

Articles

Synthesis of Carbon Nanofibers Based on Resol Type Phenol Resin and Fe(III) Catalysts

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The carbon nanofibers (CNFs) used in this study were synthesized with an iron catalyst and ethylene as a carbon source. A concentration of 30 wt % iron(III) acetylacetonate was dissolved in resol type phenol resin and polyurethane foam was put into the solution. The sample was calendered after being cured at 80 °C in air for 24 h. Stabilization and carbonization of the resol type phenol resin and reduction of the Fe³⁺ were completed in a high-temperature furnace by the following steps: 1) heating to 600 °C at a rate of 10 °C/min with a mixture of H₂/N₂ for 4 h to reduce the Fe³⁺ to Fe; 2) heating to 1000 °C in N₂ at a rate 10 °C/min for 30 minutes for pyrolysis; 3) synthesizing CNFs in a mixture of 20.1% ethylene and H₂/N₂ at 700 °C for 2 h using a CVD process. Finally, the structural characterization of the CNFs was performed by scanning electron microscopy and a synthesis analysis was carried out using energy dispersive spectroscopy and X-ray photoelectron spectroscopy. Specific surface area analysis of the CNFs was also performed by N₂-sorption.

Key Words : Phenolic resin, Iron(III) acetylacetonate, CVD, Carbon nanofibers

Introduction

A carbon fiber is a fibrous carbon material with > 90% carbon content acquired by the pyrolysis of fibrous organic precursor manufactured from polyacrylonitrile and pitch (asphalt), an oil and coal hydrocarbon residue.

Introduced in the use of filaments by T. A. Edison in 1880, carbon fibers have been developed in the US, Japan, and European countries based on the initial carbon fiber development by Union Carbide Company's Rayon in 1959 to continuous phase carbon fiber in Japan and the UK. In 1971, Toray of Japan succeeded in producing carbon fiber from acryl fiber for high intensity and high elasticity structural material. As such, it is currently widely used, though its development history is short. Average development speed is 30-50% per annum and there is wide range of studies on its stability for use as an advanced composite material reinforcing agent.¹⁻¹⁰

Chemical vapor deposition(CVD) is a carbon fiber deposition technology to form a solid membrane by reacting gas at a certain temperature. This method is used to synthesize carbon fiber by releasing hydrocarbon gas on a deposited plate to form carbon fiber using the apparatus shown in Figure 1. Carbon fiber filaments were manufactured by hydrocarbon pyrolysis in the 1960s. Normally, a catalyst metal is required for growth. The first chemical vapor deposition experiment was conducted to synthesize multiple wall nano tubes on iron particles by resolving acetylene gas. It is advantageous to perform the synthesis on a large size

plate when using this method.¹⁹⁻²²

The source gas, catalyst layer, temperature, and reaction time are important variables when synthesizing carbon fiber using chemical vapor deposition. A sputter and e-beam evaporator are prepared as a thin film for the metal catalyst. Carbon nanofibers (CNFs) are synthesized when nano size particles on the deposited catalyst metal surface are made first. As particle size affects the diameter of the CNFs, it is possible to control CNF diameter by metallic particle size. Source gases are mainly hydrocarbons such as CH₄, CO, C₂H₂, benzene, and toluene and nonreactive gases are used for delivery such as H₂, Ar, and N₂. The synthesis temperature is 600-900 °C, and catalyst metals such as Ni, Co, and Fe are essential for CNF synthesis. Selective CNF synthesis is possible by selective deposition of the metal catalyst.¹⁻⁴

Carbon nanofiber is inorganic synthetic fiber by sustaining shape of organic fiber and by carbonizing with heat welding. As oxygen, hydrogen and nitrogen are extracted during the heating, which reduces weight the carbon nanofiber is

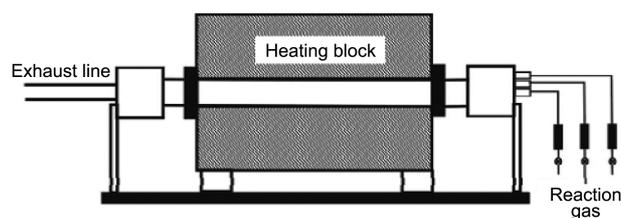
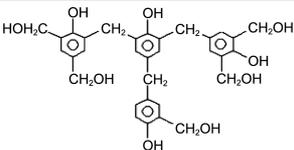
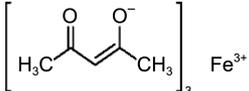
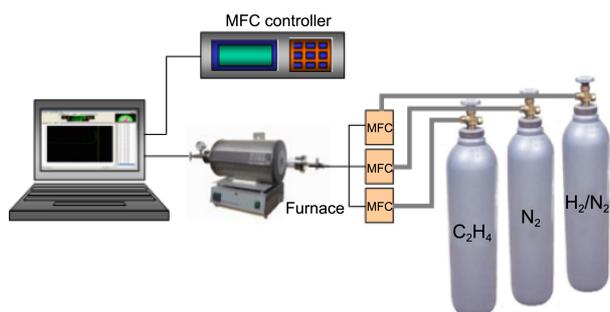


Figure 1. Schematic diagram of the chemical vapor deposition device.

Table 1. Materials used in the experiments

Name of reagent	Molecular formula	Size	Manufacturer
Resol phenolic resin (KR-65)		-	Taeyang Synthetics
Iron(III) acetylacetonate		99%	Merk

**Figure 2.** Apparatus used in the experiments.

lighter than aluminum and has better elasticity and strength than ion.

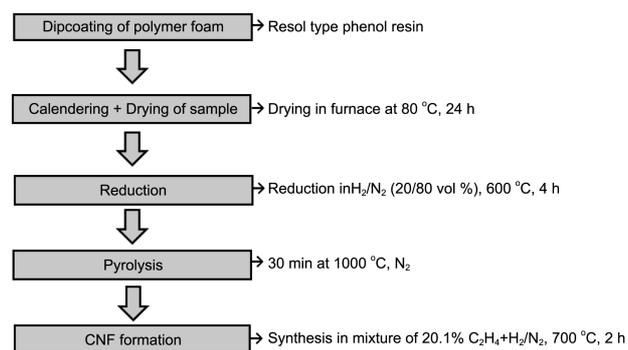
It has excellent chemical stability, electrical conduction, mechanical strength, high hydrogen storage capacity and energy efficiency, and also has extensive specific surface area. Accordingly, it enables comfortable introduction of functional group, atomic or ion reaction, and nano particle absorption. Such physiochemical characteristics can be utilized aerospace plane and automobile industry, energy saving and utilization, electronic measurement and electromagnetic wave and static control area. And it is cost effective due to mass production. With such expectations, this study began to synthesize carbon nanofiber based on resol phenol resin and Fe(III) catalyst.

Experimental

Experimental Materials and Apparatus. Table 1 and Figure 1 show the necessary materials for growing CNFs,

Table 2. Parameters to produce carbon nanofibers (CNFs)

25 PPI Polyurethane foam		
Dipcoating solution	Resol type phenol resin	Resol type phenol resin + 30 wt % Fe (acac) ₃
Dipcoating time	5 min / 30 min / 1 h / 2 h	
Drying	80 °C, 24 h	
Reduction	H ₂ /N ₂ (20/80 vol %), 600 °C (10 K/min), 4 h	
Pyrolysis	N ₂ , 1000 °C (10 K/min), 30 min	
CVD	Reduction in H ₂ /N ₂ RT to 700 °C (10 K/min) CVD in C ₂ H ₄ + H ₂ /N ₂ , 700 °C, 2 h	

**Figure 3.** Synthesis process of carbon nanofibers (CNF) without a catalyst.

and Figure 2 shows the required apparatus. This study used KR-65 resol phenolic resin as the solvent. To deposit iron, iron(III) acetylacetonate was used and a 25 PPI (pores per linear inch) polyurethane form was used as the carbon skeleton material. As gases, H₂/N₂ (20/80 vol %) and high purity N₂ and C₂H₄/N₂ (20.1/79.9%) were used.

Experimental Condition. Table 2 shows the experimental conditions. A dip coating solution with the resol phenolic resin and a dip coating solution with an iron catalyst were tested to identify the role of the catalyst. When catalyst is added, it causes a reduction in activation energy. Thus, when activation energy decreases, the reaction proceeds faster. Dip coating times were set to 5 minutes, 30 minutes, 1 h, and 2 h. The experiment could not continue after 2 h because the polyurethane form melted due to the resol phenolic resin.

Synthesis of Carbon Nanofibers Without a Catalyst.

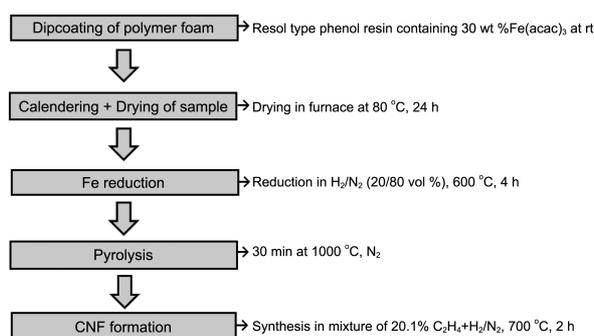
**Figure 4.** Synthesis process of carbon nanofibers (CNFs) supported on iron catalysts.

Figure 3 shows the synthesis process of carbon nanofibers without a catalyst. The resol phenolic resin solution was added to the polyurethane form. The sample was calendered and dried at 80 °C for 1 day in a furnace, followed by reduction in a high temperature furnace using the following process. First, reduce with H₂/N₂ mixed gas for 4 h at 10 °C/min up to 600 °C. Then, pyrolysis occurred for 30 minutes at 1000 °C using high purity nitric gas. Finally, CNFs were synthesized under a 2 h reduction at 700 °C using 20.1% ethylene gas and H₂/N₂ mixed gas.

Synthesis of CNFs with Fe(III) Catalyst. Figure 4 shows the synthesis process of carbon nanofibers supported on iron catalysts. The polyurethane form was put into solution after melting 30 wt % concentration iron(III) acetylacetonate in resol phenolic resin. The sample was calendered and dried at 80 °C for 1 day in a furnace. This was followed by reduction in a high temperature furnace using the following process. First, a reduction with H₂/N₂ mixed gas for 4 h at 10 °C/min to 600 °C to reduce Fe to Fe³⁺. Then pyrolysis was employed for 30 minutes at 1000 °C using high purity nitric gas. Finally, the CNFs were synthesized during a 2 h reduction at 700 °C using 20.1% ethylene gas and H₂/N₂ mixed gas.

Analysis Apparatus. Scanning electron microscopy (SEM, Hitachi, S-4300) was used to determine the change in the appearance of the carbon skeleton based on the experimental stage and the growth and diameter of the CNFs.

Energy dispersive spectroscopy (EDS, ThermoARL, ARL 3460) was used to analyze the carbon components of the nanofibers. An elemental component analysis was conducted on a specific area of SEM at 150×.

X-ray photoelectron spectroscopy (XPS, Multilab-2000) was used to analyze the chemical CNF data.

Specific surface area analyzer (BET, ASAP-2010) was used to measure the surface area (m²/g) of the CNFs.

Results and Discussion

Synthesis of CNFs Without a Catalyst. Two experiments were conducted to determine the role of the catalyst: one used no catalyst, the other used Fe(III) as the catalyst.

Change in Weight: Figure 5 shows the change in each stage of synthesizing CNFs without a catalyst. The reduction in weight was caused by removing moisture and impurities.

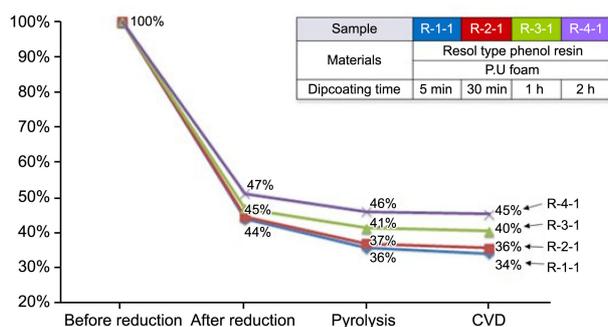


Figure 5. Weight changes in the carbon nanofibers without catalysts.

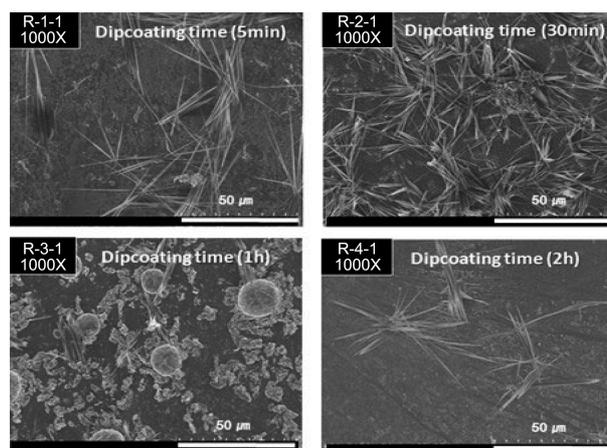


Figure 6. Scanning electron micrographs of carbon nanofibers without a catalyst.

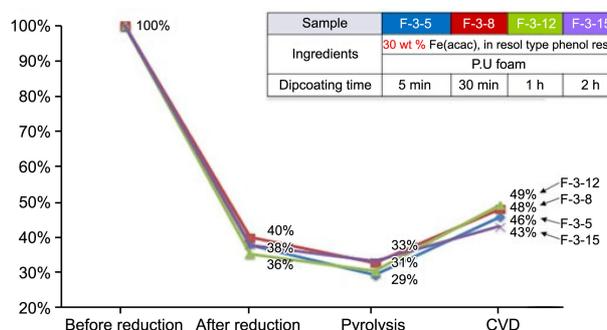


Figure 7. Weight changes in the carbon nanofibers supported on iron catalysts.

At the final CVD stage, the growth of CNFs was determined by the change in weight.

SEM: Figure 6 shows SEM images of synthesized CNFs with resol phenolic resin without a catalyst at the time of dip coating. The results show that spiculate shaped CNFs were synthesized at the time of dip coating. When SEM results are compared with the measured image at the 1000X magnifications, the highest carbon nanofiber with pointed shape was synthesized in 30 minutes of dipcoating.

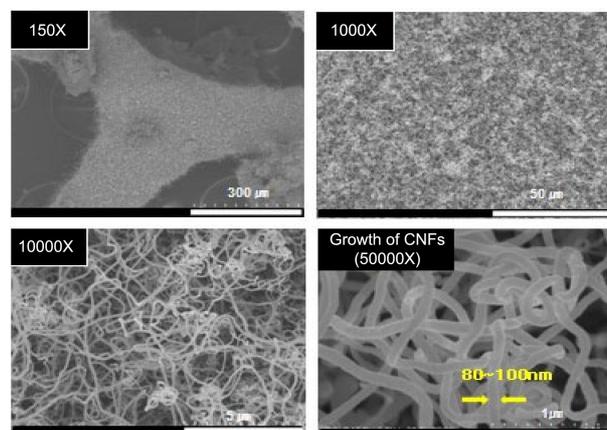


Figure 8. Scanning electron micrographs of samples at 5 min of dip coating time.

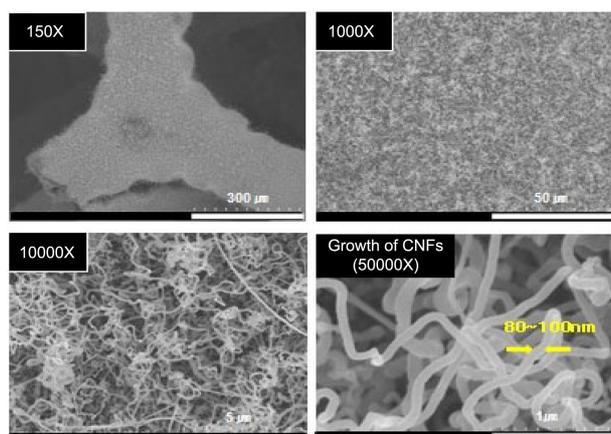


Figure 9. SEM images of samples with 30 min of dip coating time.

Synthesis of CNFs Based on the Fe(III) Catalyst.

Change of Weight: Figure 7 shows the change in each stage of synthesizing CNFs with a catalyst. The reduction in weight was caused by removing moisture and impurities. At the final CVD stage, the growth of CNFs was determined by the change in weight.

SEM: SEM images were measured to determine the growth of CNFs on overall the carbon skeleton shape and surface. Figures 8 and 9 are SEM images at 5 and 30 minutes of dip coating respectively. The overall carbon skeleton can be seen at 150 \times , whereas the overall skeleton surface could be discerned at 1000 \times . Growth of the CNFs was confirmed at 10000 \times . The CNFs had diameters of 80-100 nm at 50000 \times .

Pyrolyzed hydrocarbon synthesized carbon nanofiber by contacting metallic particle such as Fe, Co, Ni at a high temperature. Carbonaceous species which contacts metallic particle forming carbide is melted and goes beyond saturated solubility, the nucleus is formed for the growth, and fibri-form carbon is grown by continual supply of carbon source through internal dissolution carbon inside metallic particle or surface spread of metallic particle.

Carbon nanofiber synthesized in Figure 8 and Figure 9 shows well development of fiber type using iron catalyst.

Figure 10 is an SEM image at 1 h of dip coating. The overall carbon skeleton was shown at 150 \times , and the overall skeleton surface could be discerned at 1000 \times . Growth of CNFs was confirmed at 10000 \times , and the CNFs had 300 nm diameters as measured at 50000 \times .

Figure 11 is an SEM image at 2 h of dip coating. The overall carbon skeleton was shown at 150 \times , and the overall skeleton surface could be identified at 1000 \times . At 10000 \times , growth of the CNFs was confirmed, and the CNFs had 80-100 and 300 nm diameters at the same time under 50000 \times .

When SEM measurements are compared with others according to dipcoating time, it could synthesize carbon nanofiber even diameter between 80-100 nm at 5 minutes and 30 minutes of dipcoating time. On the other hand, when it becomes 1 h and 2 h, it creates larger carbon nanofiber. In particular, when dipcoating time is 2 h, it has both thin and thick diameter carbon nanofiber at the same time. The diameter of carbon nanofiber could be controlled

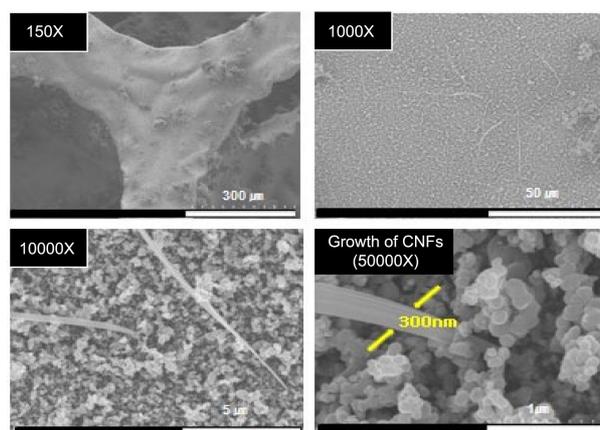


Figure 10. Scanning electron micrographs of samples at 1 h of dip coating time.

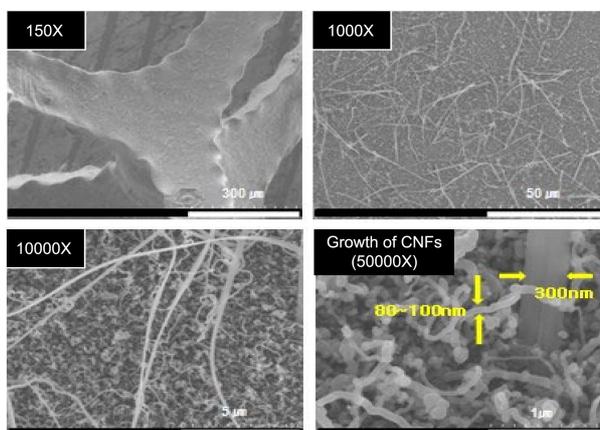


Figure 11. Scanning electron micrographs of samples at 2 h of dip coating time.

according to dipcoating time.

As physical property can vary according to internal structure, diameter can be controlled to fit for a specific purpose.

EDS: EDS was used to analyze the CNF components. The analysis was carried out on a specific area of a 150 \times SEM image. The component element peak was checked from the EDS results in Figure 12.

When dipcoating time is 5 minutes, the average value of each element(%) contains 91.41% of carbon and 8.59% of iron, and if it is 30 minutes, carbon and iron includes 71.18% and 28.82% respectively. When dipcoating time is 1 h, it contains 89.46% of carbon, 6.38% of iron and 4.16% of oxygen. When dipcoating time is 2 h, it contains 59.41% of carbon, 39.42% of iron and 1.17% of oxygen. Both carbon and iron exist together according to dipcoating time. Dip coating increased oxygen, which was measured due to the active contact with oxygen.

XPS: XPS was used to analyze the CNF elements. Figures 13, 14, 15 and 16 analyzed the binding energies of elements for synthesized carbon nanofibers between carbon and iron according to dipcoating time, while Tables 3, 4, 5 and 6 show carbon binding states according to carbon and iron binding energy.

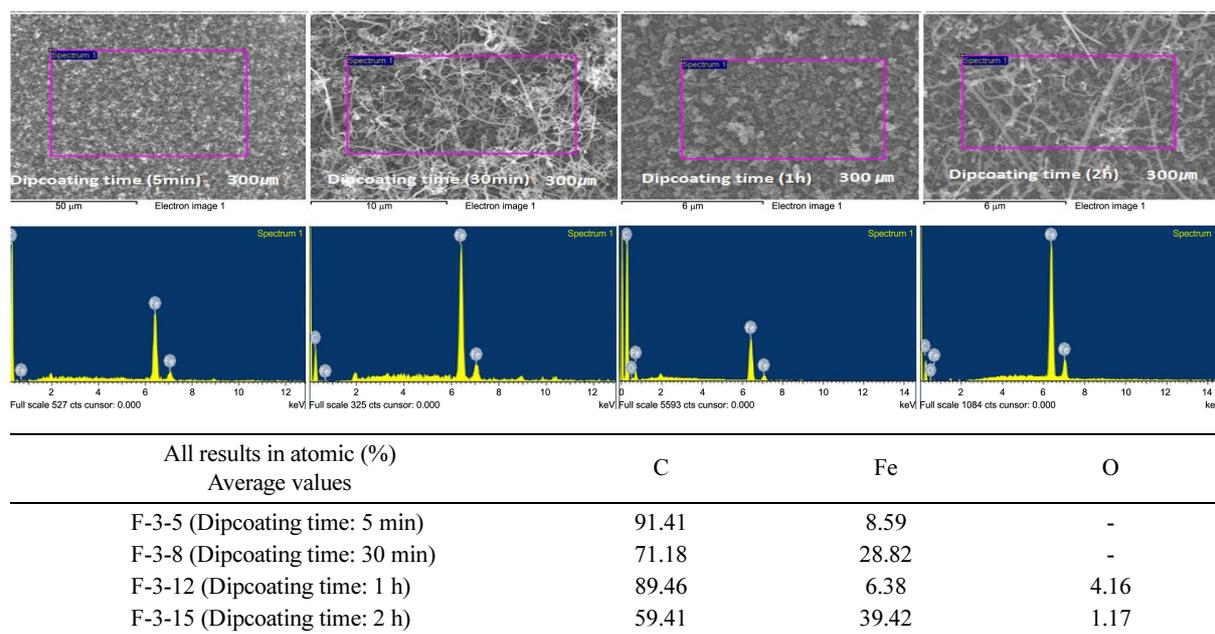


Figure 12. Energy dispersive spectroscopy results of carbon nanofibers.

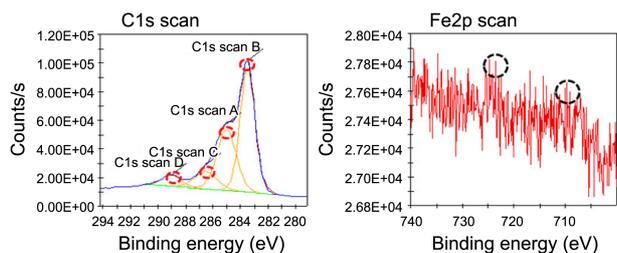


Figure 13. X-ray photoelectron spectroscopy results of samples with a 5 min dip coating time.

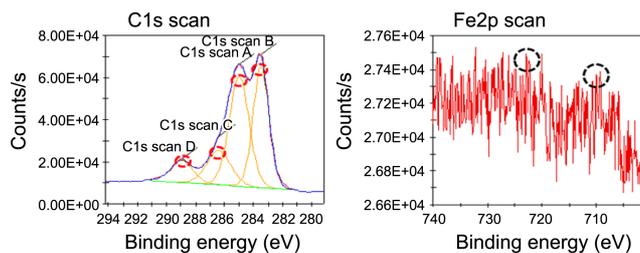


Figure 14. X-ray photoelectron spectroscopy results of samples with a 30 min dip coating time.

Figure 13 and Table 3 show that 283.49 eV was the lowest binding energy at the C1s peak of iron combined with carbon and 285.02 eV was the binding energy of the CNFs. Carbon tape and polluted carbon had peaks at 286.51 eV and 289 eV, respectively. Iron combined carbon had the lowest bond energy, because carbon has higher electronegativity than that of iron to attract more electrons. The binding

energy of the Fe2p peak occurred at 711 eV and 724 eV.

Figure 14 and Table 4 show that 283.49 eV was the lowest binding energy at the C1s peak for iron combined with carbon and 285 eV was the binding energy for the CNFs, whereas 286.39 eV and 288.95 eV were the peaks for carbon tape and polluted carbon, respectively. The peak increased at 5 minutes of deposition among the CNF peaks. The binding

Table 3. X-ray photoelectron spectroscopy results of samples with a 5 min dip coating time

Name	Peak BE	Analysis	Name	Peak BE
C1s Scan B	283.49 eV	C combined with cobalt	Fe2p Scan A	711 eV
C1s Scan A	285.02 eV	C of CNF	Fe2p Scan B	724 eV
C1s Scan C	286.51 eV	C-tape		
C1s Scan D	289 eV	Polluted C		

Table 4. X-ray photoelectron spectroscopy results of samples with a 30 min dip coating time

Name	Peak BE	Analysis	Name	Peak BE
C1s Scan B	283.49 eV	C combined with cobalt	Fe2p Scan A	711 eV
C1s Scan A	285 eV	C of CNF	Fe2p Scan B	724 eV
C1s Scan C	286.39 eV	C-tape		
C1s Scan D	288.95 eV	Polluted C		

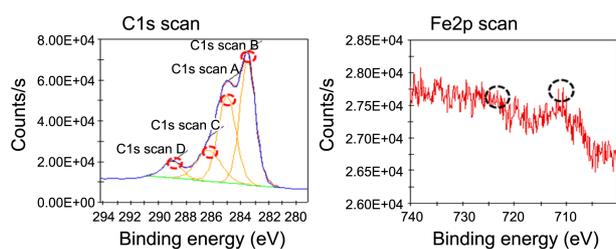


Figure 15. X-ray photoelectron spectroscopy results of samples with a 1 h dip coating time.

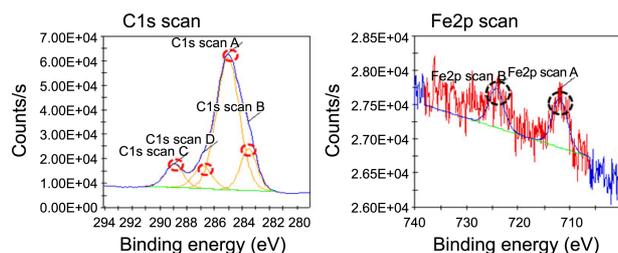


Figure 16. X-ray photoelectron spectroscopy results of samples with a 2 h dip coating time.

energy of the Fe2p peak was 711 eV and 724 eV, respectively.

Figure 15 and Table 5 show that 283.52 eV was the lowest binding energy at the C1s peak for iron combined carbon and that of the CNFs was 285.02 eV. Carbon tape and polluted carbon had peaks of 286.32 eV and 288.97 eV, respectively. The peak increased at 30 minutes of deposition among the CNF peaks. The binding energy of the Fe2p peak was at 711 eV and 724 eV, respectively.

Figure 16 and Table 6 show that 285.03 eV was the lowest

binding energy at the C1s peak for iron combined carbon and that of the CNFs was 285.3. Carbon tape and polluted carbon had peaks of 286.86 eV and 288.94 eV, respectively. The CNF peak was the highest and the combined peak of iron and carbon decreased compared to that in Figure 15. The binding energy of Fe2p peak occurred at 711.92 eV and 724.25 eV, respectively

When Figures 13, 14, 15 and 16 were compared, the peak between iron and carbon reached the highest intensity at 5 minutes, 30 minutes and 1 h. On the other hand, when dipcoating time was 2 h, carbon peak of carbon nanofiber reached to the highest intensity. Majorities were iron-binding carbon and carbon element of carbon nanofiber among carbon binding peaks.

When Tables 3, 4, 5 and 6 were compared according to dipcoating time, the carbon binding energy was measured with 283 eV and 285 eV respectively, which indicates the iron-binding carbon and carbon of carbon nanofiber. The iron binding energy was measured at 711 eV and 724 eV which indicates the iron element which is bound with carbon.

BET: Surface area (m^2/g) of the CNFs was measured using a BET specific area measuring apparatus. Table 7 shows the BET values by dip coating time. At 30 minutes of dip coating, the highest BET surface area was $130 \text{ m}^2/\text{g}$. At dip coating times of 5 minutes, 1 h, and 2 h the BET values were $112 \text{ m}^2/\text{g}$, $95 \text{ m}^2/\text{g}$, and $90 \text{ m}^2/\text{g}$ respectively. The CNFs had a relatively higher BET surface areas.

As carbon nanofiber synthesized based on resol phenol resin and iron catalyst has relatively large specific surface area, it is excellent in saving energy which can be used as electrode materials of capacitor, lead battery and lithium-ion

Table 5. X-ray photoelectron spectroscopy results of samples with a 1 h dip coating time

Name	Peak BE	Analysis	Name	Peak BE
C1s Scan B	283.52 eV	C combined with cobalt	Fe2p Scan A	711 eV
C1s Scan A	285.02 eV	C of CNF	Fe2p Scan B	724 eV
C1s Scan C	286.32 eV	C-tape		
C1s Scan D	288.97 eV	Polluted C		

Table 6. X-ray photoelectron spectroscopy results of samples with a 2 h dip coating time

Name	Peak BE	Analysis	Name	Peak BE
C1s Scan B	283.53 eV	C combined with cobalt	Fe2p Scan A	711.92 eV
C1s Scan A	285.03 eV	C of CNF	Fe2p Scan B	724.25 eV
C1s Scan D	286.86 eV	C-tape		
C1s Scan C	288.94 eV	Polluted C		

Table 7. Carbon nanofiber BET results

Sample	X wt % $\text{Fe}(\text{acac})_3$: X wt % Resin	Dipcoating time	Sample mass	Correlation coefficient	BET surface area (m^2/g)
F-3-5	30 wt % : 100 wt %	5 min	0.0110 g	0.999400	112
F-3-8		30 min	0.0060 g	0.999101	130
F-3-12		1 h	0.0140 g	0.999808	95
F-3-15		2 h	0.0140 g	0.996631	90

secondary battery.

Conclusions

We synthesized CNFs on solid carbon foam called reticulated vitreous carbon (RVC) in a simple experiment without depositing additional catalyst. When the coating was made with the resol phenolic resin on the polyurethane form without a catalyst, some spicule shape CNFs formed. In contrast, when the coating was made with resol phenolic resin in a polyurethane form with 30 wt % Fe(acac)₃, many CNFs were synthesized. Finally, when both H₂/N₂ gas and ethylene gas were released together at the CVD heating stage, no CNFs were synthesized, but CNFs were synthesized when H₂/N₂ gas was released and then ethylene gas was released at the final temperature.

The samples synthesized the most uniform and regular sized CNFs at 5 minutes (F-3-5) and 30 minutes (F-3-8) of dip coating. Among them, samples that received 30 minutes of dip coating (F-3-8) had the highest BET surface area at 130 m²/g.

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