Highly efficient growth of vertically aligned carbon nanotubes on Fe–Ni based metal alloy foils for supercapacitors

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Abstract
Supercapacitors are highly promising energy devices with superior charge storage performance and a long lifecycle. Construction of the supercapacitor cell, especially electrode fabrication, is critical to ensure good performance in applications. This work demonstrates direct growth of vertically aligned carbon nanotubes (CNTs) on Fe–Ni based metal alloy foils, namely SUS 310S, Inconel 600 and YEF 50, and their use in symmetric vertically aligned CNT supercapacitor electrodes. Alumina and cobalt thin film catalysts were deposited onto the foils, and then CNT growth was performed using alcohol catalytic chemical vapour deposition. By this method, vertically aligned CNTs were successfully grown and used directly as a binder-free supercapacitor electrode to deliver excellent electrochemical performance. The device showed relatively good specific capacitance, a superior rate capability and excellent cycle stability, maintaining about 96% capacitance up to 1000 cycles.

Keywords: vertically aligned carbon nanotube, metal alloy foils, alcohol catalytic CVD, binder-free electrodes, supercapacitor

Classification numbers: 4.02, 4.10, 5.00, 5.06, 5.14, 6.00

1. Introduction

Alternative and renewable energy systems are currently of great interest to scientists and technologists worldwide due to the decreasing reserves of fossil fuels [1]. With the increasing demand for electricity, it is important to seek clean energy sources to ensure a sustainable development in the future [2]. In particular, energy storage systems like fuel cells, batteries and supercapacitors are becoming more critical for storing energy for either short or long periods [3].

A supercapacitor (SC), also called an electrochemical capacitor, is a unique energy storage device that may replace or complement batteries due to its long lifecycle, high rate performance and sometimes higher energy density compared with batteries. It stores energy in two closely spaced layers with opposite charge, and is widely used in various applications such as portable electronic equipment, power hybrid electric vehicles and other devices. By offering fast charging and discharging rates, and the ability to sustain millions of cycles, it fills the gap between batteries and conventional capacitors [4–7]. SCs have two electrodes which are immersed in an electrolyte solution with one dielectric separator between them and two current collectors [8].

An electrochemical double layer capacitor (EDLC) may result from strong interactions between the ions/molecules in the electrolyte and the electrode surface. The physical
separation of the electronic and ionic charges is the source of the ability of an EDLC to store energy [9]. Basically, SCs can be classified into three types depending on the energy storage mechanisms: EDLCs, pseudocapacitors and hybrid capacitors [10, 11]. The behaviour of a SC can be determined by the physical properties of both electrode and electrolyte materials. However, the electrode material is the main component for charge storage and thus plays an important role in controlling the energy and power densities of the SC [12]. The charge storage performance of the SC depends on the type of the electrolyte, the structure of the surface electrode material and its pore size distribution [13].

Various materials have been used as SC electrodes. These include porous carbon materials, conducting polymers and transition-metal oxides. Among the porous carbon materials, carbon nanotubes (CNTs) have been extensively used as an electrode material due to their extraordinary electrical, mechanical and thermal properties, accompanied by a cost-effective production method and the good quality of CNTs produced. Transition metals such as Fe, Ni and Co have been extensively employed as the metal catalyst in CNT synthesis [14]. CNTs are long hollow cylinders of graphitic carbon molecules [15] and have unique properties that make them potentially useful in many technological applications [16, 17].

Basically, vertically aligned CNTs (VACNTs) give exceptionally improved electrode performance in specific capacitance and show excellent rate capability, far better than entangled CNTs, due to their mesoporosity and good conductive paths [18]. Various methods of chemical vapour deposition (CVD), including alcohol catalytic CVD (ACCVD), have been developed to produce VACNTs. ACCVD has the advantage of being economical with wide substrate selectivity. The essential parameters involved in the growth of VACNTs are the feed gas, the nature of the catalyst and the substrate temperature [19]. Various substrates such as metal alloys can act as current collectors in a SC. Remarkably, the VACNTs binder-free electrode exhibits great electrochemical performance with high capacitance and excellent cycling stability. The direct growth technique can reduce the number of process steps in device fabrication, and might avoid the incorporation of binder material, which in principle could increase the internal resistance of the device [20].

In this work VACNTs were successfully grown on various Fe–Ni based metal alloy foils, including SUS 310S, Inconel 600 and YEF 50, and were used in SC electrodes. These high-quality VACNTs were produced using a facile and low-cost ACCVD process. The VACNT growth structure makes efficient use of the advantages of the two electroactive materials such as high ion accessibility and fast ion transfer. Other than structural studies of the VACNTs, the electrochemical performance of the electrode in 6 M KOH was analysed by cyclic voltammetry (CV) and charge–discharge (CD) analyses, and showed excellent electrochemical performance with high gravimetric specific capacitance ($C_{sp}$), good rate capability and cycle stability.

2. Experimental

2.1. Direct growth of VACNTs on various Fe–Ni based metal alloy foils

VACNTs were directly grown onto metal alloy foils, namely SUS 310S, Inconel 600 (Nilaco Japan) and YE 50 (Hitachi Metals Ltd), using an ethanol based CVD technique. Prior to the growth process, a piece of each foil was cut into a round shape of diameter 15 mm using a puncher electrode. These pieces were used as the substrates. All substrates were carefully rinsed with acetone followed by cleaning with ethanol in an ultrasonic bath for 10 min. The substrates were then dried with a N$_2$ air blower until the entire surface was completely dry. Electron beam physical vapour deposition (EBPVD) (Torr International, Inc.; EB4P7C-6 KW) was used to deposit alumina (Al$_2$O$_3$, 20 nm) and cobalt (Co, 2 nm) thin films (Kurt J Lesker Company) on all substrates simultaneously with the desired nominal thickness. For CNT growth, the substrate was transferred into a CVD furnace (MILA-3000). Argon gas was flowed through during the 5 min heating process, followed by another 7 min annealing process held at the CVD temperature (700°C). After the annealing process was completed, the argon gas flow was stopped. Then ethanol vapour was immediately introduced into the furnace at flow rates around 100–200 sccm for 10 min. Similar growth processes were repeated for Inconel 600 and YEF 50 substrates.

2.2. Material characterization

X-ray photoelectroence spectroscopy (XPS; AXIS Ultra DLD; 39–306) was used to characterize the chemical state of the catalyst and catalyst-support thin films. XPS measurements were performed using Al-K$_\alpha$ as the x-ray source. The surface morphology of CNTs on all substrates was characterized by field emission scanning electron microscopy (FESEM; Hitachi, SU8000, 5.0 kV) which was used to examine the morphological characteristics of as-grown CNTs. Meanwhile, transmission electron microscopy (TEM; Hitachi, HT7700, 120.0 kV) was used to identify the submicron structures of the CNTs. Raman spectroscopy (UniRAM-3500) with 532 nm laser excitation was used to observe the quality and purity of the CNTs.

2.3. Electrochemical measurements

To investigate the electrochemical performance of the VACNT electrode, CV measurement was performed using a potentiostat/galvanostat (Metrohm; PGEAST204) in a standard two-electrode cell. These symmetrical electrodes were infiltrated by 6 M KOH as the electrolyte and were separated by a 25 μm polypropylene (Tonen) separator. The average mass of CNTs obtained from SUS 310S, Inconel 600 and YEF 50 substrates was 0.285, 0.250 and 2.270 mg, respectively. The capacitive behaviours of VACNT SCs were measured to study the stability of the electrical contact between the CNTs and substrates. To quantify the charge storage capacities, the capacitance of the SC was determined through voltammetry charges, cell potential windows and
VACNT loading. Also, the capacitive behaviours of VACNT electrodes were measured to study the stability of the electrical contact between CNTs and substrates. Due to the use of aqueous electrolyte, the CV test was conducted in potential window of 0.0–1.0 V at various scan rates from 1, 5, 10, 50, 100, 250, 500 and 1000 mV s⁻¹. Galvanostatic CD tests were conducted in a potential window of 0.0–1.0 V at various currents ranging from 0.01 to 0.5 mA. A lifecycle test to evaluate the capacitance retention of the CNT electrode was done for 1000 CD cycles with a fixed current of 0.5 mA.

3. Results and discussion

The XPS spectra of Al₂O₃ on the SUS 310S substrate without a Co catalyst after deposition by EBPVD are shown in figure 1. Four main different XPS regions were clearly observed: O 1 s, C 1 s, Al 2 s and Al 2 p (figure 1(a)). A single peak located at 531 eV was observed on the surface of the sample, which can be partly assigned to the lattice oxygen (O 1 s) of Al₂O₃ [21]. This result was consistent with previous studies on Al₂O₃ [22]. It is important that O 1 s can be represented by the oxygen gas included in the chamber environment and those attached in the Al₂O₃ structures. Meanwhile, the Al 2 p region at 71.5 eV (figure 1(b)) confirms the existence of Al 2 p, indicating the presence of stable (stoichiometric) Al₂O₃ catalyst thin films on the substrate. Other than that, the XPS spectra show signals from Co 2 p, O 1 s and C 1 s regions (figure 1(c)). From the XPS spectrum measurement two additional peaks in the region related to the Co 2 p orbital states were observed (figure 1(d)). These two spin–orbit split peaks, Co 2p₁/₂ (797 eV) and Co 2p₃/₂ (781 eV), closely match the result of previous work on standard Co showing the significant presence of Co from the substrate [23].

VACNTs were successfully grown directly on SUS 310S, Inconel 600 and YEF 50 substrates in order to investigate the influence of the substrate on CNT growth performance. Observation of the substrates showed that entire area of all substrates was covered by CNTs with similar morphology, and both individual as well as bundle CNTs have a longer length (figures 2(a)–(e)). The as-grown VACNTs were found to be well-aligned CNTs and the height of VACNTs for SUS 310S and Inconel 600 were approximately 31.68 and 10.58 µm, respectively (figures 2(b) and (d)). The vertical and denser CNTs were grown on SUS 310S and Inconel 600 substrates. Al₂O₃ is an effective support material because it is porous, and this feature is important for the growth of
VACNTs. The FESEM images give evidence of entangled CNTs homogeneously distributed on top of the sample. The height of CNT forests might be greater, but the condition inside the CVD chamber would be the main reason for the limitation of the CNT height. The FESEM images provide strong evidence that the proposed catalyst-support method is virtually devoid of metal agglomerates \cite{24}. This smooth surface, devoid of agglomerated metals, is considered to be efficient for various device applications, especially for SC applications, because agglomerated metals do not contribute to the functioning of devices. It has been suggested that the difference in the growth results is due to differences in the physical and/or chemical structure of the Al$_2$O$_3$ catalyst support and Co catalyst thin film used in the growth process.

When growing aligned CNT forests, the morphology of the catalyst and its support are very important because they determine the activity of the catalyst or, in other words, provide more nucleation sites for CNT growth \cite{10}.

In contrast, CNTs grown on YEF 50 substrate show a different morphology (figure 2(f)). However, it was found that in some areas a thicker carbon product film (forest/agglomerate) was formed. The formation of a few agglomerated CNTs on the YEF 50 substrate may be due to van der Waals forces and the entanglement among CNTs that naturally occurs to in the formation of CNT agglomerates \cite{25}. There is clear evidence of the agglomeration of large numbers of CNTs. The thickness of CNT growth is nearly 9.53 $\mu$m. It can be seen that there is a tendency for agglomeration of the

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**Figure 2.** FESEM images of the top view and tilted CNT growth on SUS 310S (a), (b), Inconel 600 (c), (d), and YEF 50 (e), (f).
particles. Also, aligned CNT growth cannot carry on for a long period of time and it falls apart and starts to form agglomeration until the CNT growth process is stopped. The formation of agglomerates may be due to the sticking together of entangled CNTs which finally develop into a CNT agglomerate [26]. The FESEM results show that it is not easy to grow CNTs on Co/Al₂O₃/YEF 50 substrate but much easier with Co/Al₂O₃ thin films on SUS 310S and Inconel 600 substrates. Thus, it is important to identify suitable metals and to control the CVD parameters under which VACNTs can directly grow on substrates.

It could be suggested that there is a Co catalyst particle at the upper part of the CNT (tip-growth). This indicates that due to a weak interaction (large contact angle), the CNTs grow by a tip-growth method in which the catalyst particle loses contact with the substrate and is pushed upward as the CNT forms beneath [27]. In the case of CNT growth on Co/Al₂O₃/SUS 310S (figure 1(a)), a Co catalyst can be observed at the top of the CNT (tip-growth). However, in most cases CNTs were synthesized by one of two main mechanisms: either the base (or root)-growth or the tip-growth mechanism. The influence of temperature on CNT growth was investigated on various substrates. It was observed that at 700 °C the ratio of carbon nanostructures produced on SUS 310S and Inconel 600 is optimal. Meanwhile, the CNTs on YEF 50 began to agglomerate at a temperature of 700 °C, which indicates that this temperature is not suitable for growing CNTs on YEF 50 substrate and further study of CNT growth on this substrate is needed. In figure 3 a scheme shows the surface change during the CNT growth process. Al₂O₃ and Co thin films started to change when further heating and annealing treatments take place. Al₂O₃ thin film changes to a porous surface, meanwhile the Co thin film was broken, becoming particles set apart from each other after annealing at 700 °C for 7 min. This corresponds to the adhesion force between Co and Al₂O₃.

In addition, the packing density and purity of the VACNTs were high for all substrates. TEM observation disclosed further characteristics of the CNT wall structures (figure 4). The TEM image reveals that the as-grown VACNTs were mainly represented by multi-walled CNTs (MWCNTs) with inner and outer diameters approximately in the range of 4 to 17 nm. MWCNTs were the dominant growth form on the substrate. There was no amorphous carbon and/or by-products, confirming the good quality and high purity of the as-grown CNTs. This is because reaction between carbon molecules and OH⁻ radical carbon that exists in alcohol etches away carbon atoms that have the tendency to develop amorphous carbon [28]. The role of the catalyst-support is to disperse the active phase and to provide the porous structure, different metals giving different results in terms of CNT quality. In many cases, CNT growth on various conducting substrates results in the formation of MWCNTs or graphite films [29]. Also, SWCNT forests can be grown on various metal alloy substrates which possess Cr–Ni–Fe composition, such as SUS 310S, NiCr, Inconel 601, YEF 50 and YEF 426 [30].

Raman spectroscopy was used to determine the types of CNT growth on the conducting substrates as well as to determine the quality of the CNTs. As shown in figure 5, there are two main features in the Raman spectra, D and G peaks [19]. The D peak is related to the breathing modes of the rings while the G peak is based on relative motion of sp² carbon atoms. A lower I_D/I_G ratio of sharp D and G peaks results in aligned and ordered CNTs [31]. Kim et al [5] reported that high G-band to D-band intensity ratio
The performance of the VACNTs in 6 M KOH was also evaluated by CD analysis for SUS 310S, Inconel 600, and YEF 50 substrates. The $C_{sp}$ was calculated according to CD measurements using the formula

$$C_{sp} = \frac{2I}{m \left( \frac{dV}{dt} \right)},$$

where $I$ is the applied current, $m$ is the average mass of the active material in each electrode, and $dV/dt$ is the slope of the discharge curve after the voltage (IR) drop [42].

The resulting $C_{sp}$ of three different substrates were 8.13 F g$^{-1}$ (SUS 310S), 7.16 F g$^{-1}$ (Inconel 600), and 9.69 F g$^{-1}$ (YEF 50), respectively. $C_{sp}$ for the YEF 50 substrate is high compared with that for the other substrates. This may be due to the CNT structures having better physical contact and attachment to the substrate surfaces, resulting in higher capacitance. The high CNT-specific surface area providing contact with electrolyte ions may influence the high value of $C_{sp}$ for the YEF 50 substrate [43]. Moreover, the particle size of the electrode material decreases to the nanosize which means it has a relatively larger specific area and can increase the contact area with the electrolyte [44].
310S substrate still shows good capacitive performance compared with Inconel 600 substrate, which may be attributed to the well-aligned CNT structure that contacts the electrolyte ions. This type of electrical/electronic characterization also confirms the electrical conductivity of the alumina film, thus making the structures suitable for use in any kind of energy storage electrode [45].

To examine the cyclic stability and further quantify the capacitance, CD measurements were performed. As shown in figure 7, the voltage increases and decreases almost linearly with time between 0 and 1.0 V. Various constant currents were applied to observe the ability of the electrodes to work from lower to higher current. The black, red, blue and green lines correspond to applied currents of 0.05, 0.10, 0.50 and 1.00 mA, respectively, for all substrates. The \( C_{sp} \) decreased with increasing current for all substrates. The discharge times at 0.05 mA of each cycle for SUS 310S, Inconel 600 and YEF 50 were 35.6 s (13.29 F g\(^{-1}\)), 49.9 s (21.88 F g\(^{-1}\)) and 54.2 s (26.57 F g\(^{-1}\)) respectively. The YEF 50 substrate shows the highest \( C_{sp} \) value compared with SUS 310S and Inconel 600 substrates. As shown in figures 7(a)–(c) the discharge times of the VACNT electrode on the different conducting substrates were nearly the same. The very rapid CD (in seconds) for all substrates is advantageous for SC applications [46]. Moreover, a dynamic long lifetime of the electrode materials can be expected from pure aligned CNTs that were produced using the ACCVD technique [47]. For SC applications using a CNT-based electrode, the ability to accumulate charge in the electrode–electrolyte interface strongly depends on the accessibility of the nanotubes to ions. Therefore, it can be suggested that the morphological structure of aligned CNTs might influence the performance of SCs, with the accessibility of ions to aligned CNTs better than that for entangled CNTs [48].

The VACNT electrode was further tested by CD for 1000 cycles in 6 M KOH electrolyte with a current of 0.5 mA in order to evaluate its performance over its lifecycle. After 1000 cycles, only a slight decrease in \( C_{sp} \) can be observed. The electrode exhibited almost lossless performance in specific capacitance after 1000 cycles; the slight decrease in \( C_{sp} \) indicates excellent stability of the aligned CNT array electrode, as shown in figure 8. High retention of \( C_{sp} \) was observed in as-grown VACNT SCs. SUS 310S, Inconel 600 and YEF 50 retained 96.1%, 100.0% and 97.4%, respectively, of the original value of \( C_{sp} \). This finding indicates excellent capacity retention and better long-term cycling stability of the VACNT electrode. Moreover, after 1000 cycles, the Co/Al\(_2\)O\(_3\) on all substrates was still strongly adhered to the CNTs [49]. Such high retention indicates the stability of this
4. Conclusions

After the deposition of Al₂O₃ and Co ultra-thin films, VACNTs were successfully grown on different Fe–Ni based metal alloy foils at 700 °C using the ACCVD technique. The CVD process resulted in similar morphological structures and good CNT distribution on all substrates, and their structures (dimension, walls) have been confirmed by means of FESEM, TEM and Raman spectroscopy. From electrochemical analyses, the CV curve shows a nearly rectangular shape up to scan rates of 1000 mV s⁻¹. It can be concluded that the aligned CNT structure produces better electrochemical performance because it allows fast ion transportation. The capacitance retention measurement for 1000 cycles proved that all substrates still had strong adhesion to the CNTs, indicating the stability of this material for EDLC applications. The performance of SCs depends on several conditions, including electrolyte and electrode material. Thus, by replacing the aqueous electrolyte with wider potential range of electrolytes, such as ionic liquids and organic electrolytes, higher SC performance may be achieved. It is necessary to use a glove-box to control the moisture and oxygen contents.

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