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Open-ended N-doped Carbon Nanotubes Array for Li-ion Battery Anode

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Abstract -Carbon nanotubes have been considered as promising candidate for anode materials of lithium ion batteries. Despite of superior electrical conductivity, the lithium ion capacity of CNTs is limited due to the closed tubular structure, restricting the use of inner surface and space as well as intercalation of lithium ion between CNT walls. Here, we present open-ended NCNT arrays maximizing the lithium ion capacity of CNT based materials. Reactive ion etching can selectively etch out the closed-tip of typical CNT arrays and enables to utilize the hidden inner surface and space for lithium ion storage. The resultant opened tubular structure shows improved the lithium ion capacity as much as 1.7 times, compared to closed-tubular structure.

***Keywords*:** Carbon nanotubes, electrode, Li-ion Battery

1. Introduction

Lithium-ion batteries (LIBs) have been successful in powering a variety of portable electronic devices in virtue of their high energy densities and reasonably long lifetime. Nevertheless, emerging large-scale applications represented by hybrid electrical vehicles (EVs) (Lu et al. 2013), stationary grid energy storage systems (Dunn et al. 2011), and advanced portable electronics (Scrosati et al. 2011) are imposing more challenging standards with regard to various cell aspects. In particular, the simultaneous increase in the energy density and cycle life are a crucial requirement for those new LIB applications. Nanostructured materials provide a potential solution to aforementioned problem. Due to their nanoscale dimensions and greatly increased surface area compared to conventional electrodes, increased energy storage capacities and rate capabilities are possible through much faster interfacial and solid-state diffusion kinetics. Typical example of nanostructured materials are actively being explored for both the negative and positive battery electrodes. (Chan et al. 2008). Along with tradition graphite and above materials as negative electrodes, recently, carbon nanotubes (CNTs) have also gained great interest (Che et al. 1998, Landi et al. 2009). Although CNTs and other anode nanomaterials have been shown to exhibit similar or greater capacities compared to the commercial lithium-ion battery standard of graphite (maximum theoretical capacity of 372 mAh/g), they do not improve on graphite’s moderate rate capability. Studies suggest that aligned CNTs could allow for better contact with the current collector and increased ion diffusivity to significantly improve bulk electron transport properties thereby allowing for improved rate capabilities (Lee et al. 2010). However, relatively low capacities at low discharge rates were observed due to poor electron transport resulting from of poor contact with current collectors and limited lithium ion storage capability arisen from closed-tips at the top of CNTs. In this study, we present the characteristics and capacitive behaviour of NCNT array before and after end-cap opening. To characterize effective lithium-ion storage of open-ended NCNT array, various analysis of SEM, TEM and XPS were carried out. The reversible capacities of open-ended NCNT array was 1080 mAh/g which is more than 2 times higher than that of NCNT array we measured (420 mAh/g) and it was remained to be 432 mAh/g which is still higher than NCNT array (251 mAh/g) after 50 cycles. The results suggest that end-cap opening utilizes lithium storage site inside the tubes which was blocked by end-cap.

2. Experimental

Fig.1 briefly illustrates the procedure for synthesis of open-ended NCNT arrays. Graphene oxide (GO) suspension prepared by Hummer's method was drop-casted on the SiO_2/Si substrate for thin film formation. Iron nanoparticles, which are catalyst for CNT growth, were formed by evaporation process with cylinder type PS-*b*-PMMA block copolymer template (Lee et al. 2009). After the growth of nitrogen doped CNTs (NCNTs) with ammonia gas (NH_3), the tip of each CNT was opened by controlled CF_4 reactive ion etching (RIE) process. The open-ended NCNT arrays on reduced graphene oxide (rGO) were transferred from SiO_2/Si onto copper current collector by selective removing the SiO_2 layer with diluted HF solution. The assembled Li ion battery cell was evaluated compared to the cell with closed-ended NCNT.

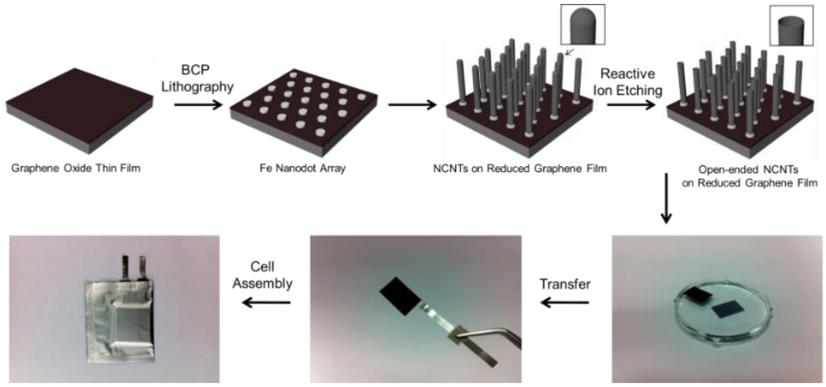

Fig. 1. Schematic illustration of synthesis of open-ended N-doped CNTs and assembly of Li ion battery half cell

2. Results and Discussion

Open-ended NCNT arrays are investigated by SEM and TEM measurement as shown in Fig 2. (a)-(d). The vertically aligned structure of NCNT arrays is maintained after opening the closed tip by RIE etching process (Fig. 2.a). Fig 2.b clearly shows the damaged tip part of NCNTs by CF_4 RIE etching process. Notably, the tip part of NCNT is selectively etched out with negligible damages on the NCNT walls (Fig. 2.d). The asymmetrical etching property of RIE process facilitates selective etching of the exposed tip part of NCNT arrays to reactive plasma. Furthermore, the curvature of the closed tip is chemically more reactive than the wall part due to the existence of a pentagon and a heptagon, which could lower the activation energy toward etching reaction(Zhang et al. 2003). Chemical structure of typical open-ended materials was characterized by X-ray photoelectron spectroscopy (XPS).

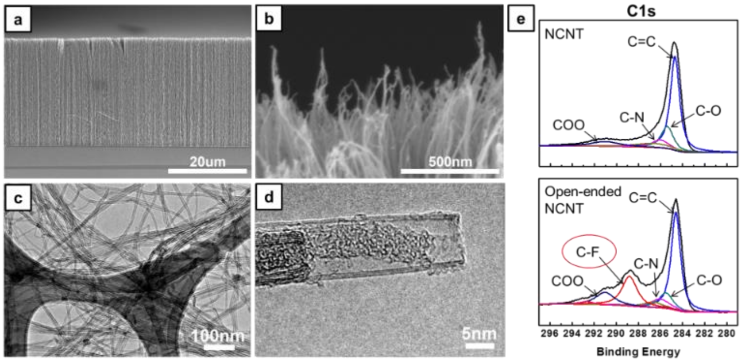

Fig. 2. SEM and TEM images of open-ended NCNT (a-d) and C1s XPS spectrum of resultant open-ended NCNTs

Deconvoluted C1s XPS spectrum (Fig. 2.e) shows the five peak for graphitic structure (C-C/C=C, 284.6 eV), carbon-nitrogen covalent bond (C-N, 286 eV), hydroxyl/epoxy groups (C-O, 285.5 eV), carboxyl group (O-C=O, 291 eV) and C-F (287.8 eV) bond, respectively. Appearance of the peaks for C-F bond in C1s XPS spectra demonstrates fluorine ion in the plasma could react with carbon atom and remove the carbon atom from the NCNT body. The opening of the closed tip part makes the inner area of NCNT accessible and enables us to utilize the hidden inner surface and space.

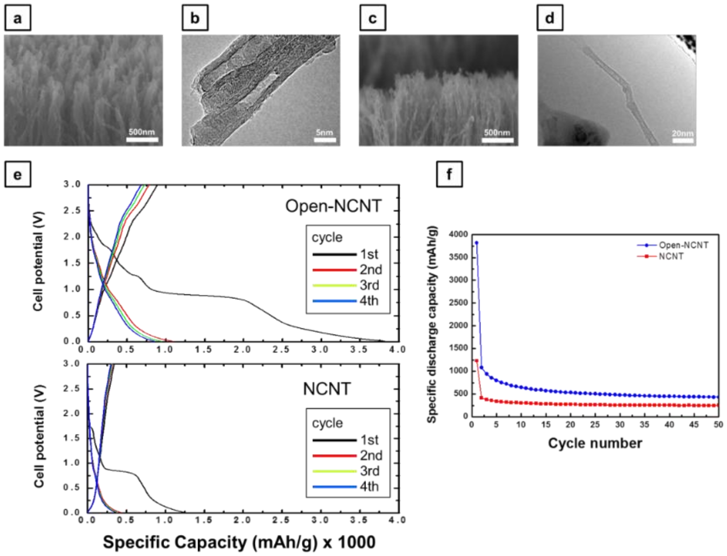

Fig. 3. TEM images of lithiation and delithiation state of open-ended NCNT arrys and electrochemical characterization of NCNT arrays and open-ended NCNT arrays.

We investigated the Li ion storage behaviour of the open-ended NCNT arrays during lithiation and delithiation reaction with TEM analysis. Fig. 3.a and b shows TEM and SEM images of the lithiation state of the open-ended NCNT arrays. It is well known that CNT based anode material mainly store the Li ions on its surface due to the closed tubular structure of CNTs(Shin et al. 2012). The closed structure restricts the Li ions to access to the inner surface and consequently the total Li ion capacity of typical CNT anode materials is limited. In case of open-ended NCNT arrays, the inner surface and space is accessible for Li ions through the passageway of opened tip part. In delithiation reaction, the stored Li ions was released into electrolyte as shown in Fig. 3.c and d

The electrochemical performances of the three electrodes were characterized in pouch-type half-cells. Galvanostatic mode was employed in the potential rage of 0.01–3.0 V (*versus* Li^+/Li) in $LipF_6$/DMC electrolyte. Lithium foil was used for reference and counter electrodes simultaneously. The working electrode consists of open-ended NCNT arrays on copper foil without any addictive and binder. The electrochemical performance of closed-tip NCNT arrays was comparatively tested to confirm the effectiveness of open-ended NCNTs. Fig 2.e shows potential profiles during the first to fourth cycles measured at a current density of 100 mA g^{-1}. As shown in Fig. 3.e, closed-tip NCNT and open-ended NCNT shows high capacity of 1,250 mAh/g and 3,800 mAh/g, respectively. Unfortunately, this high level capacity is not reproducible from second charge/discharge cycle, decreasing to 420 mAh/g and 1080 mAh/g, respectively. It is due to irreversible electrochemical reaction stemming from formation of solid-electrolyte interfaces (SEI) layer, which can be mainly formed at the defect site on the surface of carbon nanomaterials, such as edges (Xu, 2004). Appearance of the characteristic plateaus at 1.2 V and 0.8 V in the first cycle is closely related to the development of SEI layer on the carbon nanomaterials (Xu, 2004). Tthe plateau region for the SEI layer formation is proportional to the porosity of carbon nanomaterials (Fong et al. 1990). It is consistent with that open-ended NCNT shows longer plateau region that that of close-end NCNT due to enhancement of surface area. After 50 cycles, the open-ended NCNT shows 1.7 times higher Li ion capacity value (432 mAh/g) that of a closed-tip NCNT (251mAh/g) as shown in Fig. 3.f.

3. Conclusion

We have demonstrated open-ended NCNT arrays as anode materials for Li-ion battery facilitating high capacity beyond typical carbon nanotube based anode materials. The open-ended NCNT array was achieved by etching out the closed-tip of conventional NCNT arrays using reactive ion etching process with CF_4 gas. The opened tubular nanostructure allows Li ions to have access to the inner surface and space to be stored. It led to increase of Li ion capacity from 251 mAh/g to 432 mAh/g. The utilization of the inner surface and space of CNTs could be a useful and practical strategy to further improve device performance in diverse application, such as energy storage devices, catalysis, chemical synthesis in nanoreactor and so on.

Acknowledgements

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