An Effective Nitrogen Doping Technique for Improving the Performance of Lithium Ion Batteries with CNT Based Electrodes

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ABSTRACT

Lithium ion batteries are among the most used rechargeable batteries in the world. Carbon nanostructures including carbon nanotubes (CNTs) are considered as important electrode materials for this kind of batteries. Therefore improving the performance of these carbon based electrodes in Lithium ion batteries is an important issue and attracts much attention in the battery community. In this manuscript, a new method for high content Nitrogen doping on CNTs is reported as an efficient approach for enhancing the battery performance. Direct current-plasma enhanced chemical vapor deposition (DC-PECVD) system was used for nitrogen doping. Annealing with Nitrogen during CNT growth and plasma exposure after the growth has been used for Nitrogen doping of the CNTs. The growth was performed on an Indium Tin oxide (ITO) covered Silicon substrate. Implementation of Silicon substrate enables the possibility of future integration of other electronic circuits with the fabricated Lithium ion battery. Vertically aligned CNTs with an average diameter of around 150 nm and 4 um height has been obtained on this substrate. The synthesized CNTs was subsequently used as the electrode of Lithium ion battery in a half cell configuration. The results show a significant improvement of about 400% in the specific capacity of the battery as a result of Nitrogen doping. For Nitrogen doped CNT based battery, specific capacity of around 0.4 mAh/cm2 and coulombic efficiency of 97% were achieved after 28 cycles of charge/discharge with C rate of 2.5. This Nitrogen doping method is propped as an efficient technique for enhancing the performance of Lithium ion batteries with carbon based electrodes.

Keywords: Nitrogen doping, CNT, Li ion battery, Capacity, Anode electrode.

1. Introduction

CNTs are carbon based nanostructured that have been used in variety of applications due to their excellent characteristics such as good electrical conductivity, mechanical strength and electrochemical stability [1-4]. Especially for electrochemical energy storage devices, there are numerous reports on using CNTs as the electrode or for enhancing the overall performance of devices [5-12]. Today, Li ion batteries are among the most important energy storage devices in the world. They are used in many different applications from portable electronics to electrical and hybrid vehicles [13-15]. CNTs can serve as one of the potential anode materials for this kind of batteries [16-23]. Growing CNTs on Silicon wafer and then using the grown CNTs as the active anode material has the considerable advantage of the possibility to integrate other necessary devices on the same silicon wafer. However, some challenges exist in order to achieve this purpose [24-28]. The main challenge in using CNTs on a silicon wafer as the

Lithium ion battery anode is that Lithium insertion and extraction into the Silicon substrate (which occurs during the charge and discharge processes of the battery operation) results in cracking of the surface of Silicon wafer and as a result, CNTs detach from the surface [29]. For solving this problem, a proper barrier layer should be used between the CNTs as the active material and the Silicon substrate [30].

Nitrogen doping has been used extensively for improving the performance of CNT based Lithium ion batteries [31-39]. This technique enhances the electrode effective area through introducing defects in the CNTs [40-42]. Recently we have developed a nitrogen doping method that efficiently improves the supercapacitance performance of CNTs [43]. In this manuscript the effect of this Nitrogen doping has been investigated on the performance of CNTs in Lithium ion batteries. Silicon has been used as the substrate for CNT growth, and to minimize the problem of introducing the Silicon wafer to Lithium ions, we have used an appropriate barrier layer between the silicon wafer and CNTs. This makes possible both the proper growth of CNTs, and implementing the grown CNTs on the Silicon wafer as a Lithium ion battery anode. An ITO thin layer with thickness of 300 nm was used as the barrier layer, which was deposited using a RF sputtering system. DC-PECVD system was used for Nitrogen doping of the CNTs on this ITO coated Silicon wafer. The results show that this N-doping approach was really effective on the battery storage capacity so that considerable increase in the specific capacity of the battery is achieved. Scanning electron microscopy (SEM), tunneling electron

microscopy (TEM) and charge/discharge analyses have been performed to characterize the sample.

2. Materials and Methods

P type silicon wafer was used for this experiment. First the surface of the sample was cleaned using RCA#1 solution. The schematic of Nitrogen doped CNT growth process is depicted in Fig. 1 (a) to (d). As can be seen in part (a) of this figure, an ITO barrier layer was deposited on the surface of the silicon substrate using a RF sputtering system (f=13.56 MHz) to serve as a barrier layer. The thickness of this layer was about 300 nm. Next, using an electron beam evaporation system, a 9 nm Ni layer was deposited on the ITO layer as the catalyst for growth of CNTs (Fig. 1(b)).

CNT growth and nitrogen doping was performed as we reported before [20]. Briefly DC Plasma Enhanced Chemical Vapor Deposition (DC-PECVD) system was used for CNT growth. Upon heating to 680 °C under a hydrogen atmosphere, the Ni film was annealed. The hydrogen flow rate during the annealing process was set to 15 sccm. After one hour of annealing, hydrogen plasma with dc bias of 500 V and current of 30 mA was applied for 5 minutes. As a result, the Ni catalyst layer was activated and Ni nanoparticle islands were formed, which is depicted in Fig. 1 (c). After formation of Nickel Islands, nitrogen with the gas flow of 10 sccm is introduced into the chamber instead of hydrogen. Then, C_2H_2 gas with the flow rate of 6 sccm was added to the chamber. In this stage, The DC plasma voltage was set to 600 V for 10 minutes. In the next step, the synthesized CNTs was exposed to the nitrogen plasma in the DC-PECVD system.
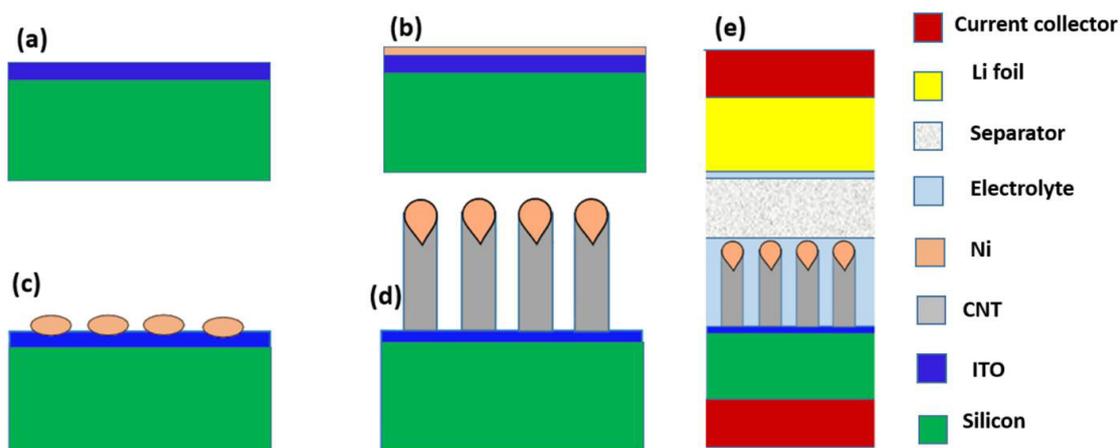

Fig. 1- Schematic presentation of CNT growth and Lithium ion battery components. (a) ITO coated Silicon substrate. (b) Nickel deposition on the substrate. (c) Forming Nickel islands, (d) Growth of CNTs and (e) Fabrication of Lithium ion battery.

The post nitrogen plasma treatment was performed with 10 sccm flow rate of nitrogen, using a power density of 0.4 W cm-2 for 10 min at 680 °C (Fig. 1(d)). At the end of the growth period, samples were slowly cooled within the furnace.

For Lithium ion battery tests, half-cell was assembled, using a home-made Swagelok-type cell. The assembly and testing of the battery was performed in an argon filled glove box, using 99.999% purity Argon. The synthesized CNTs was used as one of the electrodes while Lithium was used as the other electrode of the battery. Also, a separator layer immersed in the electrolyte was placed between the two electrodes to isolate them from each other. LiPF6 1M in (Ethylene carbonate/ Dimethyl carbonate) solution was used as the electrolyte of the battery. The schematic of Lithium

ion battery components can be seen in Fig. 1(e). The charge and discharge cycling were accomplished by a battery tester (Kimiastat 126).

3. Results and Discussions

SEM image of Nitrogen doped CNTs can be seen in part (a) of Fig. 2. The vertical nature and long range order of the CNTs are evident in this image. In addition, TEM images of the synthesized N-doped CNTs is depicted in Fig. 2 (b). Defects are obviously detected in the wall of this CNT. For comparison, TEM of bare CNT sample is also shown in part (c) of Fig. 2.

XPS result for the Nitrogen doped and bare CNT sample is shown in Fig. S3 of the supporting information file. From this analysis, the amount of Nitrogen in the Nitrogen doped sample is estimated
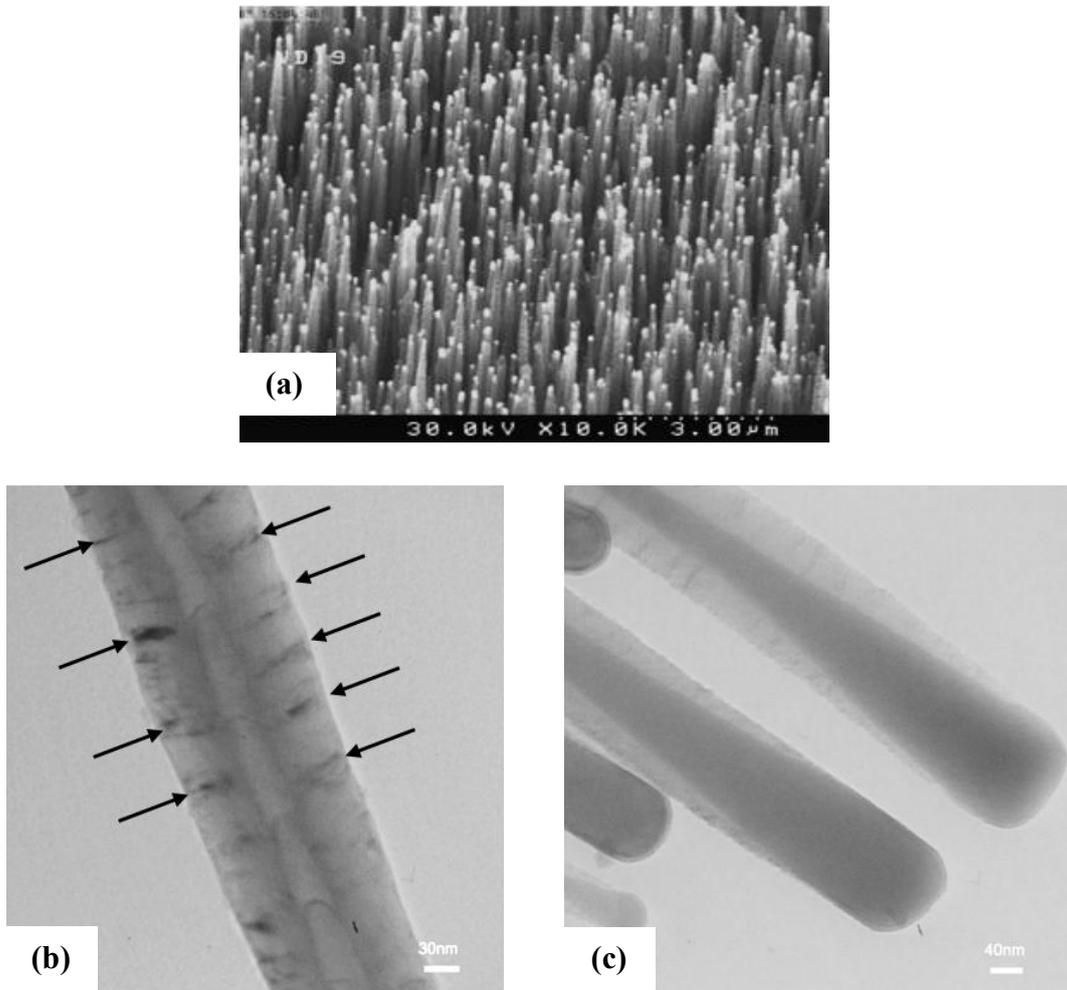

Fig. 2- (a)SEM and (b) TEM image of Nitrogen doped CNTs. (c) TEM image of bare CNTs without N-doping.

to be in the order of 14.82 at. %.

The synthesized N-doped CNTs has be exploit as the Li ion battery electrode, as depicted earlier in Fig. 1 (e). The results of this test are collected in Fig. 3. Part (a) of this figure, shows the specific capacity of the battery with current of 100 uA (equivalent to C-rate of 2.5 C) in the potential window of 50 mV - 3V, for 28 cycles. As can be seen in this diagram, the specific capacity of the battery in its first cycles are around 0.4 mAh/cm^2 and finally it reaches 0.3 mAh/cm^2 at last cycles. Coulombic efficiency of the sample is depicted in part (b) of this figure. The results show a coulombic efficiency of 65% at its first cycle that gradually reaches the value of 97% at the end of the test. Coulumbic efficiency is defined as $Q_{dis-charge}/Q_{charge}$. Although in Fig. 3 (a), the battery capacity has a decaying behavior, but with increasing the cycle number, this performance is becoming more stable and the

amount of irreversible reactions are decreasing. As a result $Q_{dis-charge}$ is going to finally reach Q_{charge}, and the amount of coulombic efficiency is high, except in the first cycle. In the first cycle, the impact of solid electrolyte interphase (SEI) formation is very efficient and as a consequent the irreversible reactions are not negligible, making the amount of coulombic efficiency low.

The cell voltage profiles in cycles 1, 5, 10 and 20 are shown in Fig. 3 (c), which again shows that as cycle number grows, the battery became more stable and the voltage curves get more close to each other. In this image a voltage plateau around 0.5 V in the charge step is distinguishable.

For comparison, the result for bare CNT based battery and N-doped CNT one is shown in a single plot in Fig. 3 (d). From this figure about 4 fold improvement in the specific capacity of the battery is evident after charge/discharge for 10 cycles.
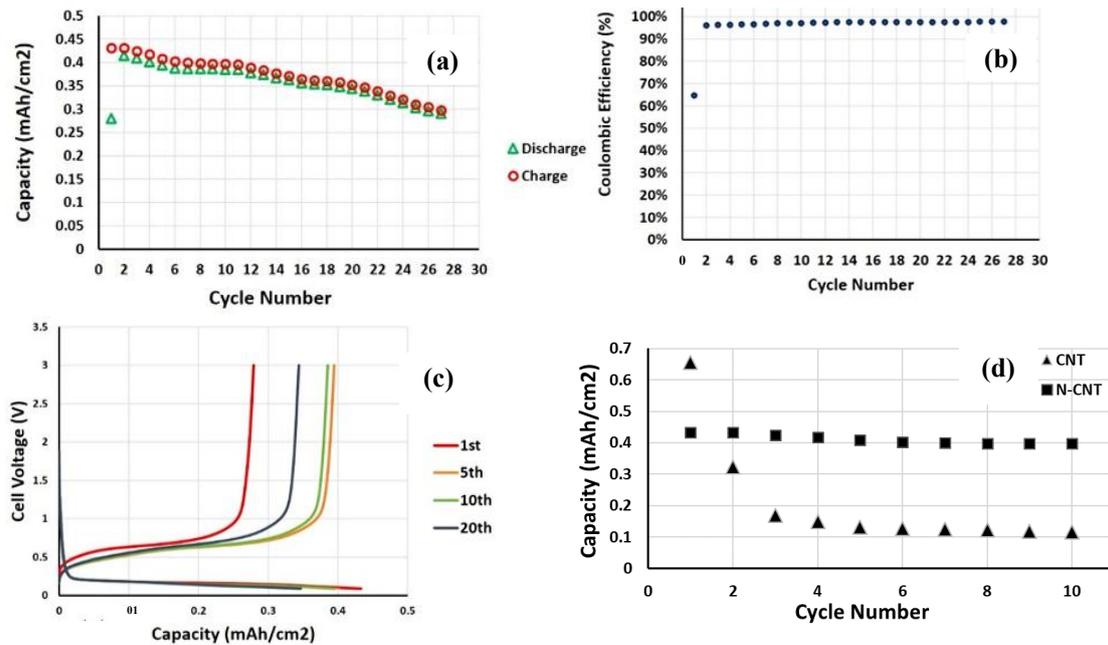

Fig. 3- The results of charge/discharge test for the Lithium ion battery. (a) Specific capacity for 28 cycles with current of 100 uA, in the potential range of 50 m to 3 V. (b) Coulombic efficiency of the cell. (c) Cell voltage profile. (d) Specific capacity in the first 10 cycles for both bare CNT and Nitrogen doped CNT based Lithium ion batteries. N-doped sample presents 4 times higher capacity at final cycles.

Table 1- Comparison of the improvement in the battery capacity when applying Nitrogen doping on the CNT based electrodes

	Q_{N-CNT}/Q_{CNT}	N-Doping Method	nitrogen content(at.%)
Ref 18	1.7	floating catalyst chemical vapor deposition	16.4
Ref 19	1.35	CCVD from toluene and acetonitrile	~ 1
Ref 22	1.5	floating catalyst chemical vapor deposition	2.83
This work	4	PECVD based doping	14.82

Doping the CNTs with Nitrogen introduces many defect sites in the CNTs, as can be seen in the TEM image of Fig. 2 (b). These centers act like channels enhancing the penetration of Lithium ions in the CNTs, therefore resulting in a much higher capacity for Nitrogen doped CNT based battery.

For comparison of the battery capacity before and after Nitrogen doping, Q_{N-CNT}/Q_{CNT} can be used as a proper figure of merit for evaluating the amount of improvement in the capacity of the Lithium ion battery. In this relation Q_{N-CNT} and Q_{CNT} are the battery specific capacities at the end of test cycles for Nitrogen doped and bare CNT samples, respectively. In this regard, table 1 compares the results of our work with related studies. To the best of our knowledge, our Nitrogen doping technique proposes considerably more improvement in the battery capacity. This table also shows the potential of high nitrogen content N-doped CNTs for resulting in better battery capacity improvement.

4. Conclusion

This manuscript reports the result of using plasma assisted Nitrogen doping on CNTs for enhancing the Lithium ion battery performance. DC-PECVD system has been exploit for annealing the CNTs in the Nitrogen ambient and also exposing them to Nitrogen plasma. Implementing this technique, high nitrogen content CNTs have been achieved with value of about 14.82 at. %. ITO coated Silicon wafer was used as the substrate for CNT growth. The TEM result show the existence of multiple defective sites on the N-doped CNT walls, enhancing the entrance/extraction of Lithium ions in the CNTs when they are used as the electrode material of Lithium ion batteries. This can result in a better performance and higher specific capacity of the fabricated battery, as was obtained in the charge/discharge analysis. The presented Nitrogen doping method resulted in a 4 fold improvement in the battery capacity which is quite outstanding in comparison with other reported values. Based on the results, this Nitrogen doping technique is proposed as an efficient approach for enhancing the performance of carbon based electrodes in Lithium ion batteries.

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