SHORT COMMUNICATION

B.V.R. Chowdari · G.V. Subba Rao · S.Y. Chow

Cathodic performance of anatase (TiO$_2$)-coated Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$

Abstract We report the use of Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ coated with different amounts of anatase (TiO$_2$) as a cathode material for lithium-ion cells. Electrochemical behavior is modified owing to coating and/or incorporation of titanium into the first few surface layers of Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$. Compositions with molar concentrations of $x = 0.005$ and 0.02 exhibit better capacity retention than the mother compound (40 cycles, 0.5 C rate, 2.75–4.30 V).

Keywords Layered oxides · Cathodes · Oxide coating · Lithium ion batteries

Introduction

Lithium nickel cobalt oxides of formula Li(Ni$_{1-y}$Co$_y$)O$_2$ ($y = 0.1$–0.4) have attracted attention as prospective cathode materials for lithium ion secondary cells. The composition with a molar concentration of $x = 0.2$, i.e. Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$, shows an initial discharge capacity of 190 mAh/g (charge cut-off voltage at 4.3 V). The electrochemical cell with Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ as the cathode and lithium metal foil as the anode retained almost 75% of its capacity over 100 cycles when cycled galvanostatically at the 1 C rate [1]. Compositions with $x = 0.1$ and 0.2 are now commercially available. Efforts have been made to further improve the electrochemical behavior of Li(Ni$_{1-y}$Co$_y$)O$_2$, especially their thermal stability in the charged state. These efforts can be categorized into two major approaches. One is to substitute some of the transition metal ions with other element(s) such as aluminum [2, 3], magnesium [4, 5] or both titanium and magnesium [6]. The second method is surface modification by way of coating the oxide powders by a layer of material such as lithium borate glass [7], crystalline MgO [8, 9] or a complexing agent [7]. Significant improvement in high-voltage stability has been reported by coating LiCoO$_2$ with SnO$_2$ [10], diamond-like carbon (DLC) [11] or LiMn$_2$O$_4$ [12]. Similarly, improvements in the cathodic performance of LiMn$_2$O$_4$ by LiCoO$_2$ coating [13], LiCoO$_2$ by Al$_2$O$_3$ coating [14], LiNiO$_2$ by DLC coating [15] and LiMnO$_2$ by Al$_2$O$_3$ coating [16] have been reported. Presently, we modified the surface of Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ particles by coating it with titanium oxide (TiO$_2$). Different amounts of anatase-type TiO$_2$ were coated and the electrochemical properties of the coated materials are compared with the uncoated mother compound.

B.V.R. Chowdari (✉) · G.V. Subba Rao
Department of Physics,
National University of Singapore,
Singapore 119260, Singapore
E-mail: phychowd@nus.edu.sg

S.Y. Chow
Institute of Materials Research and Engineering (IMRE),
3 Research Link, Singapore 117602, Singapore

Experimental

Titanium(IV) isopropoxide (TIP) (Aldrich) and commercially available Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ (OMG) (average particle size, 10 µm) were used as starting materials. The preparation process was performed under an argon atmosphere in a glove bag. TIP in liquid form was mixed with isopropanol in the ratio 1:20 (v/v) by constant stirring. A known weight of Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ (LNCO) was then added to the solution. Three batches were prepared with the mole ratio, x, of TIP:LNCO equal to 0.005, 0.02 and 0.04. The mixtures were stirred vigorously for approximately 10 h to ensure homogenous contact between the particles of LNCO and TIP. Taken out from the glove bag, the mixtures were dried in air by evaporating the solvent with constant stirring. The powders obtained were further dried in an oven at 100 °C to remove traces of isopropanol and heated at 550 °C for 10 h in air. Blank runs with TIP (without LNCO) were also done to characterize the Ti hydroxide by DTA/TGA and the final product, TiO$_2$. Structure identification as well as lattice parameters were obtained from powder X-ray diffraction (XRD) patterns (Philips X'pert unit; Cu K$_\alpha$ radiation). Electrochemical measurements were performed using 2016 coin-type cells with a Li metal foil as anode, microporous polypropylene as separator and 1 M LiPF$_6$ in EC + DEC (1:1 v/v) (Merck) as electrolyte. Fabrication details have been reported earlier [3, 6]. The cells were cycled within a voltage window of 2.75–4.30 V using computerized multi-channel battery testing units (Bitrode, USA and

MacPile, France). All cells were first cycled galvanostatically at a relatively slow rate of 0.1 C (1 C = 140 mA/g). To test the stability under repetitive lithium insertion/extraction at a high current rate, the cells were charged and discharged initially at the 0.1 C rate for 5 cycles, followed by 5 cycles at 0.2 C and finally at 0.5 C for the next 40 cycles.

Results and discussion

It is well known that Mg methoxide and metal (M) isopropoxides (where M = Al, Sn or Ti) hydrolyse when exposed to air by interaction with water molecules [8, 9, 10, 14, 16, 17]. These hydroxide species can further react with isopropoxide to form polycondensates. Finally, these polycondensates react with water to form the metal hydroxide. These gel-type hydroxides are amorphous at temperatures < 100–150 °C, but crystallize when heated to high temperature. In the presence of LNCO particles, the polycondensates of TIP can react with the surface hydroxyl groups to form gel-type $Ti(OH)_4$ with good adhesion, covering the surface. In the present case, a blank run with TIP indicated that the white powder $[Ti(OH)_4]$ obtained by drying it at 80 °C is amorphous. DTA/TGA studies in the range 80–700 °C have shown that there is a continuous weight loss up to 206 °C and no further change until 700 °C. There is a 40% weight loss. An endothermic peak at 206 °C and a strong exothermic peak at 395 °C were noted. The 206 °C peak is due to dehydration of the amorphous hydroxide $[Ti(OH)_4 \rightarrow TiO_2 + 2H_2O]$ and also partly to the decomposition of the unhydrated TIP. The strong peak at 395 °C is due to crystallization of amorphous TiO_2 into the anatase form of TiO_2. Indeed, the XRD pattern of blank-run TiO_2 heated at 550 °C could be indexed as that of the anatase form, with less than 2% of the rutile form. Thus, we conclude that the Ti compound presently coated onto LNCO is anatase TiO_2. We noted that the black-colored LNCO turns slightly gray with increasing values of x.

XRD patterns of the mother compound, $Li(Ni_{0.8}Co_{0.2})O_2$ ($x = 0$), and those with $x = 0.005$, 0.02 and 0.04, indicated that the hexagonal layer structure is retained for all values of x. The values of the unit cell parameters for the mother compound ($x = 0$; $a = 2.87$ Å and $c = 14.13$ Å) agree well with those reported in the literature [1, 6]. No impurity lines due to anatase TiO_2 have been observed even for $x = 0.04$. However, there is a slight decrease in the a and c lattice parameters: while the a value decreased by 0.2–0.3% for all x, the c value decreased by 0.10, 0.14 and 0.65% for $x = 0.005$, 0.02 and 0.04, respectively. This indicates that heat treatment of TiO_2-coated LNCO samples at 550 °C, while retaining the hexagonal symmetry of the lattice, enables Ti^{4+} ions to become incorporated. However, this doping may occur only in the first few surface layers since the compounds were heat treated only at 550 °C. Indeed, careful examination of the XRD patterns shows broadening of the peaks, especially those assigned to (003), (101) and (104) for $x = 0.02$ and 0.04. Homogeneous incorporation

into the bulk of the lattice will require higher temperatures. Coating studies by Cho et al. [10] have shown that Sn^{4+} ions become incorporated into $LiCoO_2$ only up to a depth of 2 μm in particles with an average size of 14 μm up to heat treatment temperatures of ≤ 550 °C. The slight decrease in the hexagonal a and c parameters presently observed in TiO_2-coated LNCO can be due to the changing Li content in LNCO caused by Li-ion diffusion into the anatase TiO_2.

Galvanostatic charge-discharge curves have been recorded at a low current rate (0.1 C) in the voltage range 2.75–4.30 V to obtain the maximum possible recyclable capacities for various values of x. The profiles of the charging curves are shown in Fig. 1 and the data are given in Table 1. The curves overlap up to about 80 mAh/g [corresponding to $Li_{0.7}(Ni_{0.8}Co_{0.2})O_2$] and thereafter an increased slope for $x = 0.02$ and 0.04 and a decreased slope for $x = 0.005$ are shown. This implies that the voltage needed to de-intercalate Li from the lattice increases for $x = 0.02$ and 0.04 owing to
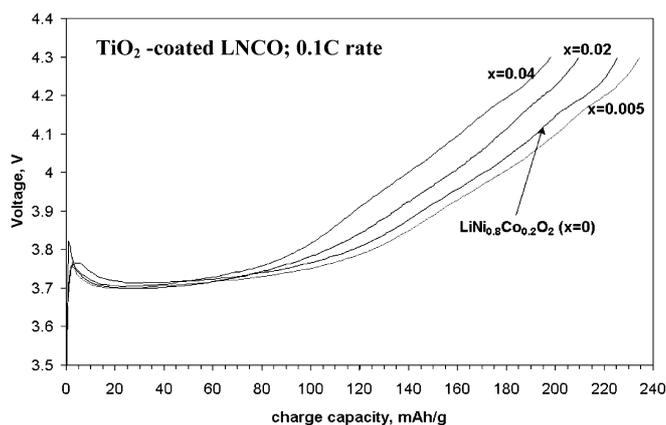
Fig. 1. Voltage profile of the first charge of TiO_2-coated $Li(Ni_{0.8}Co_{0.2})O_2$. Nominal mole ratios of TiO_2 (x) are indicated. Cut-off voltage: 4.30 V (versus Li)

Table 1. Charge and discharge capacities (mAh/g) of $Li(Ni_{0.8}Co_{0.2})O_2$ coated with TiO_2. Molar concentration (x) of TiO_2 is indicated. Theoretical values are shown in parentheses (see text)

Cathode material	$Li(Ni_{0.8}Co_{0.2})O_2$			
	$x = 0$	$x = 0.005$	$x = 0.02$	$x = 0.04$
First charge capacity (0.1 C rate)	225 (219)	234 (218)	209 (214)	198 (208)
First discharge capacity (0.1 C rate)	215	225	196	166
Irreversible capacity of first cycle	10	9	13	32
11th discharge capacity (0.5 C rate)	187	204	173	125
50th discharge capacity (0.5 C rate)	140	172	151	88
Capacity retention over 40 cycles (11th to 50th cycle, 0.5 C rate)	74.9%	84.3%	87.3%	70.4%

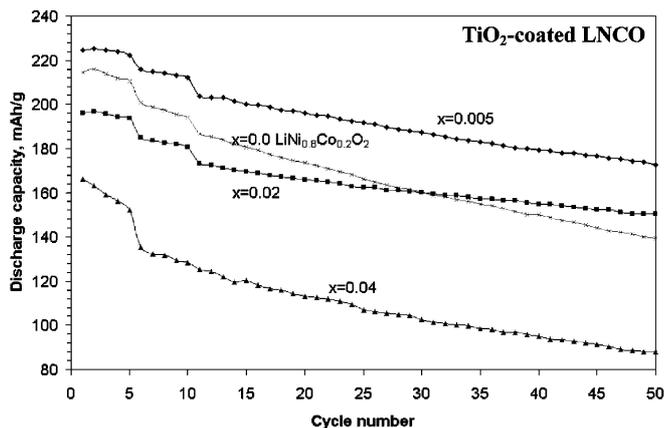**Fig. 2.** Discharge capacity versus cycle number for TiO_2-coated LNCO. Values of x are shown. Range: 2.75–4.30 V (see text)

coating/incorporation of titanium. As can be seen in Table 1, the first-charge capacity reaches 234 mAh/g for $x = 0.005$ and is more than that for $x = 0$ (mother compound). The theoretical capacities assuming only Ni^{3+} ions are participating in the charge-discharge process are also shown in Table 1. We note that Ti^{4+} ions, being electrochemically inactive, do not participate in the charging process. The higher than theoretical values noted for $x = 0$ and 0.005 indicate that some Co^{3+} ions also participate in the cycling process. However, this does not happen for $x = 0.02$ and 0.04, owing to the higher voltage needed to oxidize all the Ni^{3+} ions in the lattice (Fig. 1). The irreversible loss of capacity, which is the difference between the first charge and discharge capacities, are only 10 and 9 mAh/g for $x = 0$ and 0.005. These values are higher, i.e. 13 and 32 mAh/g for $x = 0.02$ and 0.04, respectively, indicating that some Ni^{2+} ions might have moved into the Li layer (cation mixing) during the heat treatment of TiO_2-coated LNCO samples at 550 °C. These ions, once oxidized to Ni^{3+} during charging, will not participate in the discharging process and also decrease the Li-ion mobility in the lattice [18].

Figure 2 shows the discharge capacity versus cycle number of the TiO_2-coated LNCO cathodes for various values of x. The cells were cycled at a rate of 0.1 C for the first 5 cycles, followed by a 0.2 C rate from the 6th to 10th cycles and at a rate of 0.5 C for the next 40 cycles in the voltage window 2.75–4.30 V. Capacity retention over 40 cycles (11th to 50th cycles) at the rate of 0.5 C is given in Table 1. As can be seen, the $x = 0.005$ and 0.02 compositions have superior capacity retention compared to the mother compound, $Li(Ni_{0.8}Co_{0.2})O_2$. At the end of the 50th cycle, 84.3 and 87.3% of the 11th cycle discharge capacity was retained for $x = 0.005$ and 0.02, respectively. The corresponding values for $Li(Ni_{0.8}$

$Co_{0.2})O_2$ for $x = 0$ and $x = 0.04$ are 74.9 and 70.4%, respectively.

The effect of surface coating and/or incorporation of some Ti ions into the surface layers of LNCO by anatase TiO_2 for $x = 0.005$ and 0.02 can be explained as due to the facile movement of Li ions through the anatase lattice and its behavior as a mixed (electronic + ionic) conductor when Li is intercalated. Indeed, Kavan et al. [19] reported that nanocrystalline anatase can act as a cathode material in the voltage window 1.5–2.4 V and can take up as much as 0.6Li in a reversible manner. This lower voltage window exhibited by TiO_2 compared to that of the mother compound LNCO greatly helps in increasing the charge-retention capability for $x = 0.005$ and 0.02.

To conclude, we have shown that anatase TiO_2-coated $Li(Ni_{0.8}Co_{0.2})O_2$ can be prepared and that, at molar concentrations of $x = 0.005$ and 0.02, these cathodes exhibit a better capacity retention (0.5 C rate, 2.75–4.30 V versus Li, 40 cycles).

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