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Vertically aligned carbon nanotube – Polyaniline nanocomposite supercapacitor electrodes

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ABSTRACT

We develop a fast and cost effective method for the fabrication of a nanocomposite supercapacitor electrode. In this study aluminum foils were decorated with vertically aligned carbon nanotubes (VACNT) via chemical vapor deposition (CVD) method, which was followed by the electrodeposition of polyaniline (PANI) layer on top of the VACNTs. Electrochemical behavior of the fabricated nanocomposite electrodes were evaluated through cyclic voltammetry, galvanostatic charge discharge cycles and electrochemical impedance spectroscopy method. Fabricated VACNT/PANI nanocomposite electrodes through 15 electrodeposition cycles showed significant electrochemical performance. The specific capacity of these electrodes was calculated as 16.17 mF/cm² at a current density of 0.25 mA/cm².

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Introduction

Supercapacitors (or ultracapacitors) are known as one of the most promising energy storage systems for the 21st century. Supercapacitors have received a lot of attention thanks to their high specific power and moderate energy densities. They are strong candidates to complement batteries in terms of specific power. Supercapacitors have various application areas ranging from electric vehicle, pulse power systems to portable systems and devices [1–3]. Especially their fast charge-discharge properties allow their integration into consumer electronics, mobile and renewable energy devices [4,5].

Usage of supercapacitors in many other electronic systems can also be possible if they gain novel functionalities, such as flexibility, textile integrability, environment friendliness and color indicator for charged-discharged states. The supercapacitor electrodes having these multi-functional properties will be notable for both industrial and commercial applications [6]. Hence numerous research groups are focused on the exploration of novel active materials for supercapacitor electrodes [7–11].

Recently, supercapacitors are started to be considered to complement the fuel cells to improve their power density. The fuel cell vehicle is accepted as the vehicle of the future in response to environmental, economic and political

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considerations. Most recent technology on fuel cell vehicles includes hybrid fuel cells [12]. The next generation of all-electrical cars and hybrid vehicles based on fuel cells that consume hydrogen or alcohol as the clean energy sources need supercapacitors for high fuel efficiency [13]. The fuel cell largely compensates power demand, while a small battery can be used to meet peak power requirements. Similar benefits can be observed through hybridization of fuel cells with supercapacitors [14]. Disadvantages of designing a system with a single fuel cell are the long start-up time and slow dynamic response. On the other hand, a supercapacitor is a useful device to connect in parallel with the fuel cell to form a hybrid system capable of providing both the steady-state and peak power demand [15]. Supercapacitors have some advantages over batteries in hybrid fuel cell applications. They can be charged and discharged at high rates and have a very low equivalent series resistance (ESR). One of the most visible advantages of supercapacitors is the simplicity of connection to the fuel cell system. Different from a battery, supercapacitor can be directly connected to the fuel cell without expensive components [14]. In order to determine the accuracy of the supercapacitors Shin et al. [14] designed a proton-exchange membrane fuel cell-supercapacitor hybrid system. The system consumed 6.8% less fuel with respect to a base fuel cell on average, and 17.5% at best, with a 50% improvement in peak power capacity. Harfman-Todorovic et al. [15] explained the fuel consumption decrease as a function of the frequency of the ripple current in a fuel cell-supercapacitor hybrid. This is due to the fact that the high frequency ripple current does not present a wide output voltage variation in the hybrid configuration, which directly means lower demand on hydrogen flow. As an alternative application field for fuel cells and supercapacitors Unda et al. [16] investigated the potential and limitation of a novel mechanism of hydrogen storage. This mechanism involved electrochemical division of protons and electrons on a polymer electrolyte membrane fuel cell-type electrode and then their storage in the electrical double layer of a supercapacitor-type electrode. The highest hydrogen storage capacities were determined as 0.17 and 0.13 wt% during charging and discharging, respectively. Although the H₂ storage capacities were low, the combustion energy of the hydrogen stored in this cell was still 2.6 times higher than the electrical energy stored in a symmetric supercapacitor of similar quality. A capacitance of 11 mF/cm² which is comparable to that of a commercial double layer supercapacitor was obtained using H₂SO₄ electrolyte.

According to the charge storage mechanism, there are two main groups for supercapacitor electrode active materials. Electrochemical double layer capacitors (EDLCs) store charges electrostatically in double layers; on the other hand, pseudocapacitors allow fast faradic reactions on the surface of the electrode active materials to charge and discharge. Metal oxides and conducting polymers are classified as pseudocapacitor type electrodes, while carbon based materials are known as EDLC type. Dominant aspect of EDLC type electrodes is their long-lasting life but prominent characteristic of pseudocapacitor type electrodes is their high energy density.

Carbon can be found in various crystal structures due to its different bonding configurations arisen from hybridization

[17]. Conductivity and stability of almost all carbonaceous materials are very high. Moreover, they have controllable pore size and pore size distribution, which is important for supercapacitor applications [18]. Carbonaceous materials have already been utilized or can potentially be utilized as supercapacitor electrodes in the form of activated carbons, CNTs, carbon fibers, graphene and carbon aerogels [19–23]. Among these, CNTs have low electrical resistivity due their nanoscale tubular morphology [24]. They can be visualized as graphene sheets rolled into a tube along their long axes [25]. Charge diffusion in CNTs is quite easy through their porous structure and central channels. However, entangled CNTs exhibit slower ion and electron transfer due to their complex structure, which obstructs the ion diffusion to each CNT. On the contrary, vertically aligned carbon nanotube (VACNT) based electrodes present higher conductivity across the CNT length and their specific surface area is larger than that of entangled CNTs [26].

In electrochemical devices, deposition of CNTs on metallic foils, especially on aluminum foils is very common. Huang et al. [27] used household aluminum foil as the substrate for the growth of VACNT and polyaniline arrays. In a very similar study, Dogru et al. [28] fabricated flexible supercapacitor electrodes with vertically aligned carbon nanotubes grown on aluminum foils. Despite the fact that the melting point of aluminum is quite low compared to most of the other substrate materials, direct deposition of CNTs on aluminum foils can be carried out via controlled CVD conditions. Availability, low cost and flexibility of aluminum foils make them very attractive as current collectors for supercapacitor electrodes. Thus supercapacitor electrodes with VACNT decorated aluminum foils were investigated and found to exhibit significant cyclic stability and low resistance [29]. In fact, the use of CNTs synthesized on aluminum foils not only limited to supercapacitors but also demonstrated for battery electrodes [30].

CNT growth by CVD method includes self-organization of carbon atoms around the catalytic metal nanoparticles. In other words, metal nanoparticles can be thought as templates, where carbon compounds decompose and CNT nucleation starts [31]. Moreover, while the CNT formation progresses, metal nanoparticles saturate the dangling bonds of CNTs at the edges and stabilize them [32]. As a catalyst, transition metals such as nickel, iron, and cobalt are used for CNT growth on a substrate. Methods used for the deposition of metal catalyst onto substrates involve either solution-based or vacuum based deposition routes [33]. Solution-based methods are cost-effective yet more complicated since the thickness of the metal thin film cannot be monitored simultaneously. On the other hand, vacuum based deposition techniques are more controllable. On the other hand, if the surface energy of the substrate is high, catalyst diffusion towards inner sections of the substrate can be observed. In order to prevent this problem, diffusion barrier layers having low surface energies can be coated between the substrate and catalyst [31]. At elevated temperatures, catalyst diffusion in aluminum substrates can also be valid; but, at the same time aluminum has its natural oxide on its surface. This oxide layer protects aluminum substrate from catalyst diffusion [34].

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