

# Electrochemical Properties of PPy/CNT Electrodes Prepared by Chemical Process for Ultracapacitor

Jeong-Gyun Shin and Soo-Gil Park<sup>†\*</sup>

Department of Ind. Chemical Engineering, Chungbuk National University, 12 Kaeshin, Heungduk-gu, Cheong-Ju, 361-763, Korea

<sup>†</sup>Research Center for Energy Conversion and Storage, Kwanak-gu and Seoul 151-742, Korea

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**Abstract :** Polypyrrole(PPy) was composite with MWNT to attain cycle stable by chemical method. We have been considered PPy is the ideal material for high energy density electrochemical capacitor due to pseudo capacitor reaction. In this study we found that increase in cycle life due to composite MWNT. Also PPy/MWNT composite material have resulted larger capacitance and exhibits better electrochemical behavior. The structural feature was investigated by using SEM and TEM. The PPy/CNT composite is not only a promising ultracapacitor material for energy storages but also has a good possibility because of its great capacitive properties, simple preparation and low cost.

**Keywords :** Electrochemical capacitor, Polypyrrole, Carbon nanotube, Composite material.

## 1. Introduction

Ultra capacitors are known as electrochemical capacitors, with high power density characteristics and longer cycle life time than secondly batteries, has great deal of attention in the modern society. Because of the electrical vehicles, developed potable devices and generation of power sources have pushed the development of high performance ultra capacitors as the urgent requirement.<sup>1,9)</sup> Based on the mechanisms of electrode material, ultracapacitors can be divided into two categories: Electric double-layer capacitor (EDLCs), whose mechanism of energy storage primarily involves charge stored within the electric double layers at the accessible surface area/solution, have been the subject of intensive investigation. it's important in this capacitor that high specific surface area, low cost and high durability so they are using carbon blacks, glassy carbons, activated carbons, meso carbon micro beads, carbon nanofibers, carbon nanotubes.<sup>6)</sup> But carbon material's limit of capacitance deters its high surface area. Pseudo capacitor, in which using electroactive materials with several redox states or structures, such as hydrous metal oxide, transition metal oxide and conducting polymer, show a similar charge storage mechanism of secondly batteries but they have extremely high reversibility of the superficial redox couples of certain electroactive materials. Especially ruthenium oxides are an excellent material with a remarkable high specific capacitance value, great wide potential range over reversible redox reaction. But the high cost of ruthenium metal has retarded its commercial acceptance as electrochemical capacitor. Other cheap metal oxide with equivalent capacitive characteristics is needed to be developed.

$\pi$ -conjugated polymer, such as polypyrrole, polyaniline and

polythiophene, they have relatively stable, high electrical conductivity. And they are an attractive class of electrode materials to be used in ultra capacitor due to their advantageous properties including very low cost effectiveness compared to noble metal oxide, high charge densities compared to high surface carbon, easy synthesis through chemical and electrochemical processing.

Especially polypyrrole has been the most widely studied conducting material for electrochemical capacitor. Because of their porous particles, high surface roughness, play a crucial role in high capacitance. And it's to enable local ion transfer process.<sup>2)</sup> However polypyrrole's dynamic properties are poor, particularly the long-term stability during cycling is a major demand for an industrial application. Conducting polymer suffer volumetric change on insertion/deinsertion of ions through cycling. Cause their degradation. Thus, the mechanical stress in the polymer relates directly with the cycle life of polymer based capacitor.<sup>1)</sup> So many researchers always try hard to solve this problem.<sup>1,6)</sup> For example, a combination of conducting polymer and insulating polymers with good mechanical properties or conducting polymer are deposited as a thin coating on supporting substrate. However, also such methods showed limitation of cycle life. And the preparations of these composites are usually complicated also need high cost. So in this paper, we tried to solve this problem by composite material using CNT. We expect PPy/CNT electrode has good long-term stability during cycling. The PPy/CNT electrodes not only showed good cycle life also good mechanical properties and great electrochemical performance.

## 2. Experimental.

### 2.1 Reagent

Pyrrole (98%) from Aldrich, Iron(III) Chloride (KANTO

\*E-mail: sgpark@cbnu.ac.kr

Chemical), Nitric Acid(60~62.0% Assay) from MATSUNDEN Chemical LTD, Super-P (Denki Kagaku Kogyo Co., Japan) as conducting material, and NMP(N-methyl-2- pyrrolidinone, Kanto Chemical Co. Inc. 99%) as solvent in electrode slurry, The multi-walled carbon nanotubes ( MWNTs, diameter 10-20 nm, length 10-50  $\mu\text{m}$ , BET surface area 400  $\text{m}^2/\text{g}$  ) were obtained from ILJIN Nanotech.

## 2.2 Electrode preparation

20 wt.% ethanol solution was examined as possible solvents for chemical polymerization.  $\text{FeCl}_3$  was used as the oxidant. Purified nanotubes were refluxed with concentrated nitric acid (11.8N) for 24 h at 80°C, and then washed with distilled water by filtration followed by rinsing with distilled water and drying at 60 °C, and then were treated ball milling. The ball milling treatments were performed for 48 h at room temperature. Weighted amount of the distilled pyrrole was dissolved in 20 wt.% ethanol solution along with continuous stirring at 4°C. PPy/CNT composites were prepared by immersion of MWNT into an aqueous solution of the monomer and by addition of an oxidant and dopant to this solution. PPy and PPy/CNT activate materials were used to knife casting over carbon paper substrates. Rectangular electrode, 1 cm \* 1 cm were used for three-electrode cyclic voltammetry studies in 1M  $\text{H}_2\text{SO}_4$ .

## 2.3 Electrode characterization

The binder free composite electrodes were electrochemically characterized in a three-electrode cell configuration in 1M  $\text{H}_2\text{SO}_4$ , and the capacitive properties of the composites were investigated by cyclic voltammetry method (PGZ 301 Volta lab). Electrochemical impedance spectroscopy(EIS) on a frequency response detector driving the PGZ 301 (Volta Lab). The morphology of PPy/MWNTs were followed by scanning electron microscopy(SEM) in a JEOL 6400F apparatus and transmission electron microscopy(TEM).

## 3. Result and discussion

Fig. 1 shows the FT-IR spectrum of (a) CNTs and (b) PPy/CNTs composite. The strong peak at 3428  $\text{cm}^{-1}$  implied the N-H stretch in pyrrole. The peak at 1548  $\text{cm}^{-1}$  and 1172  $\text{cm}^{-1}$  were due to the Conjugated double bond and Amines in pyrrole, respectively. C-H peak did not exist at 720  $\text{cm}^{-1}$  that detected in the pyrrole(monomer) spectrum, but absent in the polymer spectrum. It's indicating that the polypyrrole are completely coated with CNTs.

The morphology of PPy/CNTs composite with various pyrrole molecular was examined by TEM(transmission electron microscope) and SEM(scanning electron microscope) in Fig. 2. Fig. 2 shows TEM images of bare CNT (a) and PPy coated CNT (b) 0.01 M (c) 0.03 M (d) 0.05 M (e) 0.1 M and SEM image of PPy coated CNT (f) 0.3 M in 20% aqueous ethanol using different monomer concentration. TEM images of PPy/CNTs composites show various thickness by different pyrrole molecular. The nanotube's entangled network is highly porous with interconnectivity. 0.01 M PPy/CNTs composite(b) have a

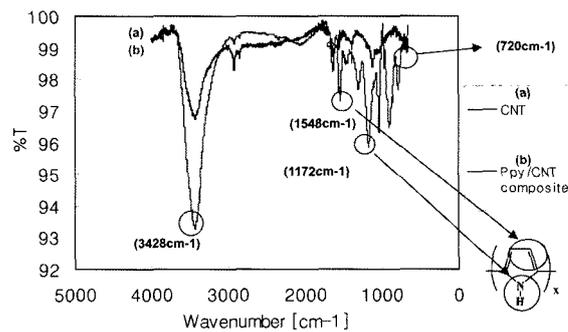
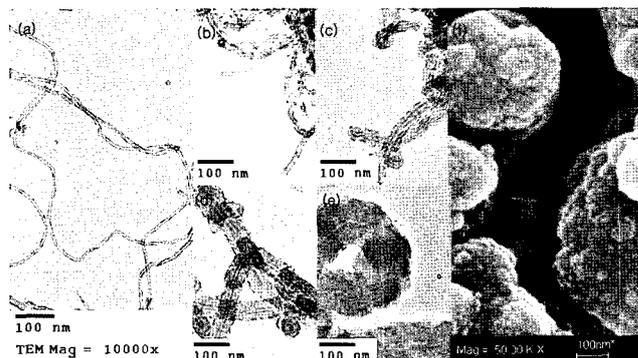


Fig. 1. The FT-IR spectrum of (a) CNTs and (b) PPy/CNTs composite.



Mag = 10.00K X TEM images of bare CNT (a) and PPy coated CNT (b) to (e) Mag = 50.00K X SEM images of PPy coated CNT (f)

Fig. 2. TEM images of bare CNT (a) and PPy coated CNT (b) 0.01 M (c) 0.03 M (d) 0.05 M (e) 0.1 M and SEM image of PPy coated CNT (f) 0.3 M in 20% aqueous ethanol using different monomer concentration.

diameter about 20 nm. It's can be seen that PPy/CNTs composite became thicker as concentration of pyrrole monomer solution increase. But in case of 0.3 M PPy/CNTs composite(f), It's look so pure PPy. This composite material, which made by higher solution than 0.3 M PPy presented a texture similar to that of the pure polymer. 0.05 M PPy/CNT composite exhibits maximal capacitance and high power density. In case of other molecular PPy/CNT composite material, PPy was coated CNT much too thin or thick. Pseudo capacitor, charge is store within the electric double layer and bulk near surface. If PPy is coat CNT much too thin, surface area to be large. But it's occurs limitation of bulk reaction. If PPy is coat CNT much too thick, surface area to be small and non-activation area is create within bulk. So we think that thickness of PPy on CNT at 0.05 M PPy/CNT composite is optimal in this study.

Fig. 3 shows the cyclic voltammograms of PPy electrode before CV and 100 cycles. Cyclic voltammetry was carried out at 100 mV/s in the potential range from -0.2 to 0.8 V for 100 cycle. The capacitance calculated from the cyclic voltammograms of PPy electrode before CV is 100.9 F/g. but after 100 cycle, it is 76.8 F/g. There is a big decrease in the specific capacitance value in the first 100 cycles. This capacitance loss indicates the electric conducting polymer degradation.

So we tried that the electrode fabrication process based on

carbon nanotube with a polypyrrole. Fig. 4 shows Cyclic voltammogram of 0.05 M PPy/CNT: Super-P=9:1 electrode. Cyclic voltammetry was carried out at 100 mV/s in the potential range from -0.2 to 0.8 V for 100 cycle. PPy/CNT composite electrode has good stability during 100 cycles. The conductivity and dispersion of polypyrrole is improved obviously by CNTs.

The loss of capacitance values during cycling for the PPy electrode is shown in Fig. 5 The capacitance calculated from voltammograms. Cyclic voltammetry was carried out at 50 mV/s in the potential range from -0.1 to 0.7 V for 1200 cycle. From the experimental data presented in Fig. 5, PPy electrode's total loss of about 46.8% of the maximum discharge capacitance is found after 1200 cycle. and PPy/CNT electrode's total loss of about 12.1% of the maximum discharge capacitance is found

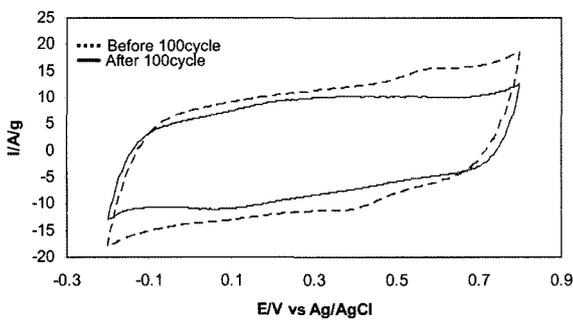


Fig. 3. Cyclic voltammogram of PPy electrode. Cyclic voltammetry was carried out at 100 mV/s in the potential range from -0.2 to 0.8 V for 100 cycle.

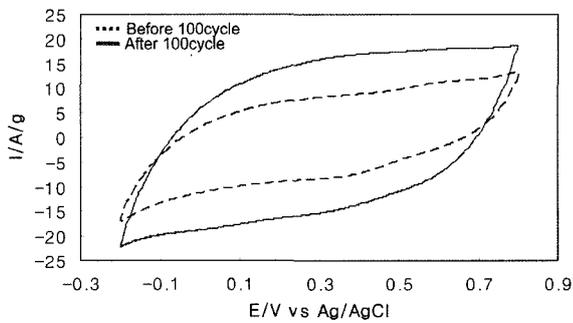


Fig. 4. Cyclic voltammogram of 0.05 M PPy/CNT electrode. Cyclic voltammetry was carried out at 100 mV/s in the potential range from -0.2 to 0.8 V for 100 cycle.

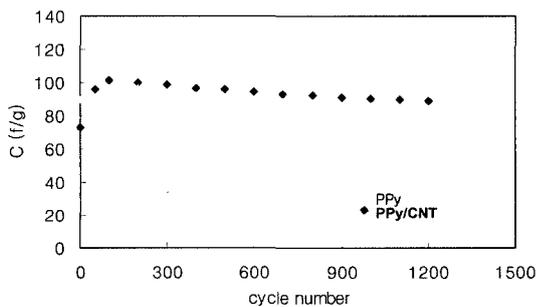


Fig. 5. Specific capacitances of PPy, PPy/CNTs electrode as a function of the cycle number.

after 1200 cycle and it showed the highest power capability. PPy/CNT electrode exhibited higher specific capacitance with a slight decent than PPy electrode during 1200 cycle. It should be concluded that the cycling life of capacitor increases dramatically after composted MWNT as activate material. Thus, PPy/CNT electrode presents a better cyclic performance than the PPy electrode.

Fig. 6 shows the cyclic voltammograms of CNT electrode and PPy/CNT electrode. Cyclic voltammetry was carried out at 50 mV/s in the potential range from  $\Delta$ 0.8 V. For PPy/CNT electrode, cyclic voltammogram with rectangular-like shape is observed at high scan rate (50 mV/s). The capacitance calculated from the cyclic voltammograms of CNT electrode is 29.8 F/g and the PPy/CNT electrode's is 121 F/g. This implies that PPy/CNT electrode has better capacitive performance than CNT electrode.

CNT, PPy, PPy/CNT electrode were prepared and tested by impedance spectroscopy in three-electrode mode. Nyquist plot of electrode(Fig. 7) shows a good capacitor-like behavior with a small diffusion limitation. The internal resistances at 10 kHz for capacitors built from CNT, PPy and PPy/CNT electrode were 1.67, 1.83 and 1.59  $\Omega$ cm<sup>2</sup> respectively. From this curve, we can see decrease of PPy's resistance after modified with CNTs, and internal resistance of PPy/CNT composite is smaller than that of PPy electrode.

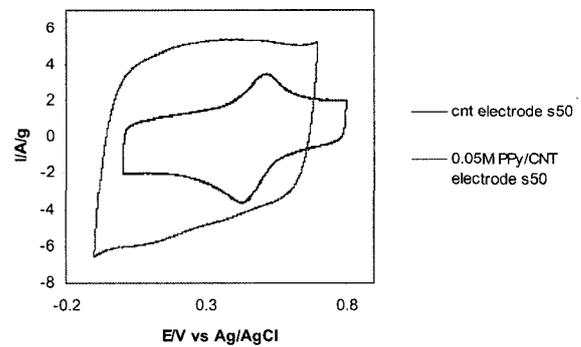


Fig. 6. Cyclic voltammograms of CNT and 0.05 M PPy/CNT electrode. Cyclic voltammetry was carried out at 50 mV/s in the potential range from -0.1 to 0.7 V.

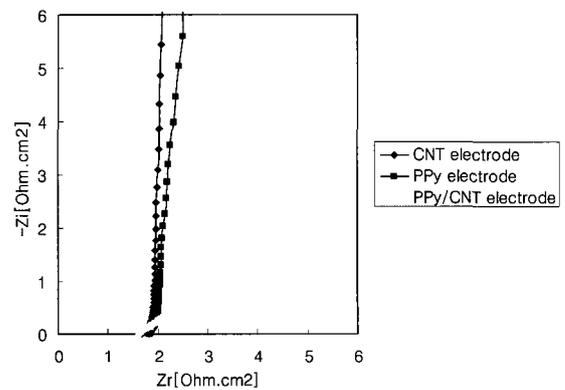


Fig. 7. Nyquist plots of CNT, PPy, PPy/CNT electrode. (100 kHz~10 MHz)

#### 4. Conclusion

Our study on polypyrrole for the supercapacitor applications demonstrates by chemical deposition of PPy on MWNT. PPy/CNT electrodes have greater performance than that of pure PPy electrode. Especially this composite shows excellent long cycle stability. The PPy/CNT composite's specific decline 46.8% after 1200 cycle on the other hand, The PPy/CNT composite's only decline 12.1% after 1200 cycle. It is ascribed to the PPy are distributed in the CNTs' matrix and covered uniformly on the surface of CNTs because of synthesized at low temperature. The PPy/CNT composite is not only a promising ultracapacitive material for energy storages but also has a good possibility because of its great capacitive properties, simple preparation and low cost.

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