Journal of Power Sources 378 (2018) 603–609

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Preparation of the polyelectrolyte complex hydrogel of biopolymers via a semi-dissolution acidification sol-gel transition method and its application in solid-state supercapacitors

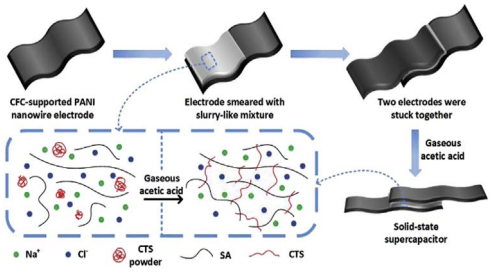
Jian Zhao[a], Yu Chen[a,*], Ying Yao[a], Zong-Rui Tong[a], Pu-Wang Li[b], Zi-Ming Yang[b], Shao-Hua Jin[a]

[a] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, PR China
[b] Agriculture Products Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, PR China

HIGHLIGHTS

- A novel SD-A-SGT method was used to prepare the PECH of natural polymers.
- The PECH with controllable sol-gel transition and uniform composition was prepared.
- The PECH was applied as the hydrogel electrolyte of solid-state supercapacitors.
- The PECH exhibited a high ionic conductivity and reasonable mechanical properties.
- The PECH SC showed large specific capacitance and excellent cycling stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrogel
Chitosan
Sodium alginate
Polyelectrolyte complex
Solid-state supercapacitor

ABSTRACT

Hydrogels have drawn many attentions as the solid-state electrolytes in flexible solid-state supercapacitors (SCs) recently. Among them, the polyelectrolyte complex hydrogel (PECH) electrolytes of natural polymers are more competitive because of their environmentally friendly property and low cost. However, while mixing two biopolymer solutions with opposite charges, the strong electrostatic interactions between the cationic and anionic biopolymers may result in precipitates instead of hydrogels. Here we report a novel method, semi-dissolution acidification sol-gel transition (SD-A-SGT), for the preparation of the PECH of chitosan (CTS) and sodium alginate (SA), with the controllable sol-gel transition and uniform composition and successfully apply it as the hydrogel electrolyte of solid-state supercapacitors (SCs). The CTS-SA PECH exhibits an extremely high ionic conductivity of 0.051 $S \cdot cm^{-1}$ and reasonable mechanical properties with a tensile strength of 0.29 MPa and elongation at break of 109.5%. The solid-state SC fabricated with the CTS-SA PECH and conventional polyaniline (PANI) nanowire electrodes provided a high specific capacitance of 234.6 $F \cdot g^{-1}$ at 5 $mV \cdot s^{-1}$ and exhibited excellent cycling stability with 95.3% capacitance retention after 1000 cycles. Our work may pave a novel avenue to the preparation of biodegradable PECHs of full natural polymers, and promote the development of environmentally friendly electronic devices.

* Corresponding author.
E-mail address: cylsy@163.com (Y. Chen).

https://doi.org/10.1016/j.jpowsour.2018.01.005
Received 13 October 2017; Received in revised form 17 December 2017; Accepted 3 January 2018
0378-7753/ © 2018 Elsevier B.V. All rights reserved.

1. Introduction

Recently, great interest has been aroused by flexible electronic equipments, such as wearable devices, rollup displays and bendable mobile phones [1]. Much progress has been made to develop high performance flexible energy storage and conversion devices [2]. Among them, supercapacitors (SCs) are emerging as an important class of energy storage devices with their many advantages, such as fast charging/discharging ability, safety and long cycling life and have shown a great potential for practical applications [3–6]. A flexible solid-state SC usually consists of flexible electrodes, a solid-state electrolyte, a separator and a flexible packaging material [7]. The solid-state electrolytes in flexible solid-state SCs reported recently are usually made with hydrogels that have the capability to fulfill multiple roles of electrolyte, separator and binder in solid-state SCs [8–11]. However, most of these hydrogel electrolytes are chemical hydrogels of synthetic polymers that are cross-linked by organic cross-linkers [9]. In contrast to chemical hydrogels, physical hydrogels, such as polyelectrolyte complex hydrogels (PECHs), are held together by noncovalent bonds without toxic organic cross-linkers needed [12]. Although a few PECHs have been used in SCs recently, these electrolytes are made with synthetic polymers, such as poly(styrenesulfonic acid) [13] and poly(ionic liquid) [11]. Therefore, these hydrogels are high cost, environmentally hazardous, and even toxic.

Biopolymer based electrolytes (BPEs) can overcome the major disadvantages of synthetic polymer electrolytes, such as high cost and environmentally hazardous [14]. Recently, many BPEs have been reported as the electrolytes of energy storage and conversion devices, such as gelatin hydrogel electrolytes for electrochemical SCs [15], and CTS hydrogel membrane electrolytes for direct borohydride fuel cells and electrical double layer capacitors [16,17]. However, to the best of our knowledge, no biopolymer based PECHs have been reported as the electrolytes of solid-state SCs.

Among various natural biopolymers, CTS and SA, two polysaccharide polymers, are the most promising raw materials of PECHs for the applications in solid-state SCs. They can form polyelectrolyte complexes (PECs) with each other without cross-linkers needed via the strong electrostatic interactions between the cationic amino groups of CTS and the anionic carboxyl groups of SA [18]. In addition, the PECH of CTS and SA is environmentally friendly, biodegradable and biocompatible. However, it is very difficult to prepare PECHs of desirable shapes and uniform compositions with CTS and SA directly because, unlike synthetic polymer hydrogels, PECHs of natural biopolymers can not be prepared by chemical polymerization [11,19]. Instead, they are usually prepared by mixing two biopolymer solutions with opposite charges [20]. The strong electrostatic interactions between the cationic and anionic biopolymers may result in precipitates instead of hydrogel [21]. Therefore, a new method is highly desired for the preparation of homogeneous PECHs of natural biopolymers.

In the present work, a novel method, semi-dissolution acidification sol-gel transition (SD-A-SGT), was developed for preparing PECHs with the biopolymers, CTS and SA. In the semi-dissolution process, a certain amount of CTS powder was uniformly dispersed in an as-prepared SA solution. The suspension of CTS power in SA solution was acidified in a gaseous acetic acid atmosphere, which gradually dissolved CTS in the SA solution and formed a PECH of CTS and SA. This novel preparation method ensures the polyelectrolytes with opposite charges uniformly dispersed before the formation of strong ionic bonds, and thus prevents possible precipitations. The application of the prepared CTS-SA PECH was explored for the first time as the electrolyte in flexible solid-state SCs. The three-dimensional cross-linking network of the CTS-SA PECH formed mainly via the strong electrostatic interactions between CTS and SA provided ion migration channels for the electrolyte ions. This novel PECH exhibited good ionic conductivity, excellent electrochemical performances and desired mechanical strength. It is believed that the CTS-SA PECH prepared via the SD-A-SGT method would have broad application prospects and can promote the development of environmentally friendly electronic and medical devices.

2. Experimental section

2.1. Materials

CTS with a deacetylation degree of 90% and an average molecular weight of 2.3×10^5 was purchased from Zhejiang Aoxing Biotechnology Co., Ltd. Analytical grade SA was purchased from Aladdin Industrial Corporation (Shanghai, China). Analytical grade acetic acid, ammonium persulfate and NaCl were purchased from Xilong Chemical Co., Ltd. (Guangdong, China). Analytical grade aniline was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Carbon fiber cloth (CFC, WOS 1002) was purchased from CeTech Co., Ltd. (China).

2.2. Preparation of CTS-SA PECH via SD-A-SGT method

CTS-SA PECHs were prepared by the SD-A-SGT method. Certain amounts of SA and NaCl were added to distilled water under stirring to form a homogeneous solution. CTS powder was then added to the SA solution and stirred for 4 h to form a slurry solution containing SA, NaCl and insoluble CTS powder. The weight percentages of both CTS and SA in the solution were determined to be 4 wt%, and that of NaCl was varied to 0, 2, 4, 6, or 8 wt%. The slurry solutions with different weight percentages of NaCl were respectively poured into Petri dishes that were then put in a larger vessel containing an appropriate amount of acetic acid and stayed at room temperature for a certain period of time until the slurry solutions were transformed into hydrogels. The hydrogels were quickly washed with distilled water to remove acetic acid residues, and sealed in valve bags before use.

2.3. Fabrication of solid-state SCs

Solid-state SCs were fabricated with CTS-SA PECH as the electrolyte and conventional PANI nanowires as the electrodes. The CFC-supported PANI nanowire electrodes were prepared as described in literature [22]. Briefly, 1.83 mL (2 mmol) aniline was added to 40 mL of 0.5 M $HClO_4$ aqueous solution. After a carbon fiber cloth (3 cm × 2 cm) was placed in the aniline solution, ammonium persulfate (304 mg, 1.34 mmol) was added to the reaction solution at 0–5 °C and mechanically stirred for 12 h. The carbon fiber cloth was then removed from the solution and washed with distilled water to form a CFC-supported PANI nanowire electrode. The average loading of the PANI on the carbon fiber cloth was measured to be 0.91 $mg{\cdot}cm^{-2}$.

SC was prepared via the in-situ SD-A-SGT of the PECH. A slurry solution of CTS, SA and NaCl was smeared on two electrodes with a thickness of 1 mm and a surface area of 2 cm × 2 cm, which were put together and placed in a larger vessel containing an appropriate amount of acetic acid. The SD-A-SGT was allowed to proceed at room temperature for a certain period of time until the CTS-SA PECH was formed between the electrodes to achieve a SC with good contact between the PECH electrolyte and electrodes.

2.4. Characterizations of CTS-SA PECH

The FTIR spectra of CTS, SA and PECH were measured on a Nicolet NEXUS-470 FTIR spectrometer (Nicolet Instrument Co., USA) in the range of 400–4000 cm^{-1} at a resolution of 6 cm^{-1} with 32 scans. CTS-SA PECHs were lyophilized before testing and the test specimens were prepared by the KBr-disk method.

Solid state ^{13}C NMR analyses of CTS, SA and freeze-dried PECH were performed on a ^{13}C NMR spectrometer (UltraShield 600 PLUS, Germany Bruker) at the recording frequency of 100.63 MHz and spinning rate of 8 kHz.

Download English Version:

https://daneshyari.com/en/article/7726199

Download Persian Version:

https://daneshyari.com/article/7726199

Daneshyari.com