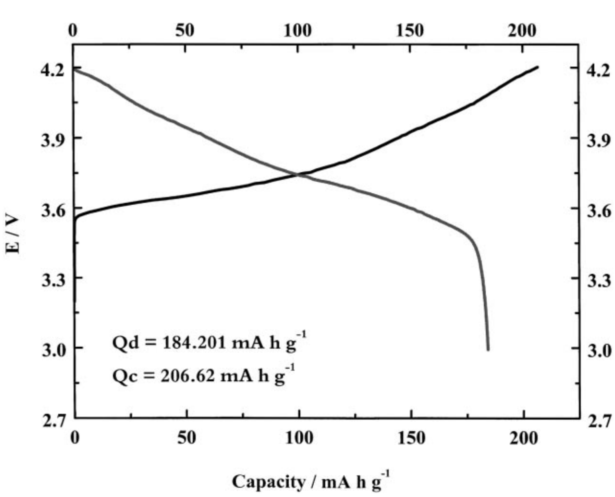

Fig. 1. Capacity of $LiNi_{1-x-y}Co_xAl_yO_2$ cathode material vs. lithium metal anode; 20°C, cycle 1, 3.0–4.2 V, $I = 0.246$ mA cm^{-2}.

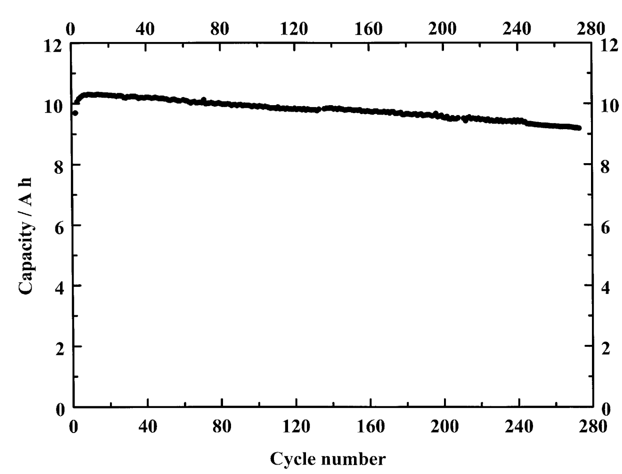

Fig. 3. *C*/5 cycle performance for 10 Ah graphitic carbon — $LiNi_{1-x-y}Co_xAl_yO_2$ Li-ion cell; 2.75–4.2 V.

projected energy density of 175 W h kg^{-1} for this cell-size is envisaged.

High energy densities of 150 W h kg^{-1} have been achieved for flat, ''soft-packaged'' 10 Ah Li-ion cells adopting a cell configuration of a $LiNi_{1-x-y}Co_xAl_yO_2$ cathode and a graphitic carbon anode. Such cells demonstrated encouraging cycle performance, as illustrated in Fig. 3.

Finally, a high capacity (75 Ah) prismatic graphitic carbon $LiNi_{1-x-y}Co_xAl_yO_2$ Li-ion metal case cell was constructed and tested and gave an energy density of 130 W h kg^{-1}. Further optimisation of the ''soft-packaged'' cell design as well as the metal case cell design is expected to lead to increased energy densities, projected to 180 and 150 W h kg^{-1}, respectively.

4. Conclusions

$LiNi_{1-x-y}Co_xAl_yO_2$ type cathode material demonstrates high reversible capacity (184 mAh g^{-1}) and stable cycle performance for application in a range of Li-ion batteries of high energy density. Such cathodes have been successfully employed in high capacity cells of different geometries. Energy densities of 160 W h kg^{-1} for a D-size cell, 150 W h kg^{-1} for a ''soft-packaged'' cell and 130 W h kg^{-1} for a metal case cell were readily achieved. Optimisation of these different cell configurations should lead to projected energy densities of 175 W h kg^{-1} for a D-size cell, 180 W h kg^{-1} for a ''soft-packaged'' cell and 150 W h kg^{-1} for a metal case cell.

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