論 文 の 内 容 の 要 旨

論文題目　Development of lightweight electrochemical capacitor electrodes based on a three dimensional carbon nanotube network capturing capacitive particles
(カーボンナノチューブ３次元ネットワークで活物質を包含した軽量な電気化学キャパシタ電極の開発)

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Chapter 1 - Introduction

Research in electrochemical capacitors as environment-friendly energy systems is currently focused on improving performance through the development of new capacitive materials, either with increased surface area in the case of electric double layer (EDL) mechanism or with redox reactions in the case of pseudocapacitive mechanisms. From the viewpoint of a conventional device architecture, which is composed of activated carbon, electrical conductive fillers and binders, changes in the configuration of their electrodes may offer another route to improve their performance. In general, the content of carbon in these devices is about 30 wt.%. By increasing the percentage of active material and reducing the amount of material that does not contribute to the capacitance, it is possible to increase the volumetric and gravimetric capacitances of complete devices using inexpensive materials. The present study analyses from the process and material perspectives the possibility of using long carbon nanotubes (CNTs) to form 3D collector matrices and to capture capacitive materials such as activated carbon (AC) and graphene oxide (GO) within it, regardless of their electrical conductivity. Such structure would not use binder and electrically conductive fillers, increasing the amount of active material. The resultant improvement of conductivity may even allow replacing the metallic current collector that has similar weight as capacitive particles in standard electrochemical capacitor devices. Furthermore, such three dimensional collector will realize practically thick electrodes of any capacitive materials (Figure 1).

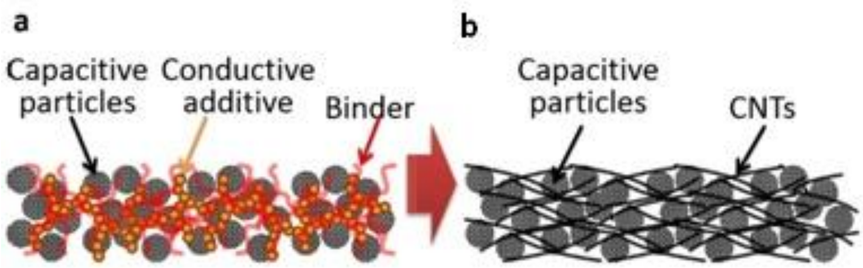

Figure 1. Comparison of traditional (left) and proposed (right) electrode configurations.

Chapter 2 - AC–CNT-based electrodes on metal current collectors

The addition of CNTs to AC in electrodes has been reported as a way to increase its electrical conductivity and replace traditional conductive fillers. Depending on the characteristics and content of CNTs, the resulting electrodes exhibit a trade-off between maximum achievable capacitance and rate performance. Also the characteristics of CNTs will impact their cost and manipulation. In this chapter, the influence of specific parameters during electrode fabrication is evaluated. Factors such as dispersant, particle size of AC, surface area of AC and CNT load in electrodes were carefully studied and their effect over the capacitance of hybrid films was determined (Figure 2a).

Excellent rate capability of pure CNT electrodes was confirmed as they exhibited specific capacitances independent of the scan rate. The amount of stored charge varied with the dispersant used for each type of CNTs. With better dispersion, higher specific surface area (SSA) was available to be used in EDL mechanism. Dispersion in aqueous solution of sodium dodecylbenzenesulfonate (SDBS) (0.5%) (H_2O-SDBS) yielded the highest performance in pure CNT electrodes. In the other hand, when used to disperse AC-CNT mixtures, it degraded the SSA of AC and thus the specific capacitance. Ethanol was suitable for hybridization of CNTs with AC because it could be easily removed from AC pores. In conclusion, single-wall CNTs (SWCNTs) having high SSA were suitable for pure CNT electrodes whereas few-wall CNTs (FWCNTs) could be dispersed in ethanol and where suitable for hybrid electrodes with AC. The results confirmed that long FWCNTs are appropriate to mechanically and electrically capture and bind the AC particles. Not only SSA but also particle size of AC influenced the performance. Enhancements in both rate performance and capacitance were confirmed by replacing big AC particles (10-60 μm) with smaller ones (~10 μm) owing to the less-interrupted network formation of FWCNTs and enhanced transport of current/ions within individual AC particles. A load as small as 5 wt% yielded self-supporting hybrid electrodes and a 10 wt% load was optimum for the best balance among capacitance, power, and small usage of FWCNTs (Figure 2b).

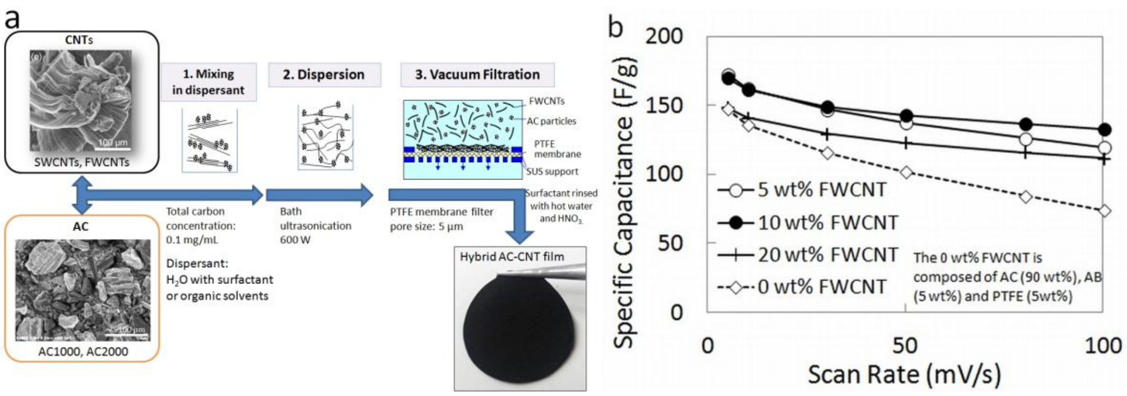

Figure 2. (a) Preparation of AC-CNT hybrid electrodes, (b) rate performance of AC-FWCNT hybrid electrodes with different FWCNT loads.

Chapter 3 - Free-standing, all-carbon AC-CNT electrodes

CNTs can increase the electrical conductivity of AC films and at the same time provide binding properties. However, no studies have been conducted to evaluate the full extent of the improvement of the electrical conductivity, *i.e.* AC-CNT hybrids without metal current collectors. In this chapter, self-supporting AC-FWCNT electrodes were fabricated and characterized in different contacts with the Ti mesh: full-contact (2D), line-contact (1D) and point-contact (0D) (Figure 3).

AC-FWCNT hybrid electrode showed almost full capacitance for any contacts for slow scan (5 mV/s equal to 320 s/cycle), and fair capacitance for line contact for fast scan (100 mV/s equal to 16 s/cycle). It should be noted that AC-CNT hybrids showed better performance even with the line contact than the conventional AC electrodes in the full contact with acetylene black (AB, conductive filler) and polytetrafluoroethylene (PTFE, binder). The AC-FWCNT hybrids showed stable capacitance for 1000 charge-discharge cycles with any contacts. Up to a fair scan rate, the heavy current collectors of metal can be largely replaced with the light-weight 3D collector of FWCNTs, which support the long-range electric conduction parallel to the electrode.

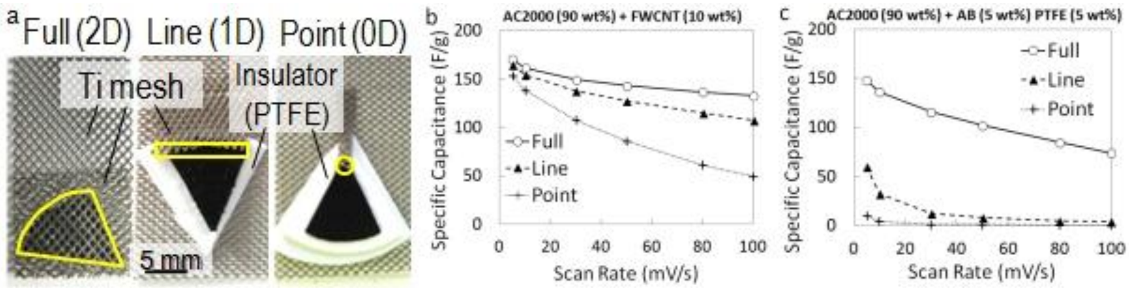

Figure 3. (a) Photographs of the different contacts to Ti mesh, (b) scan rate study with different current collector contacts for (b) AC-FWCNT hybrid and (c) conventional AC-AB-PTFE electrodes.

Chapter 4 - CNT-based electrodes with graphene oxide (GO) capacitive particles

GO has recently been extensively studied as an intermediate in the mass production of graphene. It is also attractive as a capacitive material because it has high surface area originating from a layered structure, differently from the porous structure of AC. It can also act as surfactant in liquid-solid systems facilitating dispersion, and the oxygen functional groups decorating its surface may be harvested to yield pseudocapacitance through Faradaic reactions. GO-FWCNT hybrids were made by dispersing them in water without additional surfactants followed by filtration (Figure 4).

For the GO-FWCNT hybrids, GO phase separated from FWCNT matrix and the resulting hybrid showed lower capacitance than even pure FWCNTs. GO’s properties were not utilized due to its electrically insulating nature which affected the conductivity of around half of FWCNTs. With the chemical reduction of GO in ethanol solution in the presence of FWCNTs using hydrazine as a reducing agent followed by filtration, the reduced GO (rGO)-FWCNT hybrids were fabricated. rGO uniformly mixed with FWCNTs and the hybrid had higher EDL capacitance, especially at low scan rates, than the pure FWCNTs. However, the rate performance of rGO-FWCNTs was not as good as AC-FWCNTs possibly due to the interruption of FWCNT network formation by rGO. Tailoring the degree of reduction to control the hydrophilicity as well as the degree of phase separation would be the key to utilize these "surfactant" capacitive particles effectively.

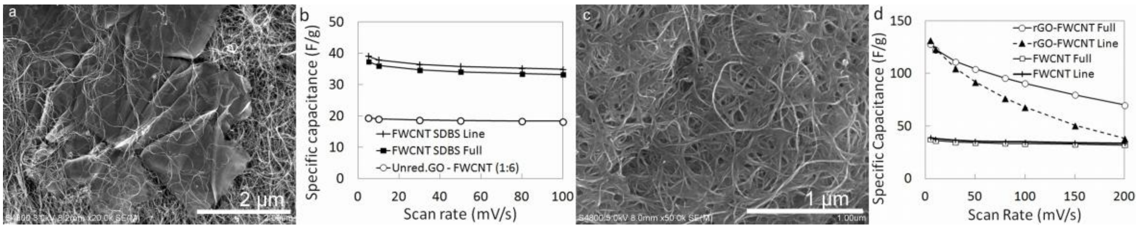

Figure 4. (a,c) SEM images and (b,d) rate performance curves of unreduced GO-FWCNTs and rGO-FWCNTs electrodes respectively.

Chapter 5 - Conclusions and perspectives

Hybrid electrodes were fabricated through a simple process (dispersion, filtration and drying). These electrodes feature a simpler architecture than the one in conventional devices: capacitive particles supported by FWCNT matrix in order to achieve higher performances. Capturing capacitive particles within FWCNT matrix without binders is effective and represents a new route to put many capacitive particles under R&D into practical use since different performances for different applications and costs can be designed. Carbon materials have different dispersion requirements and influence the final performance of electrodes. Surfactants should not be used for porous capacitive particles to avoid adsorption into the pores and FWCNTs were easier to disperse. The electrode evaluation was carried out through novel current collector connections to consider its removal in practical applications. Using the normal configuration, that is the full contact with the metallic mesh, the AC-FWCNT hybrid showed much better performance than conventional AC-AB-PTFE, which confirmed that capturing capacitive particles within a FWCNT matrix without binders is effective for simple fabrication of high-performance electrodes of practical thickness. GO disturbed the capacitance of FWCNTs, but once reduced, rGO significantly enhanced the capacitance.