

An Activated Carbon and Carbon Nanotube Composite for a High-Performance Capacitor

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A composite of carbon nanotubes (CNTs) and activated carbon (AC) is synthesized for supercapacitor applications by using a simple chemical method. Weight ratio of AC to CNT in the synthesis of the composite is changed from 0.6 to 2. The resultant capacitance increases with increasing weight ratio, but decreases when the ratio reaches 2. Too much AC can isolate the CNTs from one another, resulting in a degradation of the conductive network formed by the connected CNTs, and too little AC results in a surface area that is too small for the best performance of the supercapacitor. The resultant impedance of the composite is consistent with the result for the capacitance. The impedance decreases with increasing weight ratio due to the increase in the surface area due to the presence of AC and then starts to increase when too much AC, compared to CNT, is added to the composite, which is due to the degradation of the conductive network formed by the connected CNTs. A synergic effect of AC and CNT, *i.e.*, the large surface area of AC and the good conducting property of the CNT network, is demonstrated for supercapacitor applications.

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I. INTRODUCTION

Electric double layer capacitors (EDLCs) or supercapacitors (SCs) have become the most promising devices for energy storage devices because of their long life cycle, high power density, high specific capacitance, and environment-friendly products [1]. Although the overall performance of EDLC is determined by the physical properties of electrode and electrolyte materials, the electrode is highly important for the storage and delivery of charges, playing a crucial role in determining the energy and power densities of a supercapacitor which are main parameters for the high performance supercapacitors [2-4].

Activated carbons (ACs) have widely been used as electrode materials in supercapacitors because of their large surface area [5]. Research has shown that charges

stored in pores of 0.5 - 2 nm in size increased with decreasing pore size [6], and AC has mostly micropores [7,8] so that high specific capacitance from AC was expected. However, it leads to limited capacitance due to its relatively poor electrical conductivity. Because of the low electrical conductivity of AC, it gives low power density for the supercapacitor applications. Carbon nanotube (CNT), compared to AC, has high electrical conductivity [9,10] so that AC-CNT composites could be expected to provide a synergic effect on the supercapacitor performance.

In the report, the AC-CNT composites are synthesized by a simple chemical method and characterized for the supercapacitor applications. Weight of CNT is constant, while weight of AC is changed. The capacitances of the composites are evaluated from cyclic voltammetry and Galvanostatic charge and discharge measurement depending on the weight ratio of AC to CNT. The capacitance increases with the weight ratio of AC to CNT, and then decreases or is saturated when the ratio reaches to 2.

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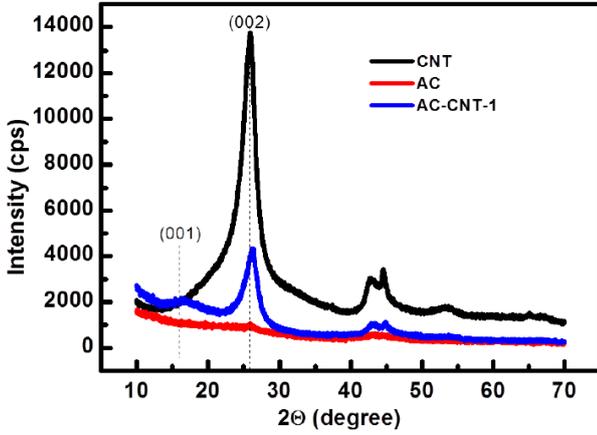


Fig. 1. (Color online) XRD of samples.

II. EXPERIMENTAL

Activated carbon (MSP-20, Kansai Coke and Chemicals, Japan) and Multi-walled CNT (MWCNT, CM-150, 87 - 93% purity, Hanwha Chemical Ltd.) were used without any pretreatment as they were. The weight of AC and CNT were measured with an analytical balance (Precisa XT220A). Three different AC-CNT composites were prepared in the ratio of AC of 0.3, 0.5, and 1.0 g to CNT of 0.5 g. In other words, the weight ratio of AC to CNT was 0.6, 1.0, and 2.0, respectively, in which the different composite was named as AC-CNT-1, AC-CNT-2, AC-CNT-3, respectively. Distilled water of 100 ml was added to each composite, and then the solution was sonicated for 2 h. The solution was then filtered using a vacuum filtration method, and the precipitated composite was dried in an oven overnight. The resultant composite was turned into a powdery form by grinding. The grinded composite was used for the characterization.

The crystalline structure of the composite was analyzed by X-ray diffraction (XRD) at 40 kV with Cu K_{α} radiation ($\lambda = 1.54 \text{ \AA}$), using an automated X-ray diffractometer (D/MAX-2500/PC, Rigaku, Japan). Scanning electron microscopy was used to investigate the morphology of the samples (SEM, S-4300, Hitachi, Japan). The electrochemical properties of the composite were measured using a three-electrode system with 1M H_2SO_4 electrolyte at ambient temperature, where platinum wire was used for a counter electrode and Ag/AgCl electrode was used as a reference electrode. Cyclic voltammetry (CV) was performed with a potential window from 0.0 to 0.8 V with a scan rate of 50

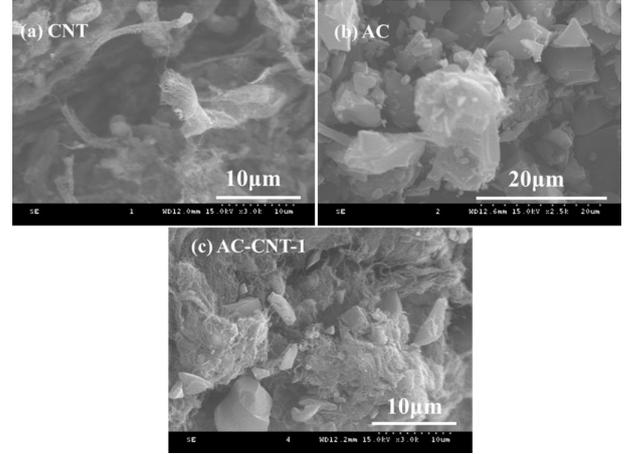


Fig. 2. FE-SEM images of the samples.

mVs^{-1} . The area specific capacitance was calculated from the CV curve using the formula below:

$$C_s = \frac{\int_{V_a}^{V_b} I d\nu}{s.m.\Delta V} \quad (1)$$

where I is the response current, s is the scan rate, A is the electrode area exposed to the electrolyte, and ΔV is the potential window. The current was integrated from 0 to 0.8 V. The current density of 5 Ag^{-1} for Galvanostatic charge and discharge (GCD) cycle was applied, and the specific capacitance was calculated using the formula below:

$$C_s = \frac{I\Delta t}{m.\Delta V} \quad (2)$$

where, I is the response current, m is the mass of the active material on the electrode, ΔV is the potential window, and Δt is the discharge time.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD results of CNT, AC, and the AC-CNT-1 composite. AC displayed an amorphous pattern because of its low crystallinity while CNT and AC-CNT-1 show the (001) and (002) diffraction peaks at 16.2° and 26.6° , corresponding to a d-spacing of 0.91 and 0.33 nm, respectively. This implies that the composite was successfully formed.

Fig. 2 shows the FE-SEM images of CNT, AC and AC-CNT-1. CNT shows long one dimensional structure and makes a bird-nest like structure, as shown

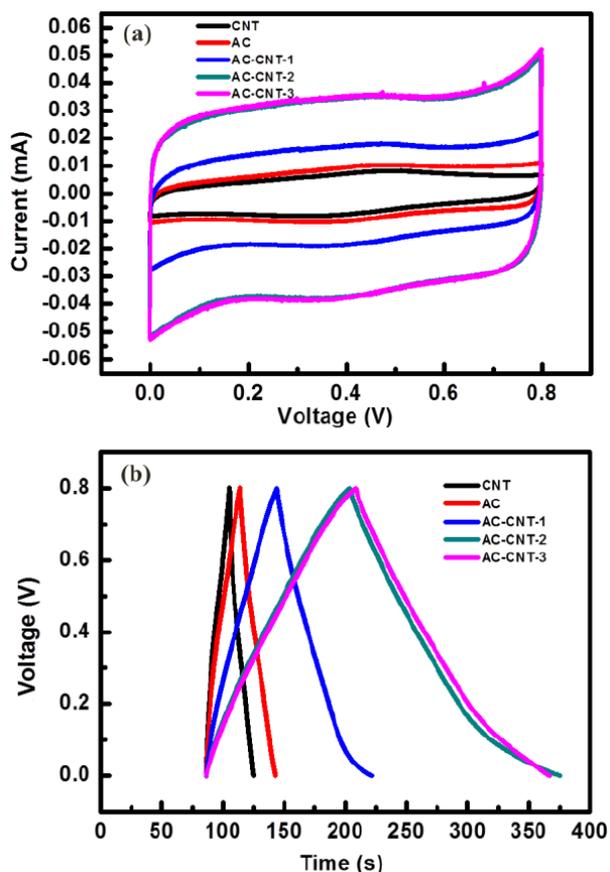


Fig. 3. (Color online) (a) Cyclic voltammetry profiles of the samples at the scan rate of 50 mVs^{-1} and (b) the GCD curves of the samples.

in Fig. 2(a). Morphology of AC is very bulky and shows three-dimensional structure with smooth surfaces in Fig. 2(b). AC-CNT-1 shows both character of CNT and AC in Fig. 2(c). The amount of CNT is more than that of AC shown because AC-CNT-1 consists of AC of 0.3 g and CNT of 0.5 g.

Fig. 3(a) shows the CV results, and the currents of the precursors (CNT and AC) were the smallest compared to the other composite samples, indicating a synergistic effect on the CV results after making the composites from the precursors. AC-CNT-2 shows the largest current among the other composites, and AC-CNT-3 also shows very similar CV curve with AC-CNT-2. The calculated capacitances are 125, 270, and 260 Fg^{-1} for AC-CNT-1, AC-CNT-2, and AC-CNT-3, respectively. The capacitance increased with the weight ratio and was maximized at the ratio of 1. It was then almost saturated at the ratio of 2. This implies that too less AC with respect to

CNT was not good because of low electrical conductivity, and too much AC also makes AC isolated without the conductive network by CNT. It is worth to note that the capacitance of AC and CNT was 36 and 24 Fg^{-1} , respectively.

A similar capacitance was also obtained from the GCD results of Fig. 3(b). The composites showed significantly longer discharging time compared with those of the precursors at the current density of 5 Ag^{-1} , resulting in the high specific capacitance of the composites. The calculated specific capacitances from the GCD results were as follows: 24, 36, 96, 213, and 204 Fg^{-1} for CNT, AC, AC-CNT-1, AC-CNT-2, and AC-CNT-3, respectively. The AC-CNT-2 composite also has the highest capacitance of 212 Fg^{-1} , consistent with the CV results.

To find the transfer kinetics and possible explanation for the difference in the electrochemical performance, electrochemical impedance study was performed. Fig. 4(a) represents the Nyquist plot of the samples. The frequency range was from 0.01 to 500,000 Hz. Slope of the line at low frequency region indicates the diffusion resistance. The composites show low impedance compared to the precursors (CNT and AC), meaning faster ion transportation in the electrodes [11, 12]. Inset of Fig. 4(a) magnified the high frequency region, which is the low impedance region, distinguishing the impedance slopes of AC-CNT-2 and AC-CNT-3. The highest slope of AC-CNT-2 demonstrated the most rapid ion transfer within the pores of the electrodes. Fig. 4(b) and 4(c) represents the Bode plot. Fig. 4(b) shows the variation of phase angle with respect to frequency. The phase angles were $-71, -77, -81, -85$ and -83 degree at 0 Hz for CNT, AC, AC-CNT-1, AC-CNT-2, AC-CNT-3, respectively, meaning that AC-CNT-2 is the closest to an ideal capacitor. Generally, a phase angle approaching to -90 degree represents a good capacitive performance and rapid-charge-discharge process [13]. From the result, AC-CNT-2 had the highest phase angle. Fig. 4(c) shows real impedance as a function of the frequency. The three composites have lower impedance when compared to the precursors, leading to the synergistic effect on the electrochemical performance. It is evident from the plot that AC-CNT-2 had the lowest impedance, and this implies the best electrochemical capacitive performance which is good for supercapacitor applications.

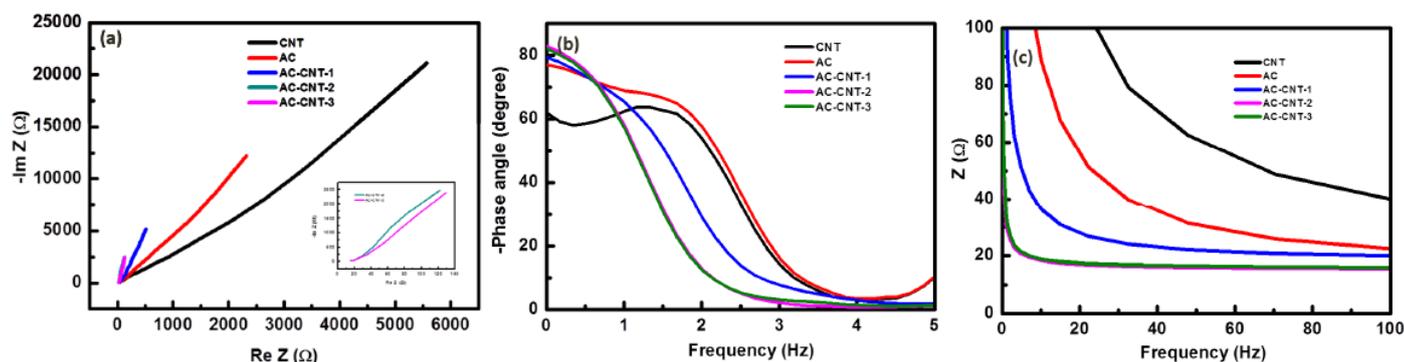


Fig. 4. (Color online) (a) Nyquist plots, (b) Bode plots of phase angle *vs.* frequency, and (c) Bode plot of impedance *vs.* frequency. The inset show the comparison between AC-CNT-2 and AC-CNT-3.

IV. CONCLUSION

The electrochemical properties of the AC-CNT composites were investigated for the supercapacitor applications. AC improved the electrochemical properties of CNT significantly due to the increase of the surface area. The electrochemical impedance of the AC-CNT composites was lower than those of the precursors such as CNT and AC. However, too much AC was not improved the electrochemical performance anymore because of loss of conductive network by CNT. Therefore, proper amount of AC with respect to CNT provides the best electrochemical performance. The capacitance was the highest when the weight ratio of AC to CNT was 1, which was 270 Fg^{-1} . The reports demonstrated that the synergic effect of AC and CNT when the precursors made the AC-CNT composites.

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