

## 전기방사를 이용한 Ru/PAN-based Carbon/MWCNT 나노섬유 복합체 Web 전극 제조

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**Preparation of Ru/PAN-Based Carbon/MWCNT Nanofiber Composite Web Electrode by Co-electrospinning**

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**1. Introduction**

A supercapacitor attracted much concern in a energy storage / conversion system because it is higher power density than battery and higher energy density than conventional dielectric capacitor [1]. supercapacitor are divided into two type, that is, electrochemical double layer capacitor (EDLC) and pseudocapacitor. Pseudocapacitor is based on the faradic mechanism and use transition metals such as rethenium, manganese, nickel oxides as electrode materials [2]. The RuO<sub>2</sub> of metal oxide showed the best capacitance as about 600 - 650 F/g. But the use of ruthenium oxide has been hesitated because of very high expensive and aomplicated manufactural process. so, many researchers have searched for the methode minimizing ruthenium. It has been studied the methode doping/alloying Ru with substrates as such carbon and carbon nanotube [3-5].

In this study, we prepared RuO<sub>2</sub>/carbon-MWCNT composites by co-electrospinning the mixed solution of both polyacrylonitrile (PAN), multi-walled carbon nanotube and ruthenium chloride hydrate (RuCl<sub>3</sub> · xH<sub>2</sub>O) in N,N-dimethylformamide (DMF). The RuO<sub>2</sub>/carbon-MWCNT nanofiber web was synthesized through stabilization, carbonization and activation. The electrochemical property of the nanofiber composite web as the electrode was carried out.

**2. Experimental****2. 1. Materials and co-electrospinning**

The multi-walled carbon nanotubes (called as MWCNT) was supplied by the Iljin Nanotech Co. (Korea). Polyacrylonitrile (PAN), N,N-dimethylformamide (DMF) and ruthenium chloride hydrate (RuCl<sub>3</sub> · xH<sub>2</sub>O) were purchased from Aldrich Chemical Co. The MWCNT was sonicated for 2 h with homogenizer (Ulso Hi-tech, Korea) in order to disperse the MWCNT before mixing with PAN. The 10 wt.% composite solution was prepared by mixing PAN and 10 to 20 wt.% RuCl<sub>3</sub> · xH<sub>2</sub>O with MWCNT dispersed in DMF. The content of MWCNT was fixed as 3 wt.%. The composite solution was spun into fiber web through a positively charged capillary using an electrospinning apparatus (NT-PS-35K, NTSEE Co., Korea). The electrospun fiber was collected on an attached aluminum foil wrapped on a metal drum rotating at approximately 350 rpm.

## 2.2. Stabilization, activation and characterization

The electrospun nanocomposite fiber web was stabilized by heating up to 280 °C at a rate of 1 °C/min and holding for 1 hr under an air atmosphere and then it was carbonized at 800 °C in the nitrogen atmosphere. The carbonized fiber webs were heated up to 800 °C at a rate of 5 °C/min and activated by supplying 30 vol.% steam for 1 hr in a nitrogen carrier gas. The micro-textural characterization of the nanostructured materials was performed by SEM.

## 2.3. Electrochemical test

Two-electrode supercapacitor cells were fabricated with two 1.5 x 1.5 cm<sup>2</sup> electrodes, a polypropylene separator (Cellgard 3501, Scimat Co., UK), and a Ni 50 nm foil as a current collector soaked in 6 M KOH aqueous solution. The electrochemical characteristics were evaluated by a galvanostatic charge/discharge and cyclic voltammetry (CV). The cell capacitance is calculated from the slope of the discharge on the basis of the equation (1)

$$C = i(t/V) \quad (1)$$

where C is the capacitance of the cell in farads; i is the discharge current in amperes (A); and t is the discharging time from 0.54 V to 0.45 V (about 50~60 % of the initial potential), V is the potential variation in the time range measured, the slope in volts per second (V/S). In a symmetrical system, the specific capacitance C<sub>m</sub> in farads per gram of samples (F/g) is related to the capacitance of the cell C in terms of the equation (2)

$$C_m = 2C/m \quad (2)$$

where m is the weight (g) per electrode of samples.

The CV of the unit cells were performed in the potential range of 0 to 0.9 V at a scan rate ranging from 1 to 500 mV/sec.

## 3. Results and discussion

Fig. 1 shows the SEM images of carbon nanofiber, and the diameter was distributed as about 500 nm. Fig. 1(a) was the SEM images of carbon-MWCNT nanofiber web. The fiber were wrinkled and showed that MWCNT was exposed on the surface of fibers. Fig 1(b)-(d) were that the content of RuO<sub>2</sub> was to be added 10, 15, 20 wt.%, respectively. The RuO<sub>2</sub> is dispersed as the particle phase on the carbon composite nanofibers. Table 1. is the element analysis of EDX about RuO<sub>2</sub>/PAN-based carbon nano-comp Fig. 2 is the XRD patterns of RuO<sub>2</sub>/PAN-based carbon nanofiber composite web with the contents of RuO<sub>2</sub>. Two peaks of  $\theta = 24$  and  $42^\circ$  is in existence in pure carbon as shown in Fig. 2(a). This mean the PAN-based carbon is crystallized. As the contents of RuO<sub>2</sub> is increased as shown in Fig. 2(b)-(d), the carbon peaks is disappeared in RuO<sub>2</sub>/carbon-MWCNT nanofiber composite web, while the RuO<sub>2</sub> peak is formed. The cyclic voltammograms (CV) of nanostructured electrodes with various contents of RuO<sub>2</sub> is compared in Fig. 3, with keeping a potential window of 0 to 0.9 V. The voltametric curve of carbon-MWCNT show the typical double layer capacitance, but the evidence of redox process shows as the content of RuO<sub>2</sub> increases. The area of current increases with increasing the content of RuO<sub>2</sub>. Fig. 4 shows the specific capacitances of the nanocomposite samples as a function of the content of RuO<sub>2</sub>. The capacitance of the nanostructured electrodes is determined from the dc discharge with a 0.9 V potential window of capacitor device. The specific capacitances of carbon-MWCNT composite is 180 F/g, while that of 10, 15 and 20 wt% RuO<sub>2</sub>/carbon-MWCNT electrodes is 323, 450 and 500 F/g, respectively. The addition of RuO<sub>2</sub> offers the electrochemical enhancement of more than 2.8 times (500/180). The reasons for this that the carbon-MWCNT exhibits only the behavior of double layer

capacitance, while the electrode added RuO<sub>2</sub> displays both double layer and pseudocapacitance. In addition, this leads to process of non-faradaic and faradaic.

#### **4. Conclusions**

The nanofiber web was prepared to do a co-electrospinning the mixed solution of polyacrylonitrile (PAN), MWCNT and ruthenium chloride hydrate (RuCl<sub>3</sub>·xH<sub>2</sub>O) in N,N-dimethylformamide (DMF). The RuO<sub>2</sub>/PAN-based carbon-MWVNT nanofiber web was synthesized through stabilization and activation. The diameter of nanofiber was below 500 nm, and the specific capacitance was 500 F/g.

#### **Acknowledgements**

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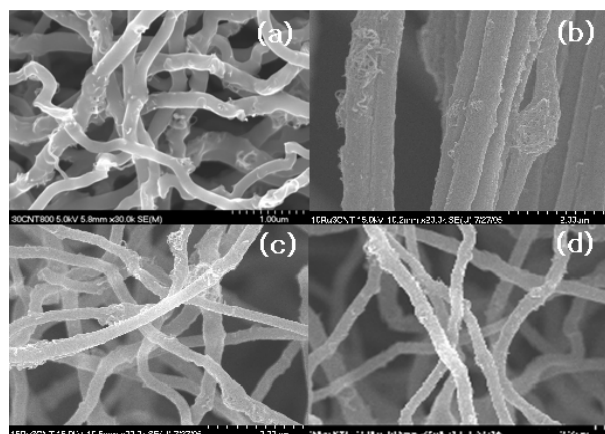


Fig. 1. SEM images PAN-based carbon (+3wt.%MWCNT) / RuO<sub>2</sub> composite nanofibers with the contents of RuO<sub>2</sub>

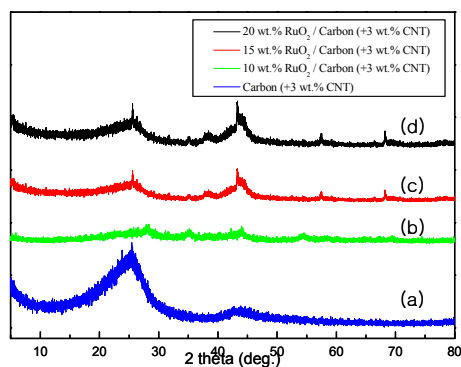


Fig. 2. XRD patterns of PAN-based carbon (+3wt.% MWCNT) / RuO<sub>2</sub> composite nanofibers with the contents of RuO<sub>2</sub>

Table 1. Elemental analysis of EDX with the contents of RuO<sub>2</sub>

Content \ Element	0 wt. %	10 wt. %	15 wt. %	20 wt. %
C	95.25	87.37	83.75	73.59
O	5.75	8.30	10.31	16.14
Ru	•	4.33	5.94	10.27
Total	100.0	100.0	100.0	100.0

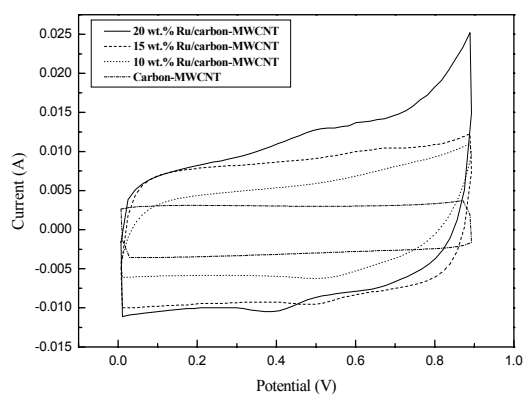


Fig. 3. Cyclic voltammograms of carbon/RuO<sub>2</sub> composite nanofibers with the contents of RuO<sub>2</sub>.

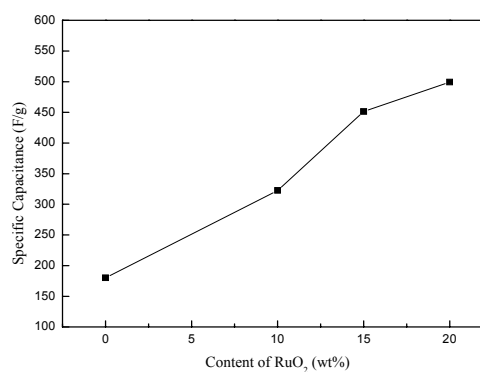


Fig. 4. Specific capacitance of carbon/RuO<sub>2</sub> composite nanofibers with the contents of RuO<sub>2</sub>.