

# Vertically Aligned Carbon Nanotube Electrode and Application to a Lithium Ion Capacitor

Yoshiaki FUKUDA\*<sup>1</sup> and Naoki TSUKAHARA\*<sup>1</sup>

\*<sup>1</sup> Institute for Super Materials, ULVAC, Inc., 5-9-6 Tohokodai, Tsukuba, Ibaraki, 300-2635, Japan

Carbon nanotube (CNT) electrodes vertically aligned on a copper foil substrate have been fabricated by using a thermal chemical vapor deposition (CVD) method. In the electrode, superior electron conduction paths are formed over the entire electrode. The electron conduction paths are due to the fact that the CNTs are vertically aligned on the substrate with strong adhesion. Such a vertically aligned CNT electrode has been applied to a lithium-ion capacitor (LIC) as a negative electrode material. The fabricated LIC shows high energy density compared to an electric double-layer capacitor (EDLC) to which a commercially available activated carbon electrode material has been applied. This fabricated LIC also demonstrates high power density compared to an LIC to which a commercially available graphite anode has been applied.

## 1. Introduction

An electric double-layer capacitor (EDLC) is a high-output capacitor with a long service life, but with the drawback of low energy density. Because policies for reducing greenhouse gas emissions have been implemented in recent years, there is a need to increase the energy density of the capacitors installed in hybrid electric and all-electric vehicles (HEVs and EVs). For this reason, companies have been actively developing lithium-ion capacitors (LICs)<sup>1,2</sup>. In an LIC, the anode of an EDLC using activated carbon for the cathode, such as the one shown in Figure 1, is replaced with a material that can be doped with lithium ions, thus improving energy density. Figure 2 shows a Ragone plot of various types of energy-storage devices<sup>3</sup>. A Ragone plot shows on the horizontal

axis the power density (equivalent to instantaneous power) and on the vertical axis the energy density (equivalent to sustaining power). Because the ideal for a device is that it is positioned in the upper right-hand corner of the Ragone plot, it can be seen that LICs have the potential to become an ideal energy-storage device with both the instantaneous power of an EDLC and the sustaining power of a lithium-ion battery (LIB).

Because of their characteristic high-power, EDLCs are already being used widely in applications such as regenerative energy systems in cars, as well as in streetcars and fixed-route buses in China<sup>4</sup>. The capability to charge EDLCs instantaneously with a large current enables them to power a vehicle to travel the predetermined distance to the next bus stop or station. Replacing these capacitors with LICs reduces the size and weight of the large number of

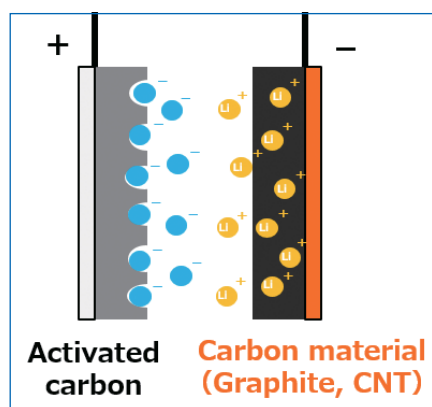


Fig. 1 Structure of Lithium-ion capacitor

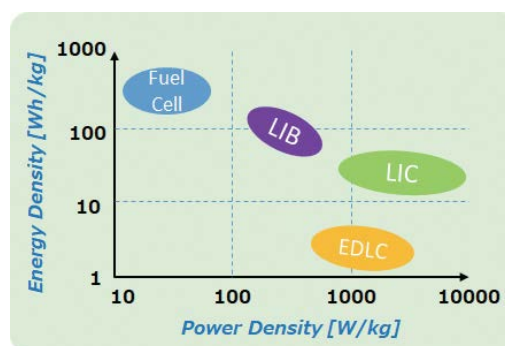


Fig. 2 Ragone plots of various storage devices (Ref. 3: Self-made with JM energy home page)

\*<sup>1</sup> Institute for Super Materials, ULVAC, Inc., 5-9-6 Tohokodai, Tsukuba, Ibaraki, 300-2635, Japan.

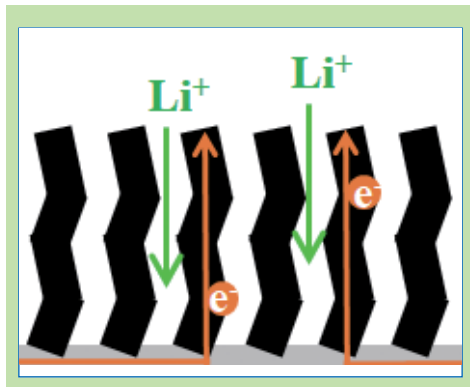


Fig. 3 Schematic diagram of CNT electrode

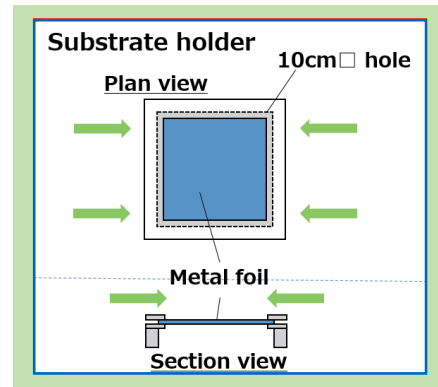


Fig. 5 Schematic diagram in the electric furnace

EDLCs installed, which also extends the cruising distance. In the future, as rapid charging/discharging becomes possible and wireless power supply technology becomes widely available even on ordinary roads, EVs relying on LICs alone could also become a reality.

Underpinning the initiation of our LIC evaluation is the fact that we had been developing a carbon nanotube (CNT) electrode fabricated using a chemical vapor deposition (CVD) method for the cathode of a next-generation battery, called a lithium-sulfur battery (LiS). One of the issues to be resolved in order to use such batteries is the need for a large volume of conductive material, because sulfur is an insulating material. Use of CNTs, which have higher conductivity than carbon materials such as acetylene black, can reduce the ratio of conductive material, which will lead to improved battery characteristics. We have so far confirmed that because CNTs fabricated using a thermal CVD method are aligned vertically on the nickel metal foil, forming a superior electron conduction path even to the top area of the electrode (see Figure 3), the sulfur filling volume can be reduced dramatically<sup>5)</sup>. This paper describes the verification results from our investigation into whether such a vertically aligned CNT electrode characterized by superior conductivity can be used as the anode material of LICs.

## 2. Deposition Method of CNT Electrode

Methods for depositing CNT films can be classified by their evaporation methods, such as the arc method and the laser ablation method, which evaporate a solid carbon source, and the chemical vapor deposition method, which fabricates CNT films by decomposing a hydrocarbon gas<sup>6)</sup>. Generally speaking, both types require metal grains (such as iron, nickel, and cobalt) that act as a catalyst. The shape (including the thickness) and the alignment of the CNTs that are grown are influenced by the substrate conditions, such as the grain diameter of the catalyst and the ease of aggregation, as well as the growing method used. Figure 4 shows the CNT growth mechanism. By using a thermal CVD method and acetylene gas and by adjusting the catalyst composition, we have already found that a long CNT film (of around 500  $\mu\text{m}$ ) can be deposited on nickel metal foil (of 20- $\mu\text{m}$  thickness). Figure 5 shows a schematic diagram of a substrate holder installed inside the thermal CVD system. Inside, a 100-mm square hole is provided in the quartz substrate holder, making it possible to grow a film on both sides of the substrate. Quartz holders can also be stacked, and because gas is supplied from four locations on the side surface, it is also possible to deposit films on multiple substrates simultaneously.

With respect to the manufacturing of CNTs, electron beam vapor deposition was used to deposit a catalyst

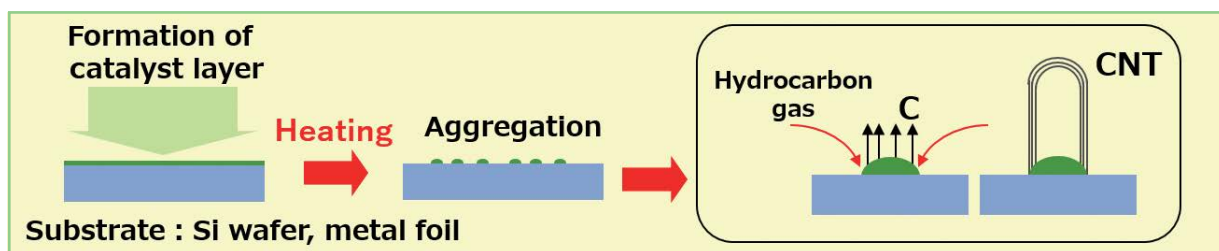


Fig. 4 Mechanism of CNT grown process on the surface of the substrate

consisting of iron, aluminum, and nickel on one side of the copper foil, and CVD was applied to this substrate under the conditions shown in Figure 6. The substrate on which a catalyst film was deposited was placed inside an electric furnace, and the film deposition temperature and acetylene gas concentration were fixed to 720°C and 2.0%, respectively. The gas supply time was varied between 30 and 60 minutes during fabrication of the CNT substrates.

Figure 7 shows a cross-sectional SEM image of the CNT substrate fabricated while supplying the acetylene gas for 30 minutes. This SEM image shows that the CNT film is vertically aligned on the substrate and has a thickness of between 400 and 500 μm.

### 3. Fabrication of CNT Capacitor and Evaluation of the Battery Characteristics

#### 3.1 Fabrication of a coin cell and lithium pre-doping

Using the aforementioned substrate, the battery characteristics of a coin cell (type 2032) were evaluated. For fabricating a coin cell, a commercially available activated carbon electrode was used for the cathode, a porous polyethylene film was used for the separator, a CNT electrode was used for the anode, and an ordinary carbonate-based product was used for the electrolyte. For comparison, we also fabricated an LIC cell using a commercially available graphite electrode for the anode and an EDLC with an activated carbon electrode for the cathode.

To fabricate such cells, it is essential to employ in advance an Li pre-doping process for supplying lithium ions to the anode of the LIC, as shown in Figure 1<sup>7,8)</sup>. In a recent experiment, we first fabricated a coin cell using a lithium metal foil and the doped anode, connected it to a charging/discharging system, and then tried Li pre-doping while controlling the system using a constant-current, constant-voltage program. Afterwards, the completely doped coin cell was disassembled, and an LIC was again fabricated using an activated carbon cathode and the doped CNT

anode or a graphite anode. Figure 8 shows a photograph of the external appearance of the electrode following Li pre-doping. On the substrate fabricated with the gas supplied for 30 minutes, only a few cracks can be detected on the CNT film. However, it can be seen on the substrate fabricated with the gas supplied for 60 minutes that stress caused part of the film to separate. Meanwhile, on the commercially available graphite electrode, a uniformly yellow surface can be observed and substrate warping was confirmed. The color of the original electrode was gray, and it is generally known that the color changes to this shade of yellow when Li doping is completed. Therefore, the graphite can also be judged from the external appearance following Li pre-doping. In the case of CNTs, it is difficult to draw conclusions from the external appearance following Li pre-doping. Other issues include the fact that the CNTs end up aggregating in the drying process following coin cell disassembly and the film hardens and tends to separate when the film deposition time becomes too long. In the case of CNTs, it is possible to tell how far the pre-doping has progressed by observing the voltage of the coin cell following Li pre-doping. While the graphite electrode ends up warping following Li pre-doping and cannot maintain flatness, hardly any warping occurs in CNTs. We have assumed that the gaps between CNTs ameliorated the stress that occurs during Li pre-doping.

#### 3.2 Evaluation of capacitor characteristics

A method called “constant-power testing” was used to evaluate the LIC as a battery<sup>9)</sup>. This constant-power test produced the Ragone plot shown in Figure 2. It is desirable that the energy density on the vertical axis not decline even when the power is increased gradually from low to high. For the test conditions, charging was performed at the same current density each time (0.5 mA/cm<sup>2</sup>), and the power was increased from 1 to 200 mW during discharging. The voltage range during discharging was set to 1.5 to 3.5 V for EDLCs, and to 2.0 to 4.0 V for LICs.

Figure 9 shows the Ragone plot obtained from the constant-power test. The light-blue curve in the

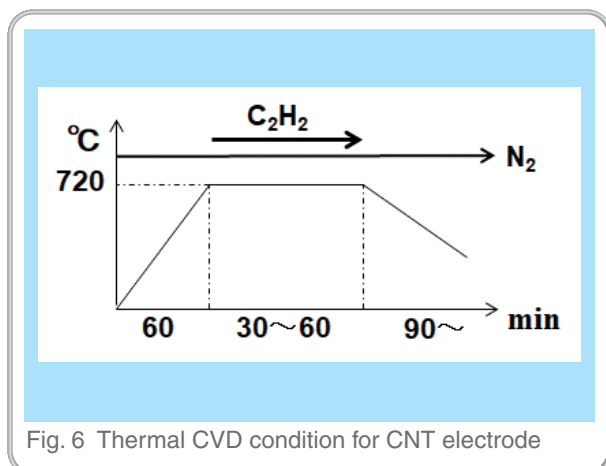


Fig. 6 Thermal CVD condition for CNT electrode

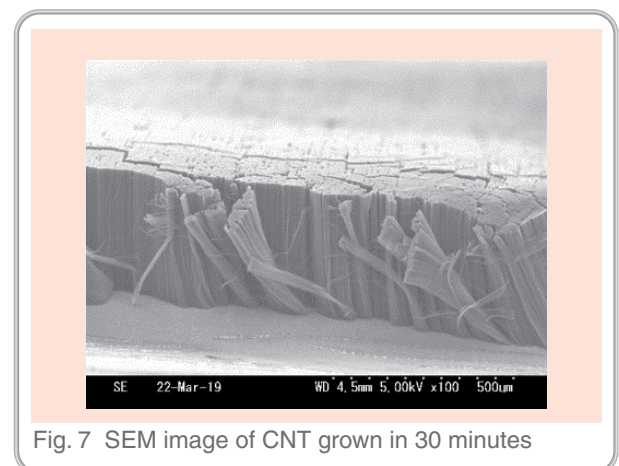


Fig. 7 SEM image of CNT grown in 30 minutes

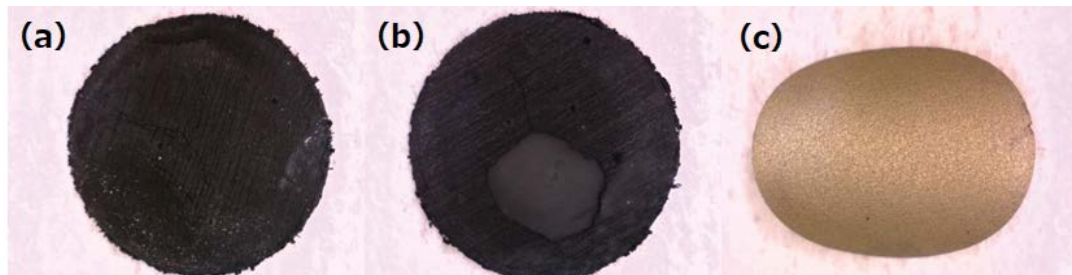


Fig. 8 Surface observation images after pre-doping of (a) CNT grown in 30 minutes, (b) CNT grown in 60 minutes, and (c) commercially available graphite electrode

graph shows the result for EDLCs fabricated using a commercially available activated carbon electrode, while for comparison the yellow curve shows the result for LICs fabricated using a commercially available graphite electrode. Because of the CNT film separation that occurred following Li pre-doping, the graph shows only the result for LICs fabricated using a CNT anode with a film fabricated with the gas supplied for 30 minutes (red curve). It shows that the energy density on the horizontal axis improved dramatically as compared to the EDLCs. Also, when compared with an LIC with a commercially available graphite anode, the energy density was about the same on the low-power side, but the LIC with the CNT anode did not show any significant deterioration in characteristics even when the load was increased to the high-power side. When an actual comparison was made at a capacity of 100 mW (the second plot from the right), the LIC with the CNT anode produced three times as much energy density (54.9 Wh/kg) as the LIC with a commercially available graphite anode (16.1 Wh/kg).

#### 4. Conclusion

We conducted an experiment to determine whether a CNT electrode aligned vertically on a copper foil using a thermal CVD method could be used as the anode of an LIC. In the course of examining whether it was possible to fabricate CNTs for the LiS battery application, which until now had been fabricated on a nickel foil, on a copper foil, which is the ordinary anode collector, we succeeded in fabricating a CNT electrode of around 400  $\mu\text{m}$  under thermal CVD conditions of 720°C, 2% acetylene gas, and a 30-minute deposition time. Furthermore, the LIC fabricated by applying Li pre-doping to this electrode showed dramatically higher energy density than an EDLC using a commercially available activated carbon electrode, as well as higher power output characteristics than an LIC using a commercially available graphite electrode.

These results seem to demonstrate that a CNT electrode aligned vertically on a copper foil using a thermal CVD method can be used satisfactorily as the anode material of an LIC. However, some issues still remain, such as the adhesion characteristic of the CNT following Li pre-doping,

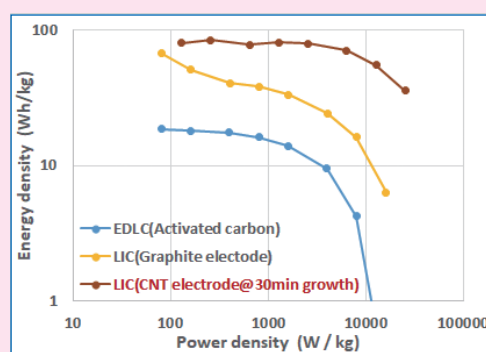


Fig. 9 Ragone plots of EDLC and LIC using CNT electrode

the fact that the CNT film is thick, and the need for a mass-production technology. For use in automotive applications, we need to evaluate the temperature characteristics of the developed CNT electrode, both under a high-temperature environment, such as in an engine compartment approaching 100°C, and in subfreezing temperatures.

LICs possess more than sufficient potential to become energy-storage devices with both power characteristics that are difficult to achieve with batteries such as LIB and a long service life. To further improve the characteristics of LICs, we must establish a mass-production technology with CNT electrode optimization and commercialization in mind.

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