

## 전기방사를 이용한 고분자전지용 Polypyrrole/SSEBS 섬유 복합체 Web 전극 제조

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**Preparation of Polypyrrole/SSEBS Nanofiber Composite Web Electrode  
by Electrospinning for Polymer Battery**

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## **1. Introduction**

Electronically conducting polymers as polypyrrole (PPy), polyaniline and polythiophene have received enormous interest due to their potential applications in the electrodes of chargeable batteries [1,2] or fuel cells [3,4], and electrochemical capacitor [5,6]. When it is used as the active material of electrodes, the dispersion of PPy influences intensively to electrochemical property. The conventional method such as slurry casting in making the electrode is subjected to enhance the dispersion of particles. This results in the decrease of the electrochemical property. In this study, the electrospinning technique is introduced to increase the degree of dispersion of PPy particles. Furthermore, in the process of the electrospinning technique, sulfonated-(styrene-ethylene-butylene-styrene) (SSEBS) is used as a cathode binder for the composite with conducting polymer because it has excellent thermal stability and very good mechanical properties and because it serves as a high molecular weight dopant. We, in this work, focus on the preparation of the doped PPy/SSEBS nanofiber composite web for polymer battery. The PPy was prepared by chemical polymerization and doped by DBSA. The nanofiber web was prepared by the co-electrospinning of the composite solution consisting of a mixture of the doped PPy, SSEBS and carbon conductor in chloroform.

## **2. Experimental**

### **2.1. Materials**

Pyrrrole as a monomer and dodecylbenzenesulfonic acid (DBSA) as both protonating agent and surfactant were obtained from Aldrich Co. The chloroform (Junsei Chemical Co.) and tetrahydrofuran (THF, Aldrich Co.) were used as solvents. Ammonium peroxydisulfate (APS) as an initiator and chlorosulfonic acid (CSA, Kanto Chemical Co.) as a sulfonating agent was used without further purification. Super-p carbon was used as an electron conductor. The cathode collector used Al mesh, and the anode collector Ni mesh

### **2.2. Sulfonation of SEBS**

10 wt.% SEBS was completely dissolved in 1,2-dichloroethane solution by mechanical mixing in a 3 neck flask at room temperature. Then, chlorosulfonic acid (CSA) was dropped slowly with vigorous

stirring under nitrogen atmosphere. The reaction was continued during 1h. The product was precipitated by boiling water and washed several times using boiling water. The SSEBS was obtained after dried for 24 h in a vacuum oven.

### 2.3. Preparation of PPy and electrode

PPy is prepared by a chemical polymerization. At first, 0.38 M of DBSA, acting as an emulsifying agent and dopant, was vigorously stirred in water in a three-neck flask, and then an aqueous solution of 0.12 M of APS in water, acting as an oxidant, was added with vigorous stirring. The molar ratio of APS/pyrrole was 0.15. After that, the solution of 5 g pyrrole was added at 0 °C with stirring. The polymerization was allowed to proceed for about 8 h. The product solution was filtered and washed with methanol. The conducting polymer powder was dried in a vacuum oven at 50 °C for one day. The cell was consisted as a system, Al mesh collector/(PPy+binder//1M LiPF<sub>6</sub> + PC/DMC//Li metal/Ni mesh collector. The cathode material was prepared as follows. At first, PPy was dissolved in chloroform, and then mixed polymer binder solution and carbon conductor (Super-P). The PVDF, sulfonated SEBS were as binders. The slurry solution cast on Al mesh, dried solvent on the vacuum oven, and then the dried electrode was used to do hot pressing at 70 °C. While the slurry 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. Li metal on Ni mesh used as a anode material. Two electrodes were assembled as a coin type and enveloped in a laminated-aluminum pouch in glove box.

### 3. Results and discussion

The electrical conductivities of PPy/PVDF, PPy/SSEBS and electrospun PPy/SSEBS web were measured by the four probes method. The electrical conductivities of PPy/SSEBS, PPy/PVDF were 0.42 and 0.23 S/cm, respectively, while that of eletrospun PPy/SSEBS was 0.52 S/cm. This is why the latter case is much better than that of the former case because the electrospinning method provides good PPy particle dispersion and excellent molecular orientation. In addition, the electrical conductivity of PPy/PVDF has the low value by the existence of phase separation because the PVDF used as only a binder is hydrophobic. On the contrary, in the case of PPy/SSEBS, the electrical conductivity is increased because SSEBS promotes the improvement of wettability and compatibility owing to the effect of coulombic interaction between PPy and SSEBS. Fig. 1 shows the views of scanning electron microscopy (SEM) for the surface of PPy/PVDF, PPy/SSEBS composite and electrospun PPy/SSEBS one. In the case of PPy/PVDF and PPy/SSEBS composites, the PPy particles are shown as small spherical granules with well-developed micro porosity. The electrospun PPy/SSEBS web is partially aligned along the winding direction of the drum winder. Fig. 2 is the cyclic voltammograms of PPy/PVDF, PPy/SSEBS, and electrospun PPy/S-SEBS electrodes in 1 M LiPF<sub>6</sub> + EC/DMC (1:1 vol.%) as an organic liquid electrolyte at scan rate of 5 mV/s in the range of 0 to 3.5 V. The range of current for oxidation and reduction reaction of electrospun PPy/SSEBS electrode is higher than other electrodes. The reason for this that PPy in the faradaic process sows the pseudocapacitance property, and SSEBS act as the additional dopant as well as the high molecular SSEBS protects the overoxidation of PPy. In addition, this is because the contact area of electrode and electrolyte is larger than that of other electrodes. Fig. 3 shows the impedance spectra by Nyquist plots in the range of 1Hz to 1 MHz for PPy/PVDF, PPy/SSEBS and electrospun PPy/SSEBS electrodes, respectively. A single semi circle high frequency region and a straight line in the low frequency region for all spectra is showed. The high frequency are is the overall contact impedance generated from the

electrical connection between conducting polymer particles, between particle and collector, and the charge transfer at the contact interface between the electrode and the electrolyte solution. The interfacial resistances of electrospun PPy/SSEBS, PPy/SSEBS and PPy/PVDF electrodes are 16, 19 and 26  $\Omega$ , respectively. The smaller interfacial resistance is the better the electrochemical performance. Fig. 4 represents the discharge profiles of Li//PPy-PVDF cell, Li//casted (PPy-SSEBS) cell, and Li//electrospun (PPy-SSEBS) cell in the range of 0-3.5 V with 0.5 mA/cm<sup>2</sup>. The discharge capacities of electrospun PPy-SSEBS, casted PPy-SSEBS and PPy-PVDF electrodes show 73, 59 and 41 mAh/g, respectively. The specific capacitance of PPy/PVDF was relatively low because PVDF played a role as only binder. On the other hand, the specific capacitance of PPy/SSEBS was very high because SSEBS act as both a binder and a dopant. In addition to, the specific capacitance of electrospun PPy/SSEBS was higher than casted PPy/SSEBS. It can be guessed that the contact area between electrode and electrolyte was increased. Fig. 5 represents the specific discharge capacities of Li//PPy-PVDF cell, Li//casted (PPy-SSEBS) cell, and Li//electrospun (PPy-SSEBS) cell with the number of cycles. The profiles of specific capacity Li//electrospun (PPy-SSEBS) cell represent good cyclability.

#### **4. Conclusions**

PPy powder was prepared by the chemically oxidative polymerization. The electrochemical performance of electrospun PPy/SSEBS electrode is better than that of casted (PPy-SSEBS) or PPy-PVDF one. The specific discharge capacity of electrospun PPy-SSEBS electrode is as high as 73 mAh/g, while that of casted (PPy-SSEBS) or PPy-PVDF one has lower values as 59 or 41 mAh/g, respectively. The electrochemical characteristics is deeply influenced by the dispersion of PPy particles and molecular orientation.

#### **Acknowledgement**

Support for this work was provided by KOSEF under Grant number R01-2003-000-10100-0.

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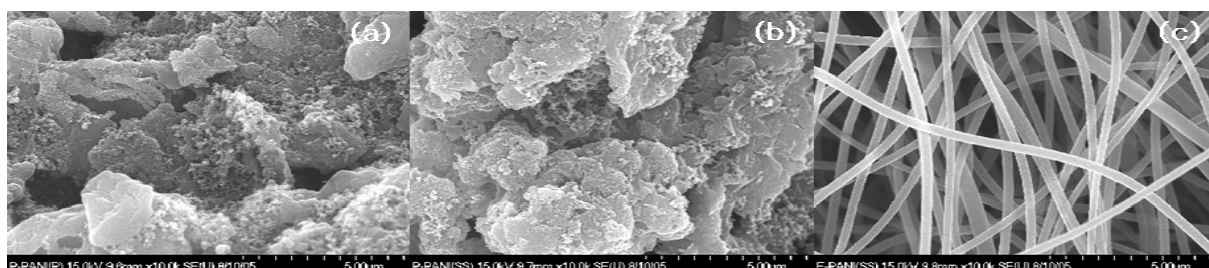


Fig. 1. The SEM images of PPy/binders ; (a) PPy/PVDF, (b) PPy/SSEBS and (c) electrospun PPy/SSEBS

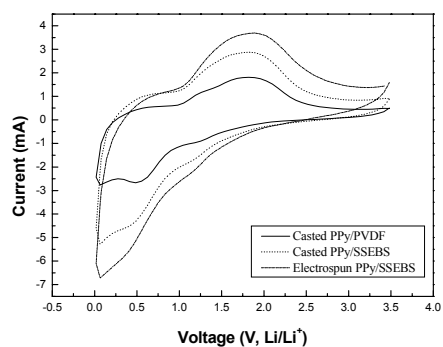


Fig. 2. The cyclic voltaammograms of various electrodes.

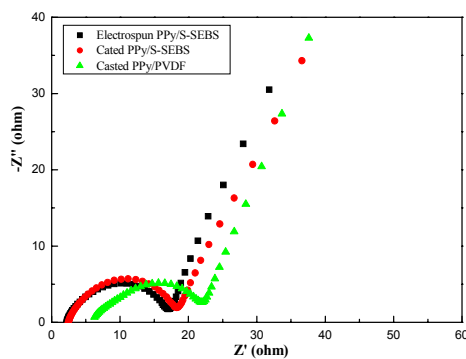


Fig. 3. The impedance spectra of various electrodes.

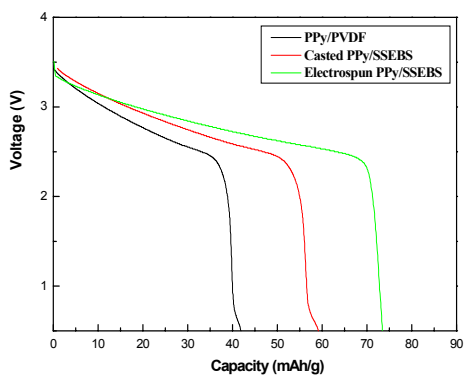


Fig. 4. The discharge profiles of various electrodes.

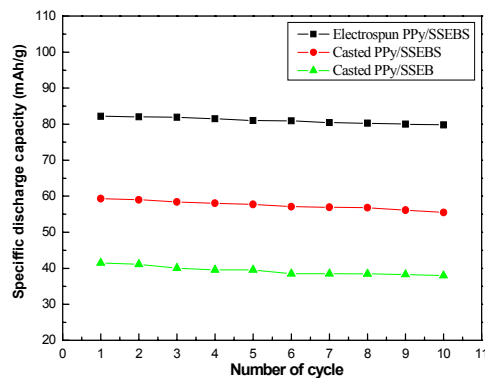


Fig. 5. The specific discharge capacities of various electrodes.