

# Supercapacitive properties of electrodeposited polypyrrole on acrylonitrile–butadiene rubber as a flexible current collector

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**Abstract** Flexible sheets consisting of acrylonitrile–butadiene rubber (NBR) and vapor-grown carbon fiber (VGCF) are newly prepared varying the composition (VGCF 10–30 wt%) for use as a current collector of supercapacitor electrodes. The electrical conductivity of as-prepared VGCF/NBR current collector can be enhanced as the content of VGCF increases. The VGCF/NBR current collector is then electrodeposited with pyrrole using a potentiodynamic cyclic voltammetry to yield a polypyrrole (PPy)/VGCF/NBR composite electrode. Cyclic voltammetry result for the PPy/VGCF/NBR composites shows that the sample with 30 wt% VGCF achieves a maximum specific capacitance ( $125.8 \text{ F g}^{-1}$ ) at  $5 \text{ mV s}^{-1}$  and reaches a lower specific capacitance at higher scan rates. In addition, the flexibility of supercapacitor electrode of PPy can also be established with a comparable capacitance value by using the NBR-based current collector.

**Keywords** Polypyrrole · Vapor-grown carbon fiber · Acrylonitrile–butadiene rubber · Flexible current collector · Supercapacitor

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## Introduction

Conducting polymers have been of wide interest in supercapacitor applications because they could conduct electricity by displaying pseudocapacitance and high specific capacitance with low cost. In particular, a decent review [1] could be beneficial to inform for the conducting-polymer-based supercapacitor devices. Of these, polypyrrole (PPy) is one of the most studied conducting polymers in the industry in that it contains a conjugated structure of alternating C=C bonds, providing specific electronic properties: notably, low-energy optical transitions and ionization potentials as well as high-electron affinities [2]. In addition, PPy shows high electrical conductivity, easy processability, and good dimensional stability under atmospheric condition. Numerous studies about PPy as a good electronic conductor [3–5] have been arising, but most of them were deficient in flexible mechanical property which is necessary for flexible energy storage devices.

Recently, the ubiquitous electronic devices including cellular phone, laptop computer, digital multimedia broadcasting (DMB), and wireless broadband internet (WiBro) are accelerating to develop smart power devices with great capacity and cycle performance. Moreover, the need of flexible power devices is going to appear to satisfy various designs of mobile electronic devices. A flexible supercapacitor with a flexible current collector can be a solution for the flexible devices such as a wearable external power sources for medical devices [6–10]. However, metallic current collectors, such as platinum foil, nickel foam, aluminum foil, and stainless steel sheet, have been mostly studied, but resulted in being inadequate to apply to flexible supercapacitor electrodes. At this stage, it will be convenient to design the flexible capacitor if a polymer-based organic current collector with a certain degree of electric conductivity is available. Moreover, polymer species with polar function groups in the main chain can give an opportunity to yield a conductive current collector if adding a certain amount of conducting carbon material.

In this study, the acrylonitrile-butadiene rubber (NBR) blended with vapor-grown carbon fiber (VGCF) is prepared as a polymer-based current collector. The NBR is a typical synthetic rubber used in automotive industry as an elastomer. Unlike other synthetic rubbers, it has polar functional groups of nitrile ( $-C\equiv N$ ), which is useful for the organic conductive matrix for flexible current collector. The VGCF plays a role of conducting additive. Using a potentiodynamic cyclic voltammetry as an electrodeposition tool, the PPy as an active material is electrodeposited on the surface of the NBR/VGCF current collector to obtain a flexible PPy/NBR/VGCF composite electrode. To characterize the supercapacitive properties, cyclic voltammetry is also performed for the prepared PPy/VGCF/NBR composite electrode. In addition, the effect of VGCF contents on the specific capacitance is examined to determine the optimal composition.

## Experimental

The NBR (KNB Series, acrylonitrile 34 mol%, Kumho Petrochemical Corp.) and VGCF (specific surface area  $13\text{ m}^2\text{ g}^{-1}$ , fiber length 10–20  $\mu\text{m}$ , aspect ratio 60–70, Showa

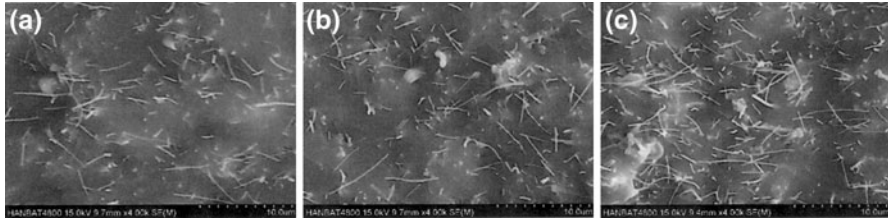
Denko) used were commercially available products. Prior to the electrodeposition, the pyrrole monomer (98.0 %, Aldrich) was purified by vacuum distillation. First, different contents of VGCF (20, 25, 30 wt%) were dispersed in 5 ml chloroform ( $\text{CHCl}_3$ , Aldrich) by stirring for 6 h. The NBR (0.4 g) was then added and vigorously stirred for 6 h to obtain viscous black slurry. The slurry was cast on a glass plate using a doctor blade apparatus to yield a current collector film (VGCF/NBR) with a thickness of 140  $\mu\text{m}$ . After drying in the air for 18 h at ambient temperature, the VGCF/NBR cast film was characterized by morphology observation using a field-emission scanning electron microscope (Hitachi S-4800). The electrical conductivity of the VGCF/NBR was examined using a four-point probe surface resistance measurement (CMT-100, Advanced Instrument Technology).

The electrodeposition of PPy on the surface of VGCF/NBR current collector film was carried out using an Autolab instrument (P/Gstat 100, Eco-Chemie). A mixture of 0.1 M pyrrole monomer and 0.05 M sodium dodecylsulfate ( $\text{NaSO}_3(\text{CH}_2)_{11}\text{CH}_3$ ) was used as an electrolyte solution. The potentiodynamic electrodeposition of PPy on the VGCF/NBR current collector as a working electrode was performed for 600 s at the current of 1 mA (vs. Ag/AgCl). The flexible PPy/VGCF/NBR composite electrode was finally obtained by washing in deionized water and drying in an oven at 40 °C for 24 h. After weighing before and after the electrodeposition, the loadings of PPy on the VGCF/NBR current collector were determined to 41.2–45.6 wt% based on total weight of the PPy/VGCF/NBR capacitor electrode. The surface morphology of the prepared PPy/VGCF/NBR electrode was also observed using a field-emission scanning electron microscope (Hitachi S-4800).

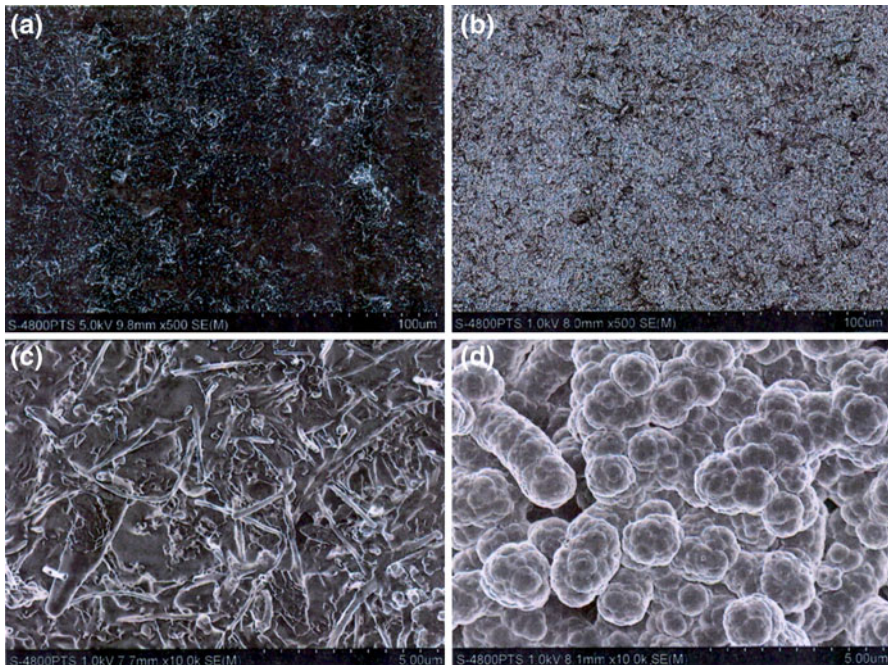
Supercapacitive properties of the PPy/VGCF/NBR as a working electrode (2 cm  $\times$  2 cm) were examined through cyclic voltammetry (P/Gstat 100, Eco-Chemie) using a three-electrode cell equipped with a Ag/AgCl reference electrode (Metrohm AG 9101 Herisau, 3 M KCl, 0.222 V vs. Ag/AgCl at 25 °C). A 2 cm  $\times$  2 cm-sized platinum plate was used as a counter electrode in the potential range of  $-0.8$  to 0.5 V at the scan rates of 5–200  $\text{mV s}^{-1}$  in a 1.0 M  $\text{Na}_2\text{SO}_4$  electrolyte solution at 25 °C. Cycle performance test was also performed at an intermediate scan rate of 20  $\text{mV s}^{-1}$  for 500 times.

## Results and discussion

Figure 1 shows cross-sectional images of the as-prepared VGCF/NBR current collectors with different contents of VGCF. The VGCF/NBR current collectors are successfully formed as self-supporting films with a certain degree of mechanical strength. It can also be seen that fibrils of VGCF are homogeneously distributed in NBR matrix and that the morphology becomes condensed with increasing the VGCF content. That is, the distance between VGCF fibrils is shortened to involve the reduction of electrical resistance of VGCF/NBR current collector. This is reflected by the increase in electrical conductivity values of 0.90, 1.55, and 3.11  $\text{S cm}^{-1}$  with increasing the content of VGCF from 20, 25, to 30 wt% in the VGCF/NBR current collector. Such conductivity values are somewhat lower than that of the active material, PPy (10–50  $\text{S cm}^{-1}$ ) [11], but they are sufficient to play



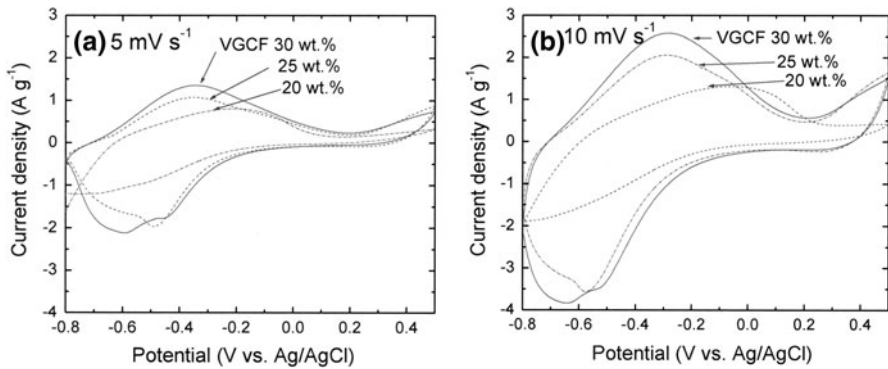
**Fig. 1** Cross-sectional images of flexible VGCF/NBR current collectors containing **a** 20, **b** 25, and **c** 30 wt% of VGCF



**Fig. 2** Surface images of **a** flexible VGCF/NBR current collector containing 30 wt% of VGCF and **b** flexible PPY/VGCF/NBR composite electrode containing 30 wt% of VGCF. **c**, **d** are enlarged views of **a** and **b**, respectively

a role of current collector, together with superior flexibility. Here, the point is a concurrent attainment of moderate conductivity value of VGCF/NBR current collector and a certain degree of flexibility. When the VGCF content exceeds 30 wt%, however, the overdose of fibril structure involves the reduction of mechanical strength so that cannot form a self-supporting film.

Moreover, Fig. 2 shows surface images of the VGCF/NBR current collector and the electrodeposited PPY/VGCF/NBR composite electrode, which are equally containing 30 wt% of VGCF. At the surface of VGCF/NBR current collector, the fibrils of VGCF are uniformly distributed in NBR matrix and entangled to form a

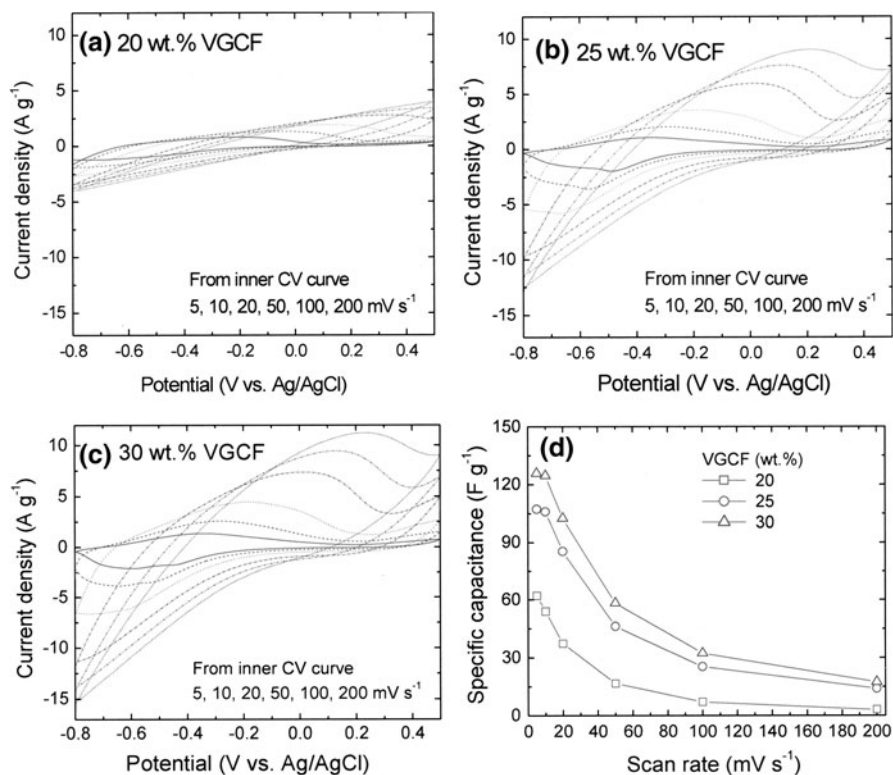


**Fig. 3** Cyclic voltammograms of PPy/VGCF/NBR composite electrodes, recorded at low scan rates: **a** 5 and **b** 10  $\text{mV s}^{-1}$

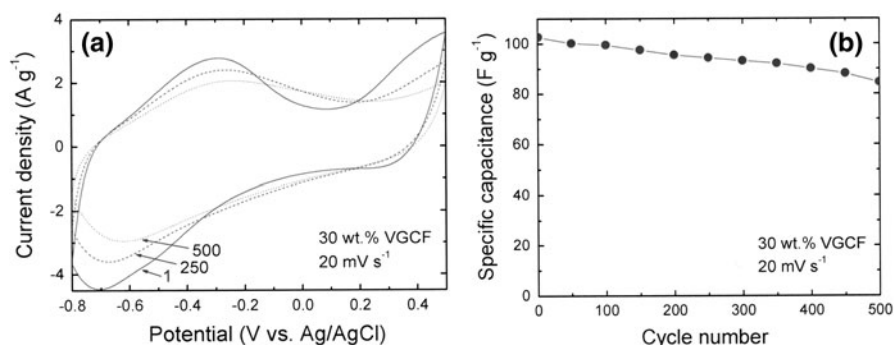
three-dimensional network. The fibrils are more strongly connected with each other in the NBR matrix, so that the current collector is highly flexible and tough enough to be folded. After the electrodeposition of PPy, somewhat coarse sphere-shaped PPy particles are uniformly deposited around the branches of VGCF. The average diameter of the PPy particles is about 0.1–0.2  $\mu\text{m}$ , yielding a microporous structure in the PPy/VGCF/NBR composite electrode.

The supercapacitive properties of the PPy/VGCF/NBR composite electrodes are investigated by cyclic voltammetry in the potential range of  $-0.8$  to  $0.5$  V (vs. Ag/AgCl) at various scan rates. It should be mentioned here that all values of current density and specific capacitance (see Figs. 3, 4, 5) are renormalized ones by the weight of active conducting polymer (PPy). Figure 3 shows the cyclic voltammograms obtained at low scan rates, reflecting slow redox behaviors at the surface of the composite electrode. PPy-based electrodes are usually known to show bulk faradaic redox behavior at potentials over 0.6 V. The redox peak position shifts with increase in VGCF content to yield a narrow potential range between the cathodic and anodic peaks, indicating a capacitance increase. The cyclic voltammograms at low scan rates, as shown in Fig. 3, agree well with the fact that the cathodic peaks in the region of  $-0.7$  to  $-0.4$  V are featured by the redox transition of PPy in its oxidation states. On the other hand, high scan rate involves fast redox behaviors becoming the  $iR$  drop significant, as shown in Fig. 4a–c. Cyclic voltammograms at high scan rates in 20 wt% of VGCF do not show redox peaks over the potential range, indicating the limited proton-diffusion migration and the  $iR$  drop in the PPy component. No redox peaks at high scan rates may involve the capacitance decrease or reveal the irreversibility. Nonetheless, as the VGCF content increases, the composite electrode of PPy/VGCF/NBR exhibits some redox behaviors even at high scan rates, greatly emphasizing in the electrode with 30 wt% VGCF content. This is due to moderate electrical conductivity of the VGCF/NBR current collector, offering good electronically conducting pathway among PPy particles. The microporous structure of the PPy/VGCF (30 wt%)/NBR composite electrode also facilitates solvated ion diffusion in the composite electrodes at high scan rates. Specific capacitances calculated by integrating the cyclic voltammograms are shown in





**Fig. 4** Cyclic voltammograms of PPy/VGCF/NBR composite electrodes with different VGCF contents: **a** 20, **b** 25, and **c** 30 wt%. The specific capacitance evolution as a function of scan rate is shown in **d**



**Fig. 5** **a** Cyclic voltammograms at 20 mV s<sup>-1</sup> and **b** specific capacitance evolution of PPy/VGCF (30 wt.%)/NBR composite electrode as a function of cycle number

Fig. 4d as a function of scan rate. Maximum specific capacitance values obtained at lowest scan rate (5 mV s<sup>-1</sup>) turn out to be 62.2, 107.3, and 125.8 F g<sup>-1</sup> for the composite electrodes adopting 20, 25, and 30 wt% of VGCF, respectively. Figure 5 shows the result of the cyclic performance for the PPy/VGCF (30 wt.%)/NBR

composite electrode. The intensity of redox peaks reduces as the cycle number increases, indicating the capacitance decrease. However, the capacitance retention ratio shows higher values of 93 and 83 % after 250 and 500 cycles, respectively, due to stable redox reaction at the surface of PPy, which is supported by the flexibility and conductivity of the VGCF/NBR current collector.

## Conclusion

In this study, a NBR-based current collector with a conducting additive is prepared for supercapacitor applications. The VGCF/NBR current collector acts as a flexible self-supporting conductive film with a moderate electrical conductivity (max.  $3.11 \text{ S cm}^{-1}$ ). The electrodeposited PPy composite electrode on the surface of VGCF/NBR current collector has a microporous structure in which the PPy particles are homogeneously deposited on the aggregated VGCF branches in the NBR matrix. The resultant PPy/VGCF/NBR composite electrodes with adequate content of VGCF (20–30 wt%) shows good specific capacitances, which are applicable to supercapacitors. Comprehensively considering, this achievement is possible by the synergistic effect consisting of (i) polarity of nitrile groups in NBR, (ii) conducting pathway of VGCF, and (iii) electroactive property of PPy. In addition, flexible supercapacitor device with wide design freedom can be possible when using the flexible electrode as the target electrode of energy storage devices.

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