Lithium ion batteries made of electrodes with 99 wt% active materials and 1 wt% carbon nanotubes without binder or metal foils

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Abstract

Herein, we propose lithium ion batteries (LIBs) without binder or metal foils, based on a three-dimensional carbon nanotube (CNT) current collector. Because metal foils occupy 20–30 wt% of conventional LIBs and the polymer binder has no electrical conductivity, replacing such non-capacitive materials is a valid approach for improving the energy and power density of LIBs. Adding only 1 wt% of few-wall CNTs to the active material enables flexible freestanding sheets to be fabricated by simple dispersion and filtration processes. Coin cell tests are conducted on full cells fabricated from a 99 wt% LiCoO₂-1 wt% CNT cathode and 99 wt% graphite-1 wt% CNT anode. Discharge capacities of 353 and 306 mAh g_{graphite}⁻¹ are obtained at charge–discharge rates of 37.2 and 372 mA g_{graphite}⁻¹, respectively, with a capacity retention of 65% at the 500th cycle. The suitability of the 1 wt% CNT-based composite electrodes for practical scale devices is demonstrated with laminate cells containing 50 × 50 mm² electrodes. Use of metal combs instead of metal foils enables charge–discharge operation of the laminate cell without considerable IR drop. Such electrodes will minimize the amount of metal and maximize the amount of active materials contained in LIBs.

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1. Introduction

To enable the wider use of lithium ion batteries (LIBs) in electric/hybrid vehicles and grid systems, great efforts have been made to increase their energy density with novel active materials, including high capacity anodes such as Si [1–5], high capacity cathodes such as S [6–9], and high voltage cathodes [10, 11]. Nanomaterials have been also extensively researched not only to activate low electrical conductivity or ion mobility materials but also to obtain higher power density [1–15]. Focusing on the electrode structure in conventional cells, which involves active material coated on metal foil with polymer binder and conductive additive, the replacement of such non-capacitive materials is another approach for improving energy density. The metal current collectors, i.e. Cu for the anode and Al for the cathode, make up 20–30 wt% of the composition of conventional lithium ion batteries [16], so a 1.3–1.4-times larger gravimetric capacity could be obtained by replacing them with lighter materials. “Carbon nanotube (CNT) three-dimensional (3D) current collectors” show promise for the replacement of heavy current collectors as well as polymer binders with a light-weight freestanding CNT network.

CNTs [5, 12–15, 17, 18], graphene [7, 12], and other hybrid carbon nanostructures [3–6, 8, 12] have been extensively investigated as electrode additives for conventional and novel active materials. Some carbon fiber additives have already been commercialized for the mechanical or electrical reinforcement of electrodes. Among these studies, some have developed binder free, freestanding electrodes composed of 3D CNT networks. For example, Luo et al. reported a freestanding cathode composed of 1–5 wt% CNTs and LiCoO_2 [13], and some groups used CNT freestanding sheets as lightweight non-metal current collectors [17–19]. However, many remaining challenges must be overcome before they can be applied to full-sized commercial batteries. To improve cell-base gravimetric/volumetric energy density, the electrodes should be prepared with suitable area and thickness, and areal/volumetric capacities

should also be improved. The cost of single-wall CNTs (SWCNTs), up to ~ 1000 USD g^{-1} , is a huge barrier to practical application. Multi-wall CNTs (~ 100 USD kg^{-1}) are now available for practical use, but their quality varies depending on their cost, so cost is still an issue for the further development of electrode performance. Additionally, the electrode and cell fabrication process must be simple and scalable. Finally, side reactions such as electrolyte decomposition accompanied by solid electrolyte interphase (SEI) formation may be enhanced on the large surface area of CNTs and/or catalyst metal nanoparticles remaining on them.

The authors have previously developed semi-continuous and batch production methods of sub-millimeter-long few-wall CNTs (FWCNTs) [20, 21] and SWCNTs [22], respectively, by fluidized bed chemical vapor deposition (FBCVD). The semi-continuous process realized a productivity of ~ 0.2 kg per L-reactor per day and a carbon yield of over 70% [20], which are similar with the commercialized MWCNTs. Although the FWCNTs are not commercialized yet, targeting at their future price of ~ 100 USD kg^{-1} , we have applied 3D networks of the CNTs to electrochemical devices [14, 15, 23–25]. The long and flexible SW/FWCNTs obtainable by these methods easily form 3D networks with submicron-sized pores and reasonable conductivity (~ 100 S cm^{-1}). 90 wt% activated carbon was captured in 10 wt% FWCNTs, and the resulting freestanding composite electrodes operated as electrochemical capacitors with fair in-plane conductivity, making them suitable as 3D current collectors [23, 24]. Pristine and surface-oxidized FWCNTs and their composites with active materials were also applied to LIB cathodes [14, 15] and pseudocapacitive electrodes [25].

In this work, we investigated the applicability of a “CNT 3D current collector” to the fabrication of lithium ion full cells without polymer binder nor metal foils. Both cathode and anode were prepared with only a minimum amount of CNTs and active materials; conventional LiCoO_2 and natural graphite were used as model electrodes. After basic coin cell tests with half cells and full cells, we fabricated laminate cells based on $50 \text{ mm} \times 50 \text{ mm}$ electrodes with and

without metal foils to demonstrate the operation of the proposed CNT 3D current collector in practical sized lithium ion batteries.

2. Experimental

2.1. Composite sheet preparation

LiCoO₂-CNT and graphite-CNT composite sheets were prepared by ultrasonication and filtration. FWCNTs prepared by FBCVD (11 nm in diameter, 370 μm long on average) [21] were added to 2-propanol (IPA, Wako Pure Chemical Industries, Osaka, Japan) at 0.02, 0.06, or 0.2 mg mL⁻¹ concentration and then dispersed for 30 min with a bath-type sonicator. Next, 2.0 mg/mL LiCoO₂ (0.5 μm average particle size, Toshima Manufacturing, Tokyo, Japan) or natural graphite (10 μm average particle size, SEC Carbon, Hyogo, Japan) powder was added, followed by dispersion for an additional 10 min and vacuum filtrating over polyvinylidene difluoride (PVDF) membrane filters (0.45 μm pore size) or cellulose filter papers (1–7 μm pore size, Advantec, Tokyo, Japan). The product was mechanically peeled off, vacuum dried at 100 °C for 1 h, and pressed at 50 kN for 30 s. The microstructure of the composite films was characterized by scanning electron microscopy (SEM; Hitachi S-4800, Tokyo, Japan), and their sheet conductivity was measured with the 4-probe method.

For comparison, conventional-type electrodes on 20- μm -thick metal foils were also prepared. For the cathode, 90 wt% LiCoO₂, 5 wt% PVDF (Sigma-Aldrich, St. Louis, MO), and 5 wt% acetylene black (AB, Denka, Tokyo, Japan) were mixed in N-methyl-2-pyrrolidone (NMP, Wako Pure Chemical Industries) and coated on Al foil. For the anode, 95 wt% graphite and 5% PVDF were mixed in NMP and coated on Cu foil. Each electrode was vacuum dried at 120 °C overnight and pressed at 50 kN for 30 s.

2.2. Coin cell assembly and electrochemical measurements

CR2032 type coin cells (Eager Corporation, Osaka, Japan) were fabricated to evaluate the performance of the electrodes as cathodes and anodes for LIBs. LiCoO₂/Li and graphite/Li half cells and LiCoO₂/graphite full cells were fabricated. For the half cells, an 8 mm ϕ working electrode, 15 mm ϕ HiporeTM (12 μ m thick, Asahi Kasei E-Materials, Tokyo, Japan) separator, and a 12-mm ϕ Li foil (500 μ m thick, Honjo Chemical, Osaka, Japan) counter/reference electrode were assembled with 1 M LiClO₄ (for the electrodes with LiCoO₂-CNT and/or graphite-CNT) or LiPF₆ (for the electrodes with LiCoO₂-PVDF-AB on Al and/or graphite-PVDF on Cu) in 1:1 v/v ethylene carbonate (EC) and diethyl carbonate (DEC) (Kishida Chemical, Osaka, Japan) as the electrolyte. For the full cells, an 8-mm ϕ cathode, 15-mm ϕ separator, and 8-mm ϕ anode were assembled with the electrolyte. The weights of the cathode and anode were adjusted to obtain a balanced capacity based on their theoretical capacities (LiCoO₂: 160 mAh g⁻¹ $\times$ 5.9 mg = 0.94 mAh, graphite: 372 mAh g⁻¹ $\times$ 2.4 mg = 0.89 mAh). Charge–discharge measurements were carried out on a charge–discharge unit (HJ1001SD8, Hokuto Denko, Tokyo, Japan) in constant current mode at 0.1C–10C and 25 °C. Here, x C rate corresponds to an applied current of 160 x mA g_{LiCoO₂}⁻¹ or 372 x mA g_{graphite}⁻¹ on the basis of the weight of the active material. Because the full cell was made of cathode and anode materials of balanced theoretical capacity, calculations based on cathode and anode weights give the same x C rate value. Cut off voltages were set at 3.0–4.2 V for the LiCoO₂/Li half cells and LiCoO₂/graphite full cells and 0.0–2.5 V for the graphite/Li half cells.

2.3. Laminate cell assembly and electrochemical measurements

Laminate cells with 50 mm $\times$ 50 mm electrodes were also fabricated with and without metal foils. Three types of current collector were prepared using 20- μ m-thick Al and Cu foils for the cathode and anode, respectively; with metal foils in full contact with the electrodes, comb structured foils (1-mm-wide wires spaced 10 mm apart) for partial contact with the

electrodes, and with 1-mm-wide wires sewn into one of the edges of the electrodes. The cells were fabricated with 1 M LiPF₆ in 1:1 v/v EC/DEC as the electrolyte and polyethylene/Al laminate film (Showa Denko, Tokyo, Japan) as packaging. Charge–discharge measurements were carried out using the same procedure as that used for the coin cells. The full cell was made with cathode at a slightly smaller load than that meeting the theoretical capacity of anode, and thus the x C rate was defined based on the cathode weight and corresponds to an applied current of $160x$ mA g_{LiCoO₂}⁻¹.

3. Results and discussion

3.1. Properties of LiCoO₂-CNT and graphite-CNT freestanding sheets

Fig. 1a and b shows photographs of 99 wt% LiCoO₂ (~11.3 mg cm⁻²)-1 wt% CNT and 99 wt% graphite (~4.6 mg cm⁻²)-1 wt% CNT composite sheets (80 mmφ) laid on a pair of tweezers. Each sheet was flexible, freestanding, and could be easily moved by hand without suffering damage. Freestanding sheets were formed at CNT contents ≥0.3 wt%, but the sheets with 0.3 wt% CNTs were too fragile, so a composition of 1 wt% or more CNTs was preferable for electrode use. Fig. 1c–f shows SEM images of the LiCoO₂-1 wt% CNT, graphite-1 wt% CNT, LiCoO₂-10 wt% CNT, and graphite-10 wt% CNT active material-CNT composite sheets, respectively. The CNTs formed a network that roughly surrounded the active material and maintained the sheet structure in the 1 wt% CNT sample whereas a large amount of CNTs covered each active material particle in the 10 wt% CNT sample. Note that such freestanding sheets can be made only with CNTs of small diameter (~10 nm or less), and cannot be made with CNTs or carbon fibers of larger diameter (~tens of nm or more) even at a high content of 10 wt%.

Fig. 1. (a, b) Photographs of LiCoO₂-1 wt% CNT (a) and graphite-1 wt% CNT (b) freestanding sheets (80 mm ϕ). (c-f) Cross sectional SEM images of LiCoO₂-1 wt% CNT (c), graphite-1 wt% CNT (d), LiCoO₂-10 wt% CNT (e) and graphite-10 wt% CNT (f) sheets. Insets show low magnification images.

Fig. 2a and b shows the thickness and packing density of pressed composite sheets with different CNT contents, respectively. Each sheet contained 11.3 mg cm⁻² LiCoO₂ or 4.6 mg cm⁻² graphite. The effective thicknesses of the active materials were calculated by dividing the areal mass by the real density of bulk LiCoO₂ (5.1 g cm⁻³) and graphite (2.2 g cm⁻³), and were 22 and 20 μ m, respectively. Note that the actual thickness was larger than the effective thickness owing to the pores present in the electrodes. The packing density of the LiCoO₂-1 wt% CNT sheet was 52%, while that of the graphite-1 wt% CNT sheet was 61% after pressing. The sheets were thicker when the CNT content was greater. With larger CNT content, the CNT network became more elastic and prevented the composite sheet from being compressed. The packing density of electrodes directly affects the volumetric energy density of the final battery, and should be at least 50 wt% for practical applications. Fig. 2c shows the sheet resistance and

Fig. 2d shows the volume resistivity of the composite sheets. The resistivity decreased as the CNT content was increased, but the LiCoO₂-1 wt% CNT sample still had a sufficiently low resistivity (sufficiently high conductivity), 79 mΩ cm, for it be useable as a lithium ion battery electrode.

Fig. 2. Properties of LiCoO₂-CNT (open red diamonds) and graphite-CNT (closed blue circles) sheets with different CNT weight ratio and 11.3 mg cm⁻² LiCoO₂ or 4.6 mg cm⁻² graphite: Thickness (a), packing density (b), sheet resistance (c), and volume resistivity (d). The error bars in (a) show the minimum and maximum thickness values for three measurement positions. The sheet resistance was very uniform for different positions (c).

3.2. Charge-discharge properties measured with coin cells

Fig. 3a shows the C-rate dependence of the charge-discharge capacity of the LiCoO₂/graphite full cell, graphite/Li half cell, and LiCoO₂/Li half cell with electrodes prepared with LiCoO₂ (11.3 mg cm⁻², effective thickness of 22 μm) or graphite (4.6 mg cm⁻² with 1 wt% CNTs, effective thickness of 20 μm). Charge-discharges were carried out at increasing C-rate

from 0.1C to 10C with two cycles for each C-rate, and the remaining cycles were carried out at 0.3C to check the stability of the cells after the series of tests (i.e., 0.1C for the 1st and 2nd cycles, 0.2C for the 3rd and 4th cycles, ..., 10C for the 47th and 48th cycles, and 0.3C for the remaining cycles). The discharge capacity at 0.1C was 353 mAh g_{graphite}⁻¹ for the full cell, 346 mAh g_{graphite}⁻¹ for the graphite/Li half cell, and 130 mAh g_{LiCoO₂}⁻¹ for the LiCoO₂/Li half cell, almost reaching the theoretical capacities. The first charge capacity exceeded the theoretical value because of the irreversible capacity originating from SEI formation. The capacity of the full cell at 1C was 306 mAh g_{graphite}⁻¹ and gradually decreased with increasing C-rate. In contrast, the capacity of the LiCoO₂/Li half cell dropped drastically at 2C, while that of the Li/graphite half cell decreased at even lower C-rate. The higher capacity of the full cell indicates a better rate performance of the LiCoO₂-CNT cathode and graphite-CNT anode in the full cell than with Li foil in the half cells, and that the capacity of the half-cells at high rates was limited by the rate performance of the Li foil counter electrode. Fairly high reversible capacities were obtained even at high rate with the freestanding electrodes containing 99 wt% LiCoO₂-1 wt% CNT and 99 wt% graphite-1 wt% CNT without the use of any polymer binders or additives. It is clear that the CNT 3D current collectors provided sufficient electrically conductive paths in the electrode even at a small content of 1 wt%.

Fig. 3b shows the average overvoltage, $\Delta V (= (V_{\text{charge}} - V_{\text{discharge}})/2)$ at each areal current density (converted from C-rate) during the charge–discharge of the full and half cells and a Li foil/Li foil symmetric cell on a single logarithmic scale. Here, V_{charge} and $V_{\text{discharge}}$ are the average charge voltage and discharge voltage, respectively. Each overvoltage value was determined from the charge–discharge voltage curve obtained at each C-rate as shown in Fig. 3c–e. At 0.1C and 0.3C, a number of plateaus and steps were clearly observed for the full cell and the graphite-CNT half cell, and a potential slope followed by a plateau was observed in the LiCoO₂-CNT half cell. The shapes of these charge–discharge curves were similar to those of conventional

cells [16, 26, 27]. In contrast, the plateaus were not clear in the 1C and 3C curves because of the high overvoltage. In each curve in Fig. 3b, the overvoltage increased monotonically with the current within a certain linear region. When polarization arises from a reaction activation barrier, i.e., negligible IR loss or ion diffusion effects, the overpotential curve can be fitted by the Tafel equation: $\Delta V = A \times \log (i/i_0)$. Note that the voltage drop by IR at 10C in the cathode in out-of-plane direction, estimated from its volume resistivity (79 m Ω cm), film dimension (8 mm ϕ , 42 μ m-thick), and applied current (8.6 mA), was 5.7 μ V, which had negligible contribution to the overall ΔV . In the case of the full cell, the linear region appeared from 0.5 to 1.7 mA cm⁻² (corresponding to 0.3C–0.9C) and the curve exceeded the line at higher current density. This suggests that the charge–discharge was reaction limited at under 0.9C and the effect of ion diffusion started to increase from 0.9C. Although the same conclusions could be drawn for the half cells, the overvoltage of Li foil was too large for the contribution of each working electrode to be observed clearly. This suggests that the reaction rate of the Li foil counter electrode was insufficient at high rate, so it was preferable to use full cells for the detailed discussion of electrode properties and cell performances.

Fig. 3. (a) C-rate dependence of the charge (●)-discharge (○) capacity of LiCoO₂/graphite full cell, graphite/Li half cell, and LiCoO₂/Li half cell with electrodes prepared by adding 1 wt% CNTs to 11.3 mg cm⁻² LiCoO₂ or 4.6 mg cm⁻² graphite (electrolyte: 1 M LiClO₄ in 1:1 v/v EC/DEC). (b) Average overvoltage of each cell and Li/Li symmetric cell at each areal current density. (c–e) Charge-discharge voltage curves of LiCoO₂/graphite full cell (c), graphite/Li half cell (d), and LiCoO₂/Li half cell (e).

The effect of CNT content on the performance of the full cells is discussed next. Fig. 4a shows the C-rate dependence of the charge–discharge capacity of LiCoO₂-CNT/graphite-CNT full cells with 1, 3, or 10 wt% CNTs in each electrode (LiCoO₂ = 11.3 mg cm⁻², graphite = 4.6 mg cm⁻²). The capacity at each C-rate of the cells with the 1 and 3 wt% CNT electrodes was similar, while that of the cell containing 10 wt% CNT electrodes was lower. Fig. 4b shows the charge–discharge voltage curves obtained at the first cycle. The difference between the charge and discharge capacities (i.e., irreversible capacity) at the first cycle was relatively high

for the 10 wt% CNT electrodes, and a large charge capacity of $\sim 100 \text{ mAh g}_{\text{graphite}}^{-1}$ was observed at 3.1–3.3 V. This result suggests the occurrence of side reactions such as SEI formation owing to the large surface area of the CNTs. Fig. 4c shows the overvoltage at each C-rate. Additionally, larger overvoltage was observed and the linear region (i.e., reaction limited) was not clear for the cell with 10 wt% CNT electrodes. This suggests that the SEI formed excessively on 10 wt% CNTs, possibly isolated significant fraction of active materials from electrolyte/conductive network, inhibited the charge–discharge reactions, and resulted in the small discharge capacity regardless of the C-rate. In contrast, the effect of side reactions was negligible when the CNT content was 3 wt% or less, and therefore it is important to add a low content CNTs for good battery performance.

Fig. 4. (a) C-rate dependence of the charge (closed symbols) and discharge (open symbols) capacities of LiCoO₂/graphite full cells with different CNT content (electrolyte: 1 M LiClO₄ in 1:1 v/v EC/DEC). Cathodes and anodes were prepared with 11.3 mg cm⁻² LiCoO₂ and 4.6 mg cm⁻² graphite, respectively. (b) Charge-discharge voltage curves of the first cycle (0.1C). (c) Average overvoltage at each C-rate.

The effect of different areal mass of active material and thus the electrode thickness on the performance of the full cell are discussed next. Fig. 5a shows the rate performance of full cells fabricated with 1 wt% CNT electrodes with LiCoO₂/graphite areal masses of 5.6/2.3,

11.3/4.6, and 28.4/10.5 mg cm⁻², respectively. The cell with thinner electrodes showed a higher gravimetric capacity than that with thicker electrodes, particularly at high C-rate. Ion diffusion between the cathode and anode through the electrolyte will limit the charge and discharge processes at high C-rate, especially when the electrodes are thick. This was also suggested by the larger overvoltage of the cell with the thickest electrodes, as shown in Fig. 5b. Commercial lithium ion batteries have electrodes of ~50-μm effective thickness, and the areal masses of 28.4/10.5 mg cm⁻² correspond to this effective thickness. Fig. 5c and d show the charge–discharge capacities and overvoltage at different C-rates of the full cells with conventional type electrodes; 5 wt% PVDF, 5 wt% AB and LiCoO₂ on Al foil for the cathode and 5 wt% PVDF and graphite on Cu foil for the anode. The cell with thin electrodes (11.3/4.6 mg cm⁻²) showed much lower capacities and higher overvoltage than those of the cell with equivalent 1 wt% CNT electrodes (Fig. 5a and b) owing to the inferior electrical conductivity of the electrodes. However, the cells with thick conventional electrodes (28.4/10.5 mg cm⁻²) showed similar performance to that of the equivalent 1 wt% CNT electrode cell because the charge–discharge processes were limited by ionic diffusion in the electrolyte. The overvoltage was similar and somewhat smaller for the thick conventional electrodes than the 1 wt% CNT ones (Fig. 5d). In filtrated films, CNTs and planar graphite particles align in parallel to the film surface (Fig. 1d), which may have increased the tortuosity and thus the overvoltage under the ionic diffusion limitation.

The 1 wt% CNT electrode-based cells showed higher capacity when the electrodes had an effective thickness of ~20 μm or less, but had similar capacity to that of the conventional cell when the electrodes were thick. Thus, to improve the power density of the cells, multilayer stack assemblies of thinner electrodes should be used. The thinning of electrodes causes a decrease in the cell-based gravimetric capacity of conventional electrodes because of the increased content of metal foil. Note that the cells with conventional type electrodes shown in

Fig. 5c contained 40 wt % metal at 28.4/10.5 mg cm⁻² active materials and 62 wt% at 11.3/ 4.6 mg cm⁻² active materials. This problem will finally be solved in the laminate cells (although the mass of separator will increase). Before discussing this, however, we next examine the cycle performance of the full cells at a high rate of 1C.

Fig. 5. (a) C-rate dependence of the charge (closed symbols) and discharge (open symbols) capacities of full cells made with 1 wt% CNT electrodes with different areal masses of LiCoO₂/graphite (electrolyte: 1 M LiClO₄ in 1:1 v/v EC/DEC). (b) Average overvoltage at each C-rate of the full cells in (a). (c) C-rate dependence of the charge (closed symbols) and discharge (open symbols) capacities of full cells with conventional type electrodes (cathode: 5 wt% PVDF, 5 wt% AB, and 90 wt% LiCoO₂ on Al foil, anode: 5 wt% PVDF and 95 wt% graphite on Cu foil) (electrolyte: 1 M LiPF₆ in 1:1 v/v EC/DEC). (d) Average overvoltage at each C-rate of the full cells in (c).

Fig. 6 shows the cycle performance of the full cells with 1 wt% CNT-based electrodes and with conventional electrodes at a high charge–discharge rate of 1C. With the conventional

electrodes, the discharge capacity dropped with increasing cycle number, because 1C charge–discharge is a severe operating condition for conventional electrodes owing to the side reactions caused by large overvoltage. Great efforts have been carried out to maintain capacity at high rate [28, 29], but a high stability of every component at high voltage, including binder, metal foil, and other additives, in the electrolyte is required. In contrast, the full cell with thin CNT-based electrodes showed a capacity drop as small as 6% after 100 cycles and retained a discharge capacity of 65% of that of the first cycle at the 500th cycle. The suppression of side reactions owing to the low CNT addition and low overvoltage owing to the good number of conductive paths formed by the CNTs might be the origins of this remarkable cycle stability. The freestanding electrodes with 1 wt% CNTs were therefore proven to effectively enhance the energy density, power density, and cycle stability of the full cells.

Fig. 6. Discharge capacity at fast charge-discharge at 1C of full cells with 1 wt% CNT-based electrodes (electrolyte: 1 M LiClO₄ in 1:1 v/v EC/DEC) and conventional electrodes (5 wt% PVDF, 5 wt% AB, and 90 wt% LiCoO₂ on Al foil and 5 wt% PVDF and graphite on Cu foil) (electrolyte: 1 M LiPF₆ in 1:1 v/v EC/DEC). Charge–discharge was conducted at 0.1C for the first cycle and 1C for the later cycles.

3.3. Laminate cells with and without metal foils

The freestanding electrodes formed of 1 wt% CNT and 99 wt% active material had rather small resistivity (79 mΩ cm as cathode and 5.4 mΩ cm as anode), indicating that the

CNT network could provide conducive paths not only in the vertical direction from the active material to the current collector but also in the in-plane direction (parallel to the electrode sheet). Thus, it was thought that the CNT-based electrodes may work with only partial contact with metal combs or wires, which have much smaller mass than the foils. To examine the effect of metal leads of different shapes (i.e., foils, combs, and lines), we fabricated laminate cells with 50 mm $\times$ 50 mm square electrode sheets.

Fig. 7a–c shows cells assembled from Cu/ graphite-1 wt% CNT/ separator (HiporeTM)/ LiCoO₂-1 wt% CNT/ Al with (a) foils, (b) combs, and (c) lines of Cu and Al and Fig. 7d–f shows the schematics of the cell assemblies. Each cathode contained 223 mg LiCoO₂, corresponding to 36 mAh theoretical capacity, and each anode contained 112 mg graphite, corresponding to 43 mAh theoretical capacity. During the electrode fabrication via vacuum filtration, some fraction of the LiCoO₂ passed through and became trapped inside the filter paper, resulting in a somewhat smaller theoretical capacity of the cathode than the anode in the laminate cells. Fig. 7g shows the charge and discharge capacities of the cells at different charge–discharge rates, and Fig. 7h shows the charge–discharge curve at the second cycle (0.1C) of each cell. The cell with comb-shaped collectors exhibited somewhat better rate performance than and similar cycle performance to that with full contact metal foils. The cell with a line-shaped collector on one edge showed reversible charge–discharge at 0.1C, but not at 0.3C or higher rates (Fig. 7g). The overvoltage of the cells with metal foils and combs was comparable, while that with the single line collector was much larger (Fig. 7h).

Fig. 7. (a–c) Laminate cell assemblies of Cu/ graphite-1 wt% CNT/ separator/ LiCoO₂-1 wt% CNT/ Al with: (a) Metal foils in full contact with the electrodes, (b) metal combs (1-mm-wide wires with 10-mm-wide spaces) in partial contact with the electrodes, and 1-mm-wide wire sewn into one of the edges of the electrodes (c) (electrolyte: 1 M LiPF₆ in 1:1 v/v EC/DEC). (d–f) Schematics of the cell assemblies in (a–c). (g) Charge–discharge capacities of the cells at 0.1C, 0.3C, 0.5C, 1C, 3C, 5C, 10C, and 0.3C. (h) Charge–discharge curve at the second cycle (0.1C).

These results show that the electron transfer length in the CNT 3D network without considerable IR drop was no less than 5 mm. Because the resistivity of the LiCoO₂-1 wt% CNT

freestanding film was 79 m Ω cm, there was an upper limit to the electron transfer length of the CNT network. In fact, the metals have a resistivity several orders of magnitude lower (1.7 $\mu\Omega$ cm for Cu and 2.3 $\mu\Omega$ cm for Al) than that of the LiCoO₂-CNT composite, which creates a tradeoff between the weight proportion of active material and the conductivity of the electrode. To solve that tradeoff, the combination of CNT 3D current collector and metal wires with certain pitch as shown in Fig. 7b is most effective, in which the CNT network works as local streets and the metal wires work as highways. In the present case, using metal combs in place of the full size foils reduced the metal content by 86%, but it could be further reduced using thinner metal wires. If the collector is fabricated with 20 $\mu\text{m}\phi$ metal wires with 10 mm pitch, the weight of the metal decreases to 0.31% of the 10 μm -thick foil, and the metal content would be less than 0.1 wt% of the total cell without a considerable IR drop. Additionally, when the electron transfer length in the CNTs is too long, the IR drop can cause an in-plane potential gradient in the electrode. Such potential gradient can produce a local overcharge that causes failure of the electrode with current control or insufficient local charge/discharge with voltage control. So, the combination of CNT 3D collector and metal wires is necessary when considering cycle stability, safety and performance.

For the future development of energy storage technology, the present binder free, metal foil free cells based on CNT 3D collectors will be beneficial for secondary batteries with novel active materials. High capacity materials such as Si or S are less conductive and have shorter cycle lifetime owing to their large volume change. Flexible networks of soft CNTs will hold such materials together while providing good conductive pathways and reduce the stress created by volume changes. Another approach for improving energy density is increasing the battery voltage by using 4.5- or 5-V class cathode materials, but the degradation of the binder, electrolyte, and current collector is a problem. Some of the salt in the electrolyte causes the corrosion of Al. Simplified battery components to only CNTs and active materials will provide

more choices for electrolytes. More stable but heavier metals such as stainless steel will be made available if the full sized metal foil is replaced by metal wires of much smaller weight.

4. Conclusions

Binder free, metal foil free LIBs were proposed and demonstrated using electrodes based on “1 wt% CNT 3D current collectors”. Flexible freestanding electrodes were fabricated by adding only 1 wt% FWCNTs to the active material particles. Owing to the flexibility and conductivity of the small diameter FWCNTs, their 3D network wrapped the 99 wt% active material in reasonably conductive paths. In a series of coin cell tests using LiCoO₂/graphite full cells, electrodes containing 1 wt% CNTs not only showed fine performance in LIBs but also exhibited positive effects on both rate performance and cycle stability. A discharge capacity of 353 mAh g_{graphite}⁻¹ based on the anode weight at 0.1C and 306 mAh g_{graphite}⁻¹ at 1C were achieved with a capacity retention of 65% even at the 500th cycle. A CNT content of ~1 wt% is preferable because excess CNTs (i.e., 10 wt%) cause additional side reactions because of their large surface area. Thinner electrodes are required to improve the rate performance, and the present metal foil free electrodes have great advantages in reducing the electrode thickness without significant loss in the weight fraction of active material in the total cell. Laminate cells with 50 × 50 mm² electrodes were fabricated to apply the freestanding electrodes to a practical size, and to demonstrate the performance of 1 wt% CNT 3D network in carrying current in the in-plane direction. The cell with a comb-shaped metal current collector with 10 mm-wide spaces showed good rate performance and cycle stability, whereas that with a metal line at one of the electrode edges did not charge and discharge electricity at 0.3C. Thus, the combination of CNT 3D current corrector and metal wires with centimeter-scale spacing were found to effectively improve the cell-base gravimetric energy density while avoiding resistivity-based power loss. The present 1 wt% CNT-based freestanding electrodes will not only improve the

performance of commercial LIBs but will aid the development of the next generation energy storage devices with novel active materials.

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active material +
binder +
conductive filler
on metal foil

Conventional

active material +
1 wt% CNT

This work

cathode

anode

Laminate cell w/o metal foil