

## IN SITU PREPARATION OF BACTERIAL CELLULOSE REINFORCED HYDROGEL ELECTROLYTE FOR FLEXIBLE SUPERCAPACITORS

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### Abstract

Due to their quasi solid state and high ionic conductivity, hydrogel electrolytes have great potential to be used in flexible supercapacitors (SCs) which is an important group of energy storage systems for portable devices. However, most hydrogels perform low mechanical properties and bad contact to flexible electrodes, especially under various deformations. Herein, we have prepared one hydrogel electrolyte with a double network created by poly acrylic acid (PAA) and sodium alginate (SA). PAA was chemically crosslinked by poly(ethylene glycol) diacrylate (PEGDA), where SA was ionic crosslinked by Ca<sup>2+</sup>. This hydrogel is also reinforced by bacterial cellulose (BC) clusters. *In-situ* polymerization was conducted to directly prepare this hydrogel electrolyte in the presence of two graphene based flexible electrodes. The resultant hydrogel was characterized by ATR-FTIR and scanning electron microscopy (SEM). Its shrinkage, mechanical property and ionic conductivity in KCl were also investigated. The electrochemical performance of assembled SC was subsequently studied. The results show our prepared hydrogel electrolyte has a promising application in flexible SCs.

**Keywords:** Flexible supercapacitors, hydrogel electrolyte, bacterial cellulose, *in-situ*

### 1. INTRODUCTION

Supercapacitors (SCs) possessing high power density, fast charge-discharge rates, and long cycle life, compared to batteries, are one promising candidate for novel energy storage devices [1]. Recently, in order to meet the rapid development of portable electronics, SCs are required to be light-weight, thin and flexible as well [2]. Flexible SCs mainly consist of two components, flexible electrodes and solid-state electrolytes. For solid-state electrolytes, they prevent the leakage of conventional liquid electrolytes when flexible SCs deform, and simplify their fabrication and packaging procedure. However, solid-state electrolytes display poor ionic conductivity, limiting the performance of assembled devices and their own use.

Hydrogel electrolytes prepared by synthetic polymers such as poly acryl acid (PAA) and poly acryl amide (PAAM) have a high porous structure and contain abundant electrolyte solution, providing comparable ionic conductivity into the corresponding electrolyte solution [3]. Unfortunately, they have low mechanical properties. Sodium alginate (SA) has a chain comprising mannuronic acid (M unit) and guluronic acid (G unit). The G blocks can form an ionic crosslink through divalent cations such as Ca<sup>2+</sup>, resulting in a network. Creation of an alginate network (natural polymer) into synthetic hydrogels/polymer to form a double network is an effective approach to improve their mechanical property [4].

In this paper, a bacterial cellulose (BC) reinforced novel hydrogel electrolyte with a double network structure created by PAA and SA is reported. The PAA network was covalently crosslinked by PEGDA, while the SA network was ionically crosslinked by Ca<sup>2+</sup>. Moreover, BC clusters (biosynthesized in Herstin-Schramm nutrient medium by *Gluconacetobacter xylinus*), a biopolymer having an inherent network structure was also added to reinforce further its mechanical property. Finally, PAA/SA-Ca/BC, a flexible SC was achieved directly by *in-*

*situ* preparation of this hydrogel electrolyte on two graphene based flexible electrodes. The resultant hydrogel demonstrates an improved mechanical property and promising performance in flexible SCs.

## 2. EXPERIMENTAL

### 2.1. Preparation of hydrogel electrolytes

Procedure for the preparation of hydrogel electrolytes was as follows: 3.6 g acryl acid was dissolved in 2.5 mL water and neutralized by 2.86 g KOH. Then, 1 g PEGDA, 0.06 g  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , 7.5 g BC suspension and 25.6 mg (Potassium persulfate) KPS was added into this solution. Finally, the obtained solution was dropped into 18.4 g 5 wt% of SA solution under stirring. The mixture was casted into a mold and kept in the oven for 1h at 80 °C. The gained hydrogel was immersed into 1M  $\text{CaCl}_2$  solution for 2 days and then in 2M KCl for 1 day. SA cross-linked by  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  was designated as “SA- $\text{CaSO}_4$ ”, and cross-linked by  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CaCl}_2$  was named as “SA-Ca”.

### 2.2. Fabrication of flexible supercapacitors

The flexible reduced graphene oxide (RGO) electrode with graphite current collector was achieved by vacuum filtration. Two these flexible electrodes were face to face placed and separated by above mixture solution. This fixture was moved into a mold and cured. The formation of hydrogel occurs in the presence of two flexible electrodes. Obtained SC was immersed into  $\text{CaCl}_2$  and KCl solution similar way as mentioned above.

### 2.3. Characterization

The resultant hydrogel was characterized by ATR-FTIR (Nicolet iS5). Their morphology was investigated by scanning electron microscopy (SEM, FEI Nova NanoSEM 450). The compression test was conducted by Testometric MT350-5CT. The electrochemical characterization was carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) using Autolab PGSTAT128N (Metrohm, Netherlands).

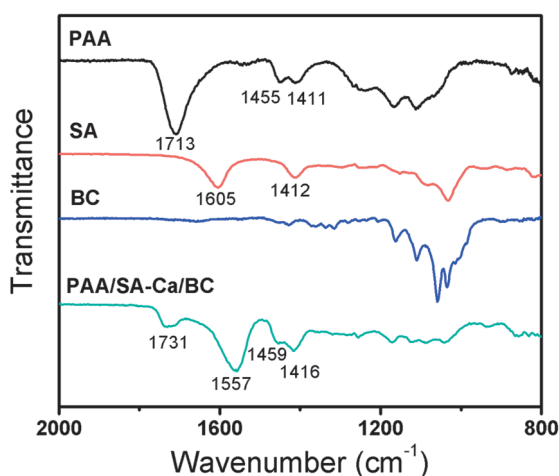
## 3. RESULTS AND DISCUSSION

### 3.1. ATR-FTIR

The ATR-FTIR spectrum of PAA/SA-Ca/BC is shown in **Figure 1**. For comparison, the spectra of pure PAA, SA and BC are also included. For pure PAA, the peak centered at  $1713 \text{ cm}^{-1}$  was assigned to the associated carboxylic acid groups [5]. For SA, the peak for carboxylate group appears at  $1605 \text{ cm}^{-1}$ . These corresponding peaks are obviously found in the spectrum of PAA/SA-Ca/BC. However, the peak for carboxylate group is altered slightly to  $1557 \text{ cm}^{-1}$  due to the ionic crosslinking with  $\text{Ca}^{2+}$  [6]. The presence of BC is hardly proved by ATR-FTIR because of its low content.

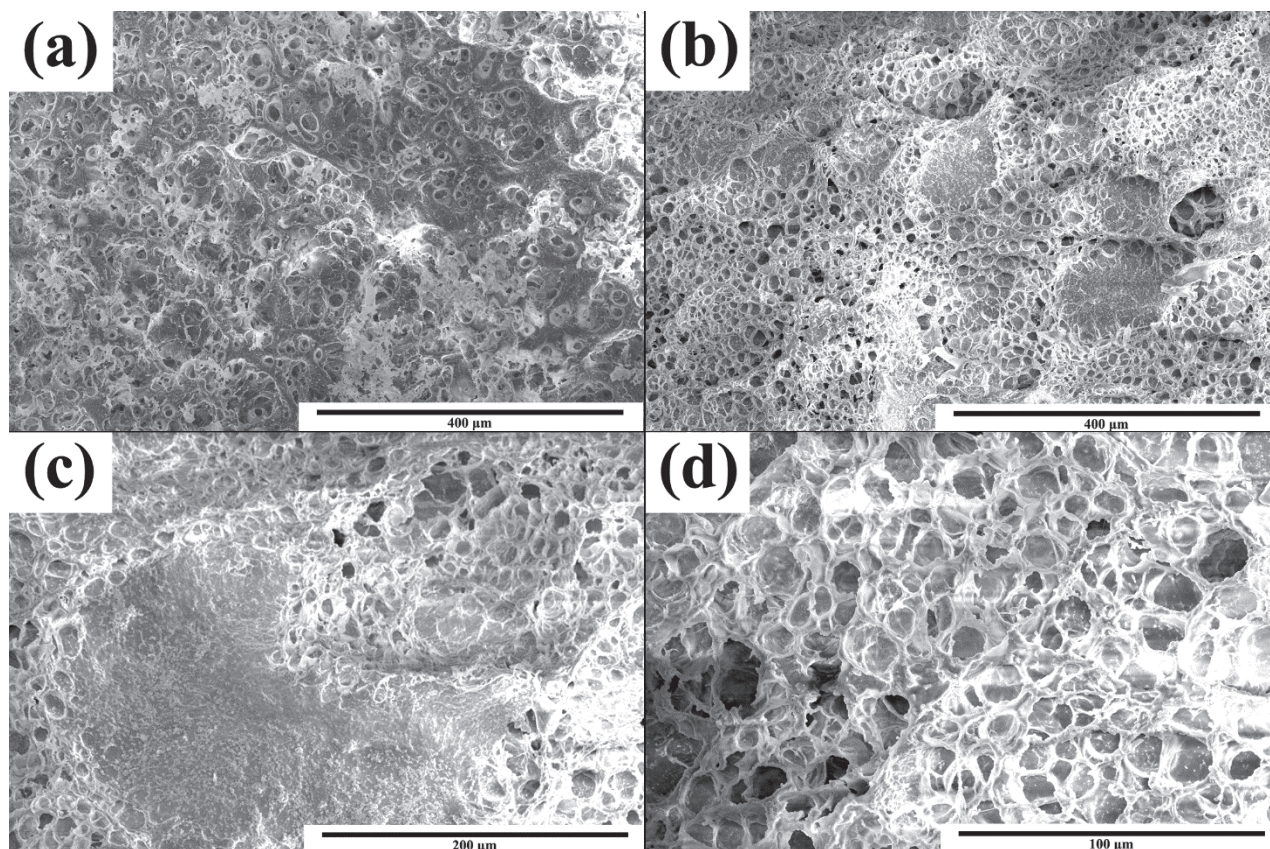
### 3.2. SEM

The morphology of PAA/SA-Ca and PAA/SA-Ca/BC was shown in **Figure 2**. It can be seen in **Figure 2a** and **b** that both the hydrogels exhibit high porous structure. In case of PAA/SA-Ca/BC shown in **Figure 2b**, BC clusters present in the network, acting as knots, which indicates that BC



**Figure 1** ATR-FTIR spectra of pure PAA, SA, BC and PAA/SA-Ca/BC

improve the mechanical property. The size of BC clusters are about 200  $\mu\text{m}$  presented in **Figure 2c** whereas, PAA/SA-Ca/BC exhibits more uniform porous structure shown in **Figure 2d**. The diameter of each pore is about 13.5  $\mu\text{m}$ . A uniform and highly porous structure endows hydrogel electrolytes (PAA/SA-Ca/BC) having a high ionic conductivity as well.



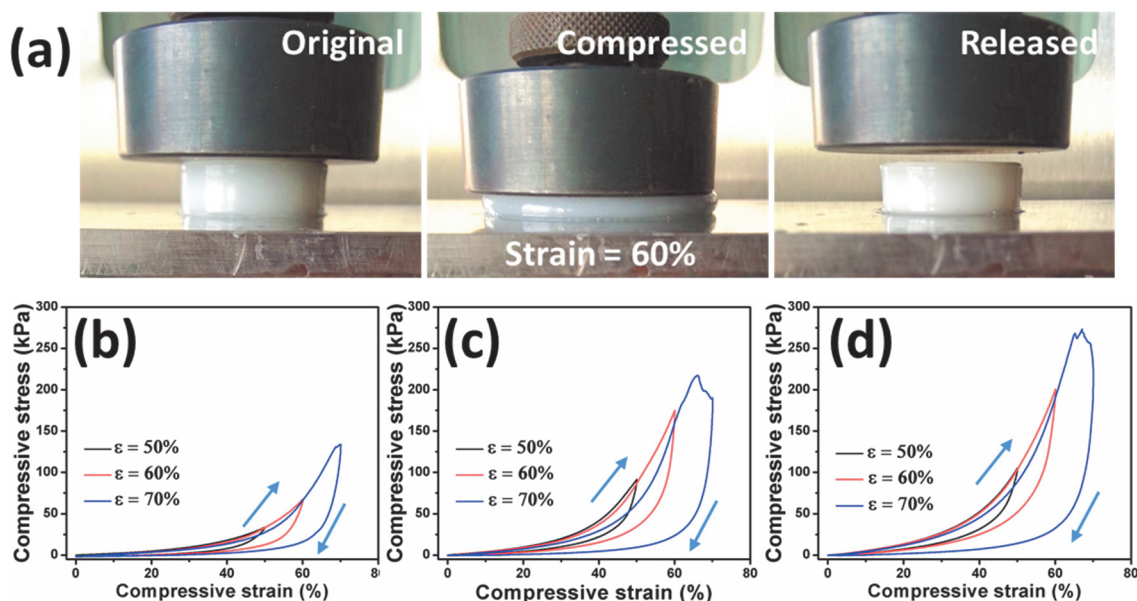
**Figure 2** SEM images of (a) PAA/SA-Ca and (b) (c) (d) PAA/SA-Ca/BC

### 3.3. Shrinkage and Mechanical property

The ionic cross-linkage of SA with  $\text{Ca}^{2+}$  ion was successively conducted by  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CaCl}_2$ . The slow  $\text{Ca}^{2+}$  releasing of  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  makes a gradual crosslink of alginate, resulting in a homogeneous hydrogel. High soluble  $\text{CaCl}_2$  conducts a fast and further crosslink of alginate. The rearrangement of G units in alginate chains makes the hydrogel shrink, which is negative to *in-situ* preparation. For PAA/SA-Ca/BC, it shrinks about 83.3% of the initial in 1M  $\text{CaCl}_2$  and then 93% in 2M KCl.

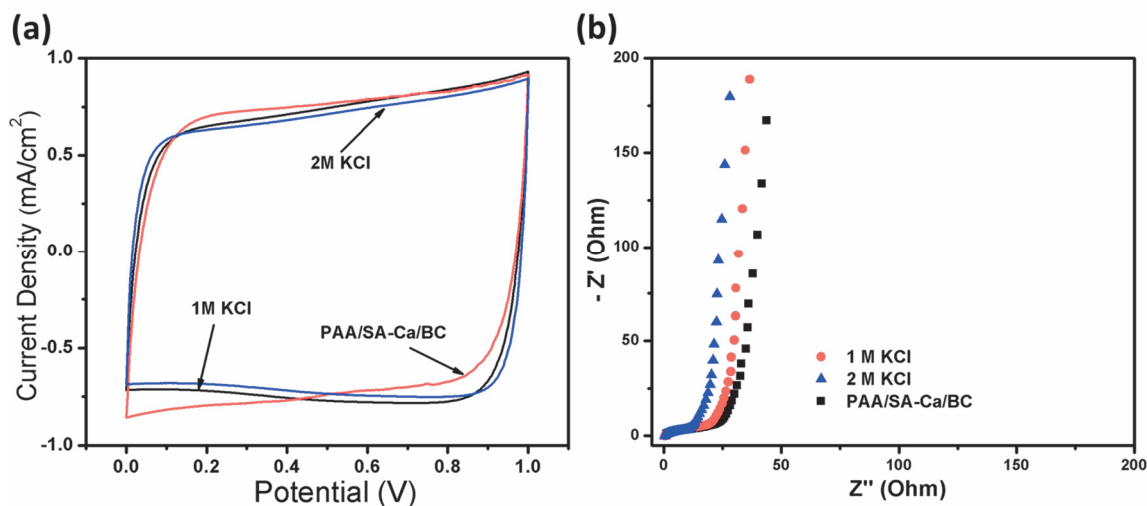
**Figure 3a** shows the process of compressive test using an example of PAA/SA-Ca/BC hydrogel. The hydrogel was compressed to the required strain and then released to the initial state. Several cycles (strain = 50%, 60% and 70%) have been conducted until the hydrogel being fractured. PAA/SA-Ca/BC hydrogel exhibits excellent compressive property with a strain of 60% shown in **Figure 3a**.

Three samples exhibits similar compressive behaviors shown in **Figures 3b, c** and **d**. They have good reversibility within strains of 50% and 60% and break down when the strain goes up to 70%. However, the maximum compressive stress of each cycle is different. With the assistance of further ionic cross-linkage of  $\text{CaCl}_2$ , PAA/SA-Ca achieved a compressive stress up to 217 kPa, compared to PAA/SA- $\text{CaSO}_4$  of 134 kPa. On the other hand, with the reinforcement of BC clusters, PAA/SA-Ca/BC exhibits a compressive stress of 273 kPa.



**Figure 3** Compressive mechanical properties of prepared hydrogel electrolytes. (a) Images of compressive process of PAA/SA-Ca/BC hydrogel. Compressive stress as a function of strain from cycling compressive test of (b) PAA/SA-CaSO<sub>4</sub>, (c) PAA/SA-Ca and (d) PAA/SA-Ca/BC

### 3.4. Ionic conductivity and electrochemical performance



**Figure 4** (a) CV curves and (b) Nyquist plots of SCs with electrolyte of 1M KCl, 2M KCl and PAA/SA-Ca/BC, respectively

Ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) 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 ionic conductivity of PAA/SA-Ca/BC is  $0.035 \text{ S cm}^{-1}$ , compared to that of 2M KCl ( $0.04 \text{ S cm}^{-1}$ ), which is appropriate to be used in SCs. **Figure 4a** shows the CV curves of assembled SCs with electrolyte of 1M KCl, 2M KCl and PAA/SA-Ca/BC, respectively. They exhibit rectangular shapes, which are typical for carbon materials due to electric double-layer mechanism. Rare difference is observed between these three electrolytes. **Figure 4b** displays their Nyquist plots. In the region of low frequency, they perform nearly perfect capacitive behavior. In the high frequency region, they have almost same bulk solution

resistance ( $R_s$ ), and the charge transfer resistance ( $R_{ct}$ ) of PAA/SA-Ca/BC is just a little higher than others. It indicates that our prepared PAA/SA-Ca/BC hydrogel electrolyte has a very similar electrochemical performance to their liquid electrolytes.

#### 4. CONCLUSION

PAA/SA-Ca/BC hydrogel electrolyte has been prepared with an improved mechanical property. Its mechanical property highly improved not only due to ionic cross-linkage of SA but also the reinforcement of BC clusters (200  $\mu\text{m}$ ). The compressive stress can reach up to 273 kPa. This hydrogel electrolyte exhibits a low shrinkage of 93% in 2M KCl. Moreover, it has a high ionic conductivity of 0.035 S  $\text{cm}^{-1}$ . Subsequently, PAA/SA-Ca/BC was *in-situ* prepared into a flexible SC device, which displays similar electrochemical performances to liquid electrolyte. It indicates that PAA/SA-Ca/BC hydrogel electrolyte has a positive possibility to replace liquid electrolyte and be used in flexible SCs.

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