A strong and sticky hydrogel electrolyte for flexible supercapacitors

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A strong and sticky hydrogel electrolyte for flexible supercapacitors

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Abstract. With the rapid development of flexible supercapacitors (SCs), there is increasing demand for high-performance solid electrolyte to replace the conventional liquid electrolyte. Hydrogel electrolyte is one of the promising candidates, which possesses solid state but contains plenty of water within its highly porous structure. In this paper, a strong and sticky hydrogel has been synthesized using bacterial cellulose (BC) and poly (acrylic acid) (PAA). The results of attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectroscopy shows that two components are well combined. Scanning electron microscopy (SEM) test shows that BC/PAA has a highly porous structure, which is modified by the interaction between BC nanofibers and acrylic acid monomer. Double network created by BC and PAA not only enhances the mechanical property of PAA but also improves the anti-compression ability of BC. Moreover, a sticky property is recognized within BC/PAA due to PAA, which can prevent the spilt of two flexible electrodes. The high ionic strength makes PAA shrink in 1M Na_2SO_4. However, the swelling ratio of BC/PAA could still reach to approximately 500% and its ionic conductivity is about 0.06 $S{\cdot}cm^{-1}$. This prepared BC/PAA hydrogel electrolyte has a great potential to be used in flexible SCs

Keywords: Bacterial cellulose, ploy(acrylic acid), flexible supercapacitors, hydrogel electrolyte, ionic conductivity
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INTRODUCTION

In order to meet the rapidly growing demand for portable electronic devices such as mobile phones, wearable electronics, and flexible displays, the development of high performance and reliable power sources with light-weight, excellent flexibility and safety is essential [1]. Supcapacitors (SCs), one of the most promising energy storage devices, have drawn a great deal of attention due to their high power density, long life cycles and high efficiency [2].

Flexible SCs, one functionalized SCs for portable devices, are mainly composed of two components, flexible electrodes and solid-state polymer electrolyte [3]. Nowadays, more and more attention has been paid to the study of electrodes. Solid-state polymer electrolyte, however, is another important aspect [4]. Despite the requirement of high ion conductivity to ensure excellent electrochemical performances of assembled SC, the solid-state polymer electrolyte should also have a good mechanical property and high adhesion ability to avoid the short circuit and split of two electrodes when the flexible SC under deformation [5]. Hydrogel electrolyte usually has a porous structure filed with electrolyte solution, having high ion conductivity and remaining solid-state, but their mechanical properties are mostly weak. On the other hand, in order to solve the issue of network destruction in physical cross-linked hydrogel when temperature rises up, the chemical cross-linking is applied, however, it dramatically weaken the adhesion of original gels.

PAA has abundant groups of COO-, which are easy for ions to store and transfer. Interestingly, it is still adhesive after chemical crosslinking [6], but its mechanical property is low. In case of BC, it has a rigid and tough structure constructed by crystalline nano cellulose fibers, which can serve as a skeleton of BC/PAA hydrogel. Meanwhile, the soft PAA hydrogel can fill into the void to enhance the anti-compression ability of BC [7]. Moreover, BC is a degradable material, which is friendly to the environment [8].

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In this paper, we prepared a novel composite hydrogel electrolyte of PAA and BC with 1M Na_2SO_4. This neutral and partially degradable electrolyte with a double network structure, exhibiting high mechanical property and staying adhesive, has a large potential in portable electronic devices.

EXPERIMENTAL

Materials

Acrylic acid, N, N'-methylenebis (acrylamide), potassium persulfate and sodium sulphate were purchased from Sigma-Aldrich. BC pellicle was biosynthesised in our lab [9].

Preparation of BC, PAA and BC/PAA

Pure BC was obtained by treating the collected BC pellicles with NaOH. It was freeze-dried and cut into squares (size: 1cm × 1cm). BC/PAA was prepared by initiating the polymerization of acrylic acid in the original network of pure BC. Pure PAA were also gained during this preparation. Steps are shown as follows: 0.9 mL of acrylic acid and 9 mg N, N'-methylenebis (acrylamide) were dissolved in a glass vial with 6 mL deionized water. Then a piece of water-swelled BC was kept in this solution at the temperature of 4 ^oC for 1 h. After that, 7.2 mg of potassium persulfate was added. The solution was incubated for 30 min. Then the soaked BC was taken out and put into the space between two glass slides separated by Para-film and kept into the oven at the temperature 70 ^oC for the occurrence of polymerization to gain BC/PAA. Meanwhile, the remained solution was injected in another space for reaction to obtain pure PAA.

Characterization

BC, PAA, and BC/PAA were analyzed by ATR-FTIR. Surface and cross sectional morphologies of freeze-dried PAA and BC/PAA were evaluated by SEM analysis. The amount of electrolyte (1 M Na_2SO_4) absorbed in BC/PAA was calculated using the following equation: *Absorptivity % = (Ws-Wd) / Wd x 100*, where "*Ws*" is the weight of absorbed BC/PAA hydrogel, and "*Wd*" is its dried weight. The thicknesses of BC, PAA and BC/PAA in different solution (deionized water, monomer solution and 1 M Na_2SO_4) were measured to evaluate the shrinkage properties. The mechanical and adhesive properties of BC/PAA were presented qualitatively/ apparently. Ionic conductivity was measured by CHI 600 and calculated using the following equation. $\sigma 0 = L/RA$, where L, R and A are the thickness, bulk resistance and area of the hydrogel electrolyte, respectively. The thermal stability of BC and BC/PAA were evaluated by thermogravimetric (TGA) analysis (10 ^oC/min, 25 ~ 650 ^oC).

RESULTS AND DISCUSSION

Physical-Chemical nature of BC, PAA and BC/PAA

The ATR-FTIR spectra of BC, PAA, and BC/PAA samples are shown in Figure 1. In the case of BC, the identified band at 1060 cm^{-1} is due to the C-O-C pyranose ring skeletal vibration. The typical band of pure PAA at 1710 cm^{-1} corresponds to the C=O stretching. They both appear in the spectra of BC/PAA, which proves that these two components are well combined.

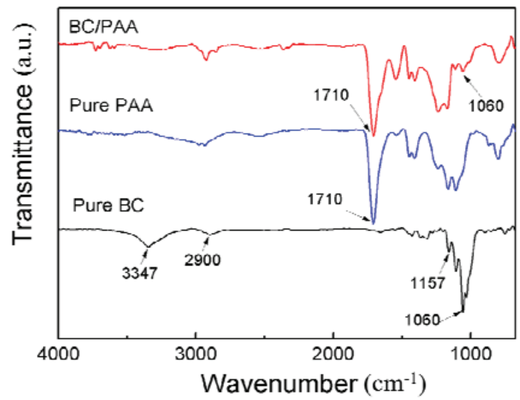

FIGURE 1: ATR-FTIR spectra of pure BC, pure PAA and BC/PAA.

Morphologies of PAA and BC/PAA

The morphologies of PAA and BC/PAA composite were studied using SEM. Figure 2 (a) and (b) show the surface images of freeze-dried PAA and BC/PAA, respectively. They present like wrinkled silk cloth. The existence of PAA in the surface of BC/PAA can make it sticky to flexible electrodes. Figure 2 (c) and (d) display their cross sectional images. PAA has huge pores with soft supports. In case of BC/PAA, the fragments of PAA get smaller and align along with BC nanofibers, the pores generate based on the porous structure of BC. It indicates that abundant hydroxyl groups in BC nanofibers surface attract acrylic acid monomers to react close to them.

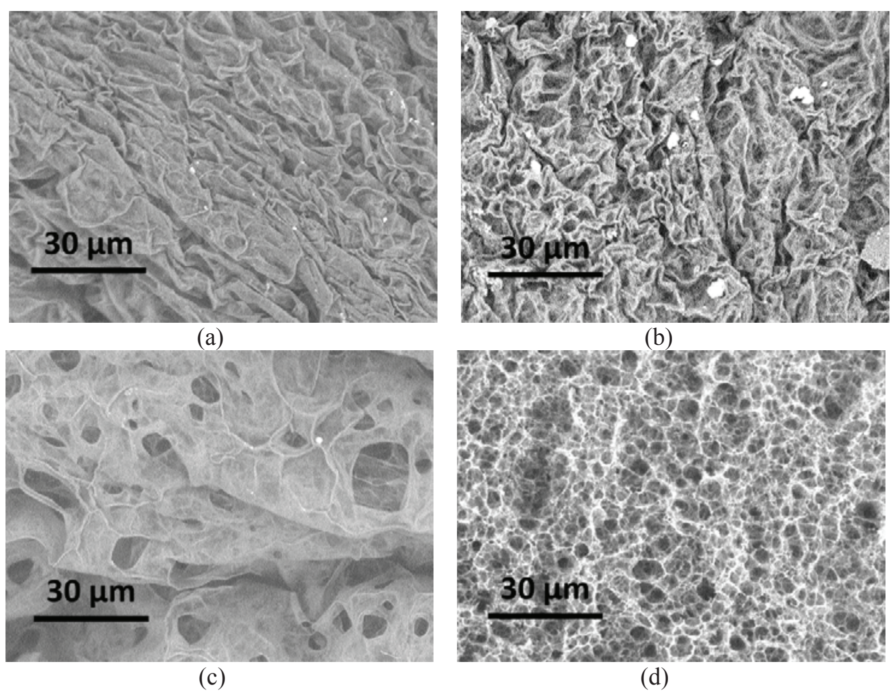

FIGURE 2: SEM images of PAA (a), BC/PAA (b) [surface] and PAA (c), BC/PAA (d) [cross-sectional].

Compression and Adhesion Properties

Double network with rigid and soft components in BC/polymer composite highly improves the anti-compression ability of original BC, which has been widely investigated [7]. The improvement of mechanical property of BC/PAA equilibrium swelled in 1 M Na_2SO_4 is shown in Figure 3 (a). BC is squeezed out under a modest compression and cannot recover, while BC/PAA is elastic. The adhesion of BC/PAA is also presented in Figure 3 (b), which proves that it is sticky. This property can prevent the split of two flexible electrodes when the assembled SC bends.

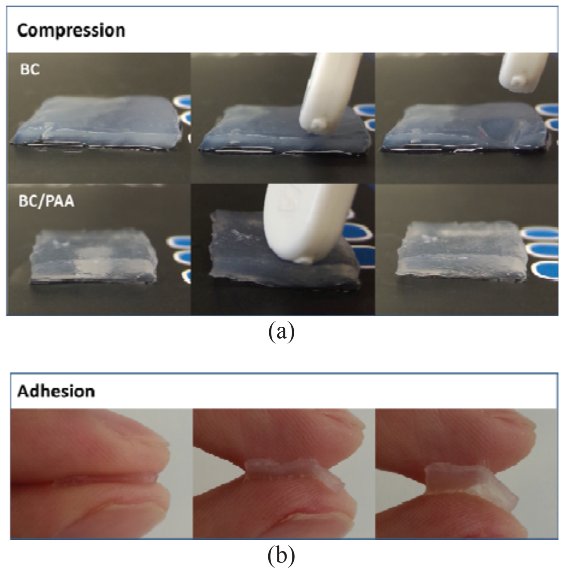

FIGURE 3: Visual images of compression ability of BC and BC/PAA (a), of adhesion ability of BC/PAA (b).

Effects of Electrolyte (1 M Na_2SO_4) on ionic conductivity

To prepare hydrogel electrolyte, BC/PAA was soaked in 1 M Na_2SO_4 electrolyte solution. However, the influences of ionic concentration on swelling behaviour of BC and PAA are different. PAA is a polyelectrolyte; its swelling ratio highly depends on the ionic concentration. In our study, PAA shrinks about 20 % in 1M Na_2SO_4 from the original size, while BC slightly changes. The shrinkage of PAA makes the BC/PAA composite electrolyte more compact but decreases the retention of electrolyte solution. But the retention (%) of BC/PAA can still reach approximately~500%. Its ionic conductivity can achieve to 0.06 $S\cdot cm^{-1}$.

Thermogravimetric Analyses

The TGA curves of pure BC and BC/PAA are presented in Figure 4. Pure BC underwent a single step of de - composition with a range from 245 to 378 °C, which confirms the purity of pure BC. BC/PAA exhibits three steps of decomposition. The first step is predominantly associated with the release of H_2O (120 °C); the second weight loss is assigned to the decomposition of carboxyl groups of PAA (230-280 °C); the third weight reduction in the region (360-500 °C) is likely due to the decomposition of the polymer backbone and hydroxyethyl groups. The influence of BC on the thermal stability of BC/PAA is not significant due to its little amount in the composite.

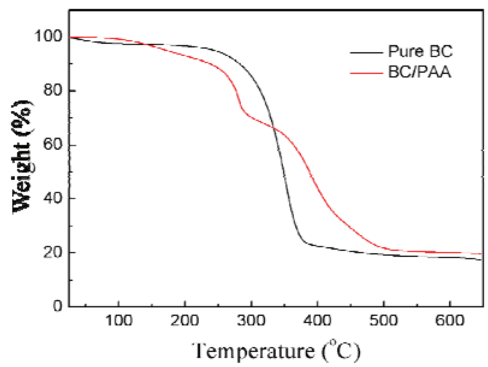

FIGURE 4: TGA curves of pure BC and BC/PAA

CONCLUSION

The BC/PAA composite hydrogel electrolyte was prepared using BC and PAA. It shows a highly porous structure, which is beneficial to the ion store and transfer. BC/PAA shrinks in 1M Na_2SO_4. However, its electrolyte retention capacity (%) reach approximately ~500 %, and the ionic conductivity is more or less 0.06 S cm^{-1}. Double network created by BC and PAA give this composite hydrogel a better mechanical property. Meanwhile, the incorporation of PAA makes BC/PAA sticky, which can be used to unify the two flexible electrodes. Those properties make this prepared BC/PAA hydrogel electrolyte a potential candidate for flexible SCs. But more work has to be done to investigate the performance when it is applied in flexible SCs.

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