

Capacitance behaviors of conducting polymer-coated graphene nanosheets composite electrodes containing multi-walled carbon nanotubes as additives

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Article Info

Received 23 February 2017

Accepted 8 May 2017

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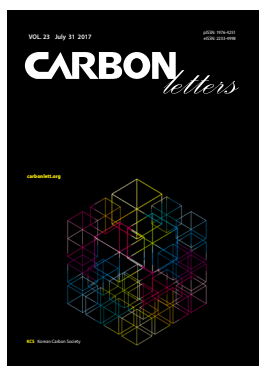
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Open Access

DOI: <http://dx.doi.org/10.5714/CL.2017.23.063>

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<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

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Global warming is rapidly becoming a major concern as a result of the continuing emissions of greenhouse gases generated by the combustion of fossil fuels. To resolve this problem, various studies on efficient energy storage devices have been undertaken. Electronic technologies are increasingly used in electronic products and systems, and they require effective energy storage [1,2]. Supercapacitors are energy storage devices with high power density and long cycle life, and have been spotlighted in recent years because of their promising applications in portable devices, electric vehicles, transportation systems, digital devices. The two main types of electrochemical capacitors are electrical double-layer capacitors (EDLCs) and pseudo-capacitors. The operating mechanism of the electric double-layer capacitors depends on the pore structure of the electrode materials, while the operating mechanism of pseudo-capacitors is based on their active electrode materials, where faradic redox processes occur [3-6]. In EDLCs, the charge is stored by an electric double layer at the electrode-electrolyte interface. The charge storage mechanism is a non-Faradaic process, and carbon-based materials such as 2-D graphene and 1-D carbon nanotubes (CNTs) are frequently employed as the electrode material for this type of supercapacitor. Because of the electrical charge separation at the interfaces between the electrically conductive electrode and the electrolyte, they exhibit high power density [7,8]. In pseudo-capacitors, to accommodate the fast and reversible redox reaction process, transition metal oxides [9,10] or conducting polymers [11-13] are used as electrode materials, and capacitance is formed at the interface of the electrode and electrolyte by a reversible faradaic process. To enhance their energy performance, a recent trend in supercapacitor research has focused on hybrid capacitors, which combine pseudo-capacitance materials with a double layer capacitor [14-16]. To develop supercapacitors with high performance, various materials have been examined as possible electrode materials. Among them, graphene and other carbon-based materials, which have a large surface area, good mechanical properties and high conductivity, have been most widely used [17,18]. Graphene, a two dimensional one-atom-thick planar sheet of sp² bonded carbon atoms, exhibits excellent electrical and mechanical stability, and large specific surface area. Another carbon-based material, CNTs, are known for their outstanding physical properties, but they also have problems with agglomeration and water-insolubility, which impedes their homogeneous dispersion in a polymer matrix. Many studies have investigated ways of modifying CNTs to address these limitations, and their application in supercapacitor electrodes [19,20]. Conducting polymers are well known as supercapacitor electrode materials because of their simple preparation, good conductivity, low cost, fast redox rate, and relatively high capacitance. However, their electrochemical performances are limited by poor cycling stability, and the structure of the materials can be easily damaged during the redox processes [21,22]. To solve these problems, polypyrrole (PPy) and composites formed with various carbon-based materials, including graphene nanosheets (GNS) and multi-walled carbon nanotubes (MWCNT), have been studied as electrode materials for supercapacitors to produce high specific capacitance and long cycling stability. To prepare PPy/GNS

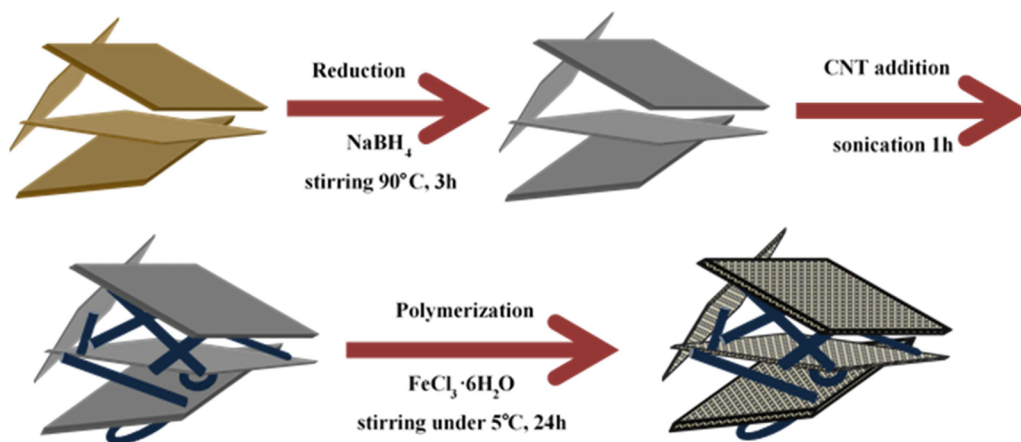


Fig. 1. Schematic diagram of the synthesis route of the PPy/GNS/MWCNT composites. PPy, polypyrrole; GNS, graphene nanosheets; MWCNT, multi-walled carbon nanotubes.

composites, the in situ chemical oxidative polymerization of pyrrole has been attempted in the presence of graphene. We considered adding MWCNTs into such PPy/GNS composites. By adding MWCNTs, it was expected that the undesirable GNS restacking could be reduced by the fiber-like CNTs, acting as spacers. Another effect would be the development of an electron conduction path based on networks of the highly conductive MWCNTs. Furthermore, the combination of PPy and GNS were expected to provide synergetic effects, including the prevention of agglomeration or restacking of the graphene layers, as well as enhancement of the pseudo-capacitance of the PPy itself. As a result, the composites would be expected to induce higher electrochemical performance, such as enhanced capacitance. For synthesizing composite material, graphite oxide (GO) was synthesized by the modified Hummers and Offeman method [23] as previously reported [24]. First, graphite powder (1 g), NaNO_3 (1 g), and 46 mL H_2SO_4 were put into an Erlenmeyer flask in an ice bath to prevent increasing temperature. After stirring for 15 min, KMnO_4 (5 g) was added to the mixture and the mixture was stirred again for 15 min at 35°C for 2 h. The mixture became a brownish solution after the addition of 140 mL H_2O , and the color of this solution changed into bright yellow after adding 5.2 mL of 30% H_2O_2 . The resultant solution was filtered and washed with hydrochloric acid. The products were washed with distilled water and ethanol, and then freeze-dried overnight. 0.1 g of the prepared GO was dispersed in 100 mL distilled water. Then the GO solution was sonicated for 90 min. Then the GO solution was reduced with sodium borohydride (NaBH_4) as described elsewhere [24]. It was stirred at 90°C for 3 h and then the reaction mixture was filtered and washed several times with ethanol and water. Finally, black powders were obtained after being freeze-dried for 24 h. PPy/GNS/MWCNT composites were synthesized by a facile chemical polymerization of pyrrole. Firstly, 0.5 mL of pyrrole and certain amounts of GNS and MWCNT were dispersed in 100 mL of 0.2 M hydrochloric acid. The added amounts of GNS and MWCNT were various weight percent per weight of pyrrole, and the samples were designated PPy/GNS/MWCNT. Then the mixture was sonicated for 1 h to obtain a homogeneously

dispersed solution. Then, 6.08 g of ferric chloride hexahydrate dissolved in 60 mL of 0.2 M hydrochloric acid was dropwise added into the above solution. The oxidation polymerization process lasted for 24 h in the ice bath. We finally obtained and collected black deposits which were washed sequentially with ethanol and water several times and dried in a vacuum oven at 60°C for 12 h. For comparison, pure GNS without PPy, and pure PPy, were also synthesized. To study the morphology of the PPy/GNS/MWCNT composites, a field emission scanning electron microscope (SUPRA 40VP with EBSD; Carl Zeiss, Germany) was used. We also measured structural properties using Fourier transform infrared spectroscopy (Spectrum GX; Perkin Elmer, USA). Electrochemical measurements by cyclic voltammetry (CV) were carried out on a potentiostat/galvanostat (IviumStat, the Netherland) with a three electrode system. We used the three-electrode method for electrochemical analysis. The counter electrode was a Pt wire, the reference electrode was a saturated calomel electrode (SCE) and the working electrode was prepared by the following procedure. The synthesized composites, carbon black (Super-P) and polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) solvent at a ratio of 85:10:5. Next the slurry was spread on a 1 cm by 1 cm nickel foam current collector and dried in a vacuum oven at 80°C for 12 h. All of the electrochemical analyses were performed in a 1 M NaNO_3 aqueous electrolyte at room temperature. CV and galvanostatic charge-discharge (GCD) were measured by Potentiostat/Galvanostat (Ivium-Stat). CV tests were processed at a scan rate of 10 mV s^{-1} . GCD curves were measured at a current density of 0.5 A g^{-1} . The voltage windows of the CV and GCD tests were set with a potential range of -0.2 to 0.8 V . The synthesis route of the PPy/GNS/MWCNT composites is illustrated schematically in Fig. 1. First, the GNS and carbon nanotubes were hydrolyzed into a solution of 0.2 M hydrochloric acid containing pyrrole. Then, the PPy/GNS/MWCNT composites were prepared by adding ferric chloride hexahydrate dissolved in 0.2 M hydrochloric acid solution into the above solution. The FT-IR spectra of the PPy, GNS and the PPy/GNS/MWCNT composites are shown in Fig. 2a. The spectrum of the PPy showed

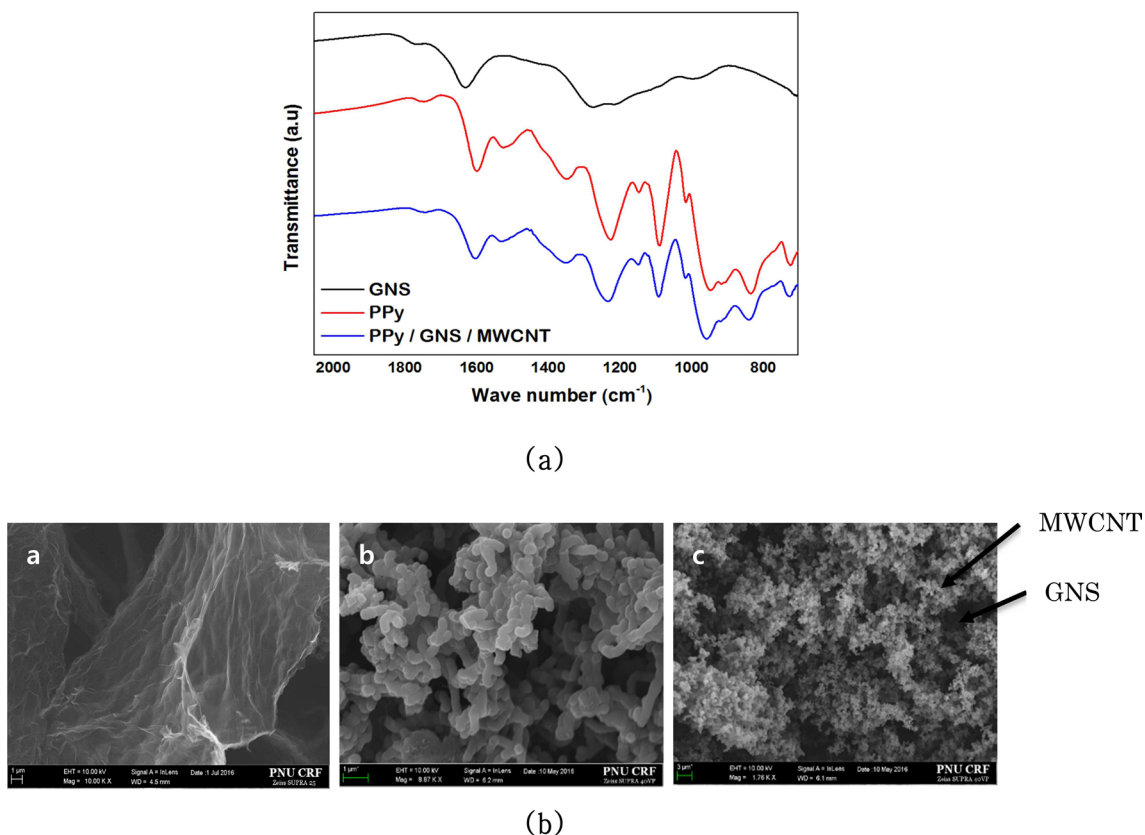


Fig. 2. (a) FT-IR spectra of GNS, pure PPy, PPy/GNS/MWCNT composite and (b) FE-SEM images of GNS, pure PPy, PPy/GNS/MWCNT. FT-IR, Fourier transform infrared spectroscopy spectra; GNS, graphene nanosheets; PPy, polypyrrole; MWCNT, multi-walled carbon nanotube; FE-SEM, field emission scanning electron microscope.

the peaks at 1549 and 1458 cm^{-1} representing the C–N and C–C asymmetric and symmetric ring-stretching vibrations of the pyrrole rings, respectively. The presence of oxygen-containing functional groups on the GNS was found at around 1500 cm^{-1} . The series of 1316, 1202, 1049, 922, and 790 cm^{-1} are the typical characteristic peaks of PPy. The PPy/GNS/MWCNT composites were confirmed by the spectrum of PPy/GNS/MWCNT showing characteristic peaks [25]. The morphologies of the prepared PPy, GNS and PPy/GNS/MWCNT composites were investigated using the SEM images shown in Fig. 2b. Fig. 2b (a) clearly shows the GNS, and Fig. 2b (b) shows pure PPy particles with a globular-like appearance. Fig. 2b (c) shows the GNS, PPy particles, and the layered morphology of the graphene, confirming the preparation of PPy/GNS/MWCNT composites. It was thought that the PPy was probably coated on the surface of the graphene and carbon nanotubes. The PPy and carbon nanotubes were considered spacers to help prevent the aggregation of the GNS, resulting in an enhancement in the specific area of the graphene. Accordingly, the PPy/GNS/MWCNT composites were expected to have a higher surface area for electrochemical reactions due to the exfoliated GNS structure.

Electrochemical testing was carried out using CV and GCD techniques to measure the electrochemical behavior of the prepared sample in the three electrode electrochemical system. The

specific capacitance values were calculated from the GCD using the following equation:

$$\text{Specific Capacitance}(C_s) = \frac{I \times \Delta t}{m \times \Delta V}$$

where I is the current density, Δt is the discharge time, m is the mass of the active material in the working electrode, ΔV is the potential window. As shown in Fig. 3a, the CV of the pure pyrrole, PPy/GNS and PPy/GNS/MWCNT composites electrode was tested, with a scan rate of 100 mV s^{-1} in the potential range from -0.2 to 0.8V (vs. SCE) in 1 M NaNO_3 aqueous electrolyte at room temperature. This result showed the composite sample had a higher capacitance than pure pyrrole or pyrrole graphene composite. Fig. 3b shows the CV graphs of the composites electrode with various scan rates of 5 to 100 mV s^{-1} . All of the CV curves are close to a rectangular shape, indicating that the sample has a unique capacitive characteristic, such as an electrical double layer. The composites showed that adding graphene and carbon nanotubes enhanced capacitance. The composites containing graphene and carbon nanotubes achieved the highest capacitance compared to the pure PPy and the PPy/GNS composite. The high electrochemical performance of the PPy/GNS/MWCNT composite is related to the exfoliated graphene sheets and the carbon nanotube and PPy network chain. As

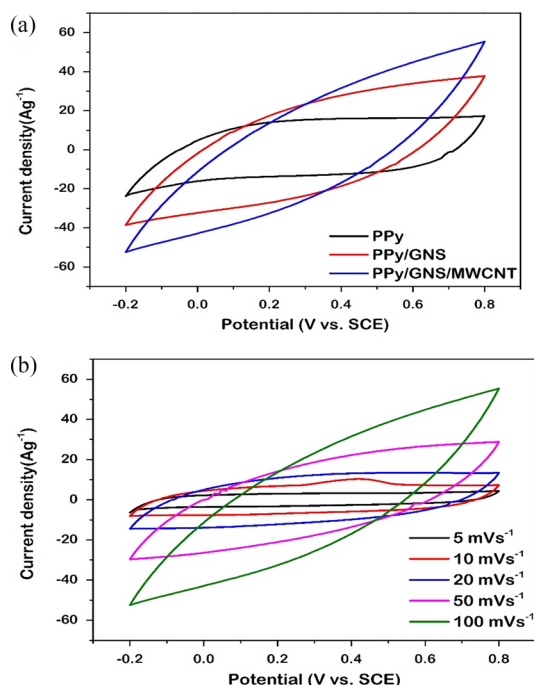


Fig. 3. (a) Cyclic voltammetry (CV) curves of the samples at a scan rate of 100 mV s^{-1} in 1 M NaNO_3 electrolyte and (b) CV curves of the PPy/GNS/MWCNT composites at different scan rates ($5, 10, 20, 50,$ and 100 mV s^{-1}). PPy, polypyrrole; GNS, graphene nanosheets; MWCNT, multi-walled carbon nanotubes; SCE, Saturated calomel electrode.

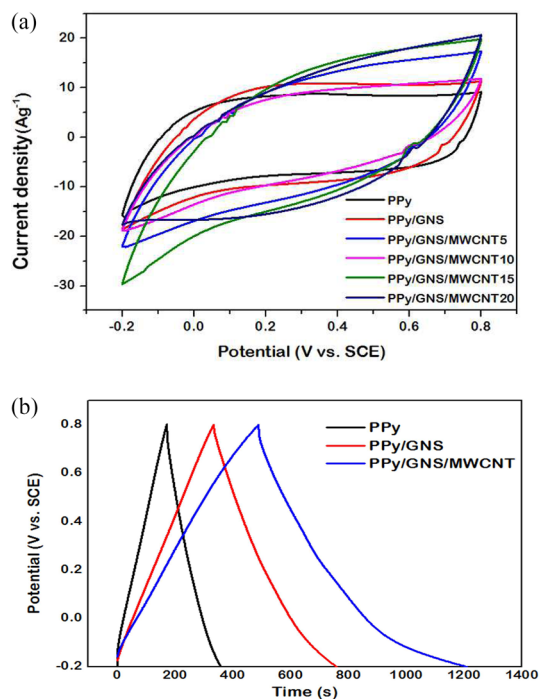


Fig. 4. (a) Cyclic voltammetry curves of the PPy/GNS/MWCNT composites with different MWCNT contents at the scan rate of 20 mV s^{-1} and (b) galvanostatic charge-discharge curves of PPy/GNS/MWCNT and PPy/GNS at the same current density of 0.5 A g^{-1} . PPy, polypyrrole; GNS, graphene nanosheets; MWCNT, multi-walled carbon nanotubes.

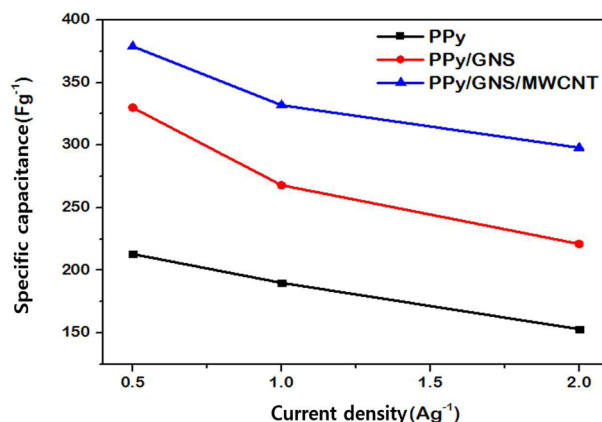


Fig. 5. Specific capacitance of PPy, PPy/GNS, and PPy/GNS/MWCNT as a function of the various current densities. PPy, polypyrrole; GNS, graphene nanosheets; MWCNT, multi-walled carbon nanotubes.

expected, the carbon nanotube additives acted as a bridge between graphene sheets, which was beneficial for improving the conductivity of the composites and the specific capacitance. Fig. 4a shows the CV graphs of the composites electrode with various amounts of MWCNTs, at 5, 10, 15, and 20 wt% per weight of pyrrole, which were designated PPy/GNS/MWCNT ($x \text{ wt}\%$, $X=5, 10, 15,$ and 20). CV curves were obtained at a scan rate of 20 mV s^{-1} . The composites showed increased capacitance as the amount of MWCNTs was increased. However, the capacitance decreased when the amount of MWCNTs was too high. The composite prepared with 15 wt% of MWCNT achieved the highest capacitance among the various composites. The high electrochemical performance of the PPy/GNS/MWCNT composite is related to the use of MWCNTs as conducting additives. The graphene sheets provide a large number of active sites, resulting in a synergetic interaction between the PPy and GNS surface. This allows a significantly greater number of charge transport channels, which are related to higher electrical or ionic conduction. As we expected, the added MWCNTs acted as spacers, preventing the restacking of the GNS layers. The spacers increase the space between graphene layers, resulting in much higher mass transfer. This can change or promote the development of electrolyte ion channels for ion transport. In addition, the MWCNTs themselves can provide an effective conducting path for electrons due to their highly conducting behavior. These dual effects are related to the improved capacitance values and rate-capability. Fig. 4b shows the GCD profiles at the current density of 0.5 A g^{-1} for the pure PPy, PPy/GNS and PPy/GNS/MWCNT (20 wt%). The PPy/GNS/MWCNT composite electrode exhibits a discharge capacitance that is higher than the other samples. Fig. 5 shows the GCD profiles at different current densities from 0.5 to 2 A g^{-1} for pure PPy, PPy/GNS and PPy/GNS/MWCNT, respectively. The result exhibits the same tendency as those of the CV curves. The PPy/GNS/MWCNT electrode exhibited a discharge capacitance of 379 F g^{-1} , which was higher than the PPy/GNS electrode (331 F g^{-1}). This could be attributed to the increased electrical conduction network of the graphene

and carbon nanotubes, which enhanced charge transport. It could also suggest an intimate interaction between the pyrrole and GNS, resulting in better charge transfer due to defect assisted propagation [26]. From these curves, we were able to determine the specific capacitance value of the composite.

In summary, PPy/GNS/MWCNT composites were successfully prepared by the facile method of in-situ polymerization of pyrrole. The MWCNTs played a crucial role in stabilizing the PPy/GNS/MWCNT, enhancing the composite's electrochemical properties and by preventing the aggregation of graphene layers. The specific capacitances of the PPy/GNS/MWCNT composites were remarkably enhanced, compared with individual PPy and GNS. The reason for this could be due to the synergistic effect between the carbon-based materials and PPy. The PPy/GNS/MWCNT composite electrode showed enhanced specific capacitance, higher rate performance, and better charge-discharge stability, which suggests it can be applied as electrode materials for electrochemical supercapacitors. Further improvement in performance can be expected by optimizing the composites electrode, and electrolyte formulation. We believe that our composites can be applied to broad applications in lithium ion batteries and energy storage devices.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technology (Korea) (Nuclear Power Research Base Development Project, Grant No: 2016M2B2A4910820).

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