



# High performing all-solid electrochemical capacitor using chitosan/poly(acrylamide-co-diallyldimethylammonium chloride) as anion conducting membranes

Bei Ao <sup>a</sup>, Yanan Wei <sup>a</sup>, Min Wang <sup>a</sup>, Yixiao Cai <sup>a, b, d, \*</sup>, Keryn Lian <sup>c</sup>, Jinli Qiao <sup>a, b, \*\*</sup>

<sup>a</sup> State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China

<sup>b</sup> Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

<sup>c</sup> Flexible Electronics and Energy Laboratory, Department of Material Science and Engineering, University of Toronto, 184 College St., Toronto, ON, Canada, M5S 3E4

<sup>d</sup> NUS Environmental Research Institute, National University of Singapore, 1 Create Way, Singapore 138602, Singapore

## ARTICLE INFO

### Article history:

Received 19 December 2017

Received in revised form

17 April 2018

Accepted 19 April 2018

Available online 21 April 2018

### Keywords:

Anion-exchange membrane

Double cross-linking

Alkaline and oxidative stability

Specific capacitance

All-solid electrochemical capacitor

## ABSTRACT

The aim of the present work is to demonstrate a novel alkaline anion-exchange membrane composed of chitosan (CS) and poly (acrylamid-co-diallyldimethylammonium chloride) (PAADDA) for electrical double layer capacitors (EDLCs). The CS-PAADDA-OH<sup>-</sup> membranes were prepared through a combined thermal and chemical cross-linking strategy and their physical-chemical properties were investigated. As a notable example, when the mass fraction of PAADDA was about 33%, the CS-PAADDA-OH<sup>-</sup> membrane exhibits excellent OH<sup>-</sup> conductivity, reaching high as 0.0151 S cm<sup>-1</sup>, while its water uptake is only about 32.23%. Such membrane also showed optimal mechanical property and excellent thermal stability, due to the compact and dense network. Moreover, all the testing membranes showed high oxidative stability in 30% H<sub>2</sub>O<sub>2</sub> solution, and a robust alkaline stability in 8 M KOH at 60 °C for 320 h of evaluation. The resultant EDLC device demonstrated a voltage window at about 1.2 V, sustaining a cycle-life over 2000 cycles. Even when the scan rate is up to 5 V s<sup>-1</sup>, the device still maintained excellent rate capability. This study provides feasibility of transforming bulky liquid devices to safer and solid thin devices.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

The recent boom in wearable electronics and flexible displays has raised the demand for optimization of currently available energy conversion and storage technologies. Electrochemical capacitors (ECs) are an important class of energy storage devices which have received much attention owing to their higher power density, cycle efficiency, and fast charge/discharge rates as against batteries [1,2]. According to the charge-storage mechanism, an EC stores energy using either ion adsorption (electrical double layer

capacitors, EDLCs) or fast and reversible Faradic reactions (pseudocapacitors) [3]. There is also another type of capacitor termed as “hybrid capacitor” with two dissimilar electrodes, interestingly, one is battery type and another is capacitor type [4].

Tremendous research and development efforts have been devoted to investigating the two carbon-based electrodes and an organic electrolyte in EDLCs. Unquestionably, electrolyte plays a crucial role in determining the performance of EDLCs. Previous studies have primarily focused on liquid electrolytes (LEs) such as aqueous solution, organic solution or ionic liquids [5–8]. Within commercially available EDLCs, the practicability of LE is hindered by weaknesses such as electrolyte leakage, corrosion, and environmentally hazardous. Accordingly, it is necessary to develop alternative electrolytes for EDLCs. One efficacious strategy is to use solid polymer electrolytes (SPEs) for above applications, since they are prone to solve the leakage problems, equally important, they exhibit the potential to promote capacitors to be more reliable and compact. Although, the SPE is high resistance and has relatively low

\* Corresponding author. State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China.

\*\* Corresponding author. State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China.

E-mail addresses: [yxcai@dhu.edu.cn](mailto:yxcai@dhu.edu.cn) (Y. Cai), [qiaojl@dhu.edu.cn](mailto:qiaojl@dhu.edu.cn) (J. Qiao).

melting point compared with liquid electrolytes, but affords the EDLCs flexible geometry, electrochemical stability, mechanical strength and high corrosion resistance [9,10]. However, extensive research efforts on polymer electrolytes have been mainly devoted to  $H^+$  ion-conducting systems [4–8]. Moreover, SPEs have already conveniently used in the fuel cell technology, hitherto there is limited research on developing the  $OH^-$  ion conducting analogues, especially for ECs [11,12].

In this work, we report a series of novel  $OH^-$  conducting membranes based on water-soluble quaternized copolymers and chitosan (CS). CS has been selected as the polymer matrix to prepare membrane electrolyte due to its high hydrophilicity, good film forming capability, biodegradable, economic, and non-toxic [13]. Furthermore, as a result of abundant active amino groups ( $-NH_2$ ) and hydroxyl groups ( $-OH$ ), CS possesses high hydrophilicity and can be easily cross-linked by chemical and thermal treatment [14], affording the membrane high mechanical strength and chemical resistance. At the same time, the uses of CS in supercapacitors were gradually reported, suggesting its applicable potential [15,16]. However, the pristine CS membrane shows low ionic conductivity for no mobile ions in its structure [17]. Therefore, we utilize quaternized copolymer PAADDA for its water-soluble characteristic, which is compatible with CS and offers anions as charge carriers for hydroxide ( $OH^-$ ) [18]. Upon the membrane preparation, a simple blending method is used that allows the quaternized copolymer PAADDA well incorporated into CS networks, thus forms interpenetrating polymer networks. Due to high hydrophilic properties of CS and PAADDA, the blending of two precursor solutions can be easily realized without phase separation. The membrane is further treated by thermal and chemical cross-linking methods, respectively, during which glutaraldehyde (GA) is used as a cross-linking agent. Upon the cross-linking reaction, GA tailors CS polymer into different forms. Specifically, GA obtains two aldehyde groups ( $-CHO$ ) that can attach to amino groups ( $-NH_2$ ) and hydroxyl groups ( $-OH$ ) from CS. Moreover, GA shows higher selectivity and flux than another crosslinked agents due to their higher flexibility [19,20]. Therefore, the stability and performance of CS and PAADDA are expected to be largely improved [21]. This work demonstrates

the feasibility of converting bulk liquid electrochemical devices into thin, portable and high-performing all-solid devices.

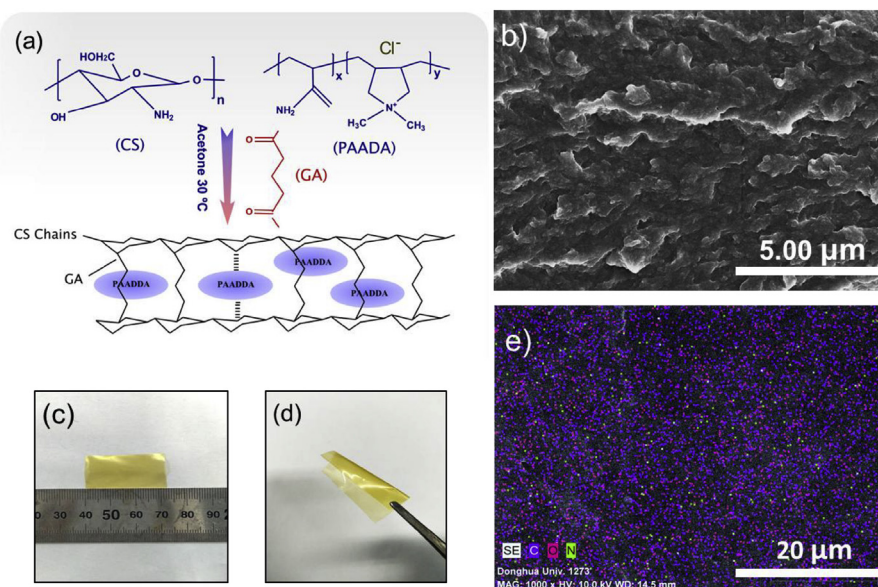
## 2. Results and discussion

### 2.1. FT-IR analysis

Fig. S1 shows the FT-IR spectra of CS/PAADDA- $OH^-$  membranes with different PAADDA contents after thermal and chemical cross-linking modifications. As reported, the chemical cross-linking occurs between the  $-OH$  of CS and the  $-CHO$  of glutaraldehyde (GA) via an acid-catalyzed reaction [22]. Here, the strong absorption peak between  $3000$  and  $3700\text{ cm}^{-1}$  is clearly observed, which corresponds to the stretching vibration of  $-OH$  from CS or the bound water. The peaks at  $2943$  and  $2873\text{ cm}^{-1}$  arise from the stretching of  $-CH_3$ ,  $-CH_2$ , and  $-CH$  groups, and the sharp absorption peaks at  $1660$  and  $1564\text{ cm}^{-1}$  can be assigned to the stretching vibrations of the I belt  $\nu(C=O)$  and the II belt  $\nu(C-N)$  absorption from PAADDA can be clearly observed due to the cross-linking reaction. The enhancement of the  $C-O-C$  ester mode at  $1100\text{ cm}^{-1}$  is most likely due to the presence of cross-linking network between CS and GA. Moreover, the peak intensities of I belt  $\nu(C=O)$  and the II belt  $\nu(C-N)$  are increased significantly with the PAADDA content increases. These results clearly confirm successful incorporation of the quaternary ammonium groups into the CS/PAADDA- $OH^-$  membranes.

### 2.2. SEM studies of CS/PAADDA- $OH^-$ membranes

All the membranes prepared are translucent with a pale yellow, and one typical sample is shown in Fig. 1(c). Fig. 1(d) reveals the flexible nature of these membranes. The cross-sectional SEM images of these membranes are summarized in Fig. S2. Generally, each CS/PAADDA- $OH^-$  membrane reveals a dense structure, while no obvious surface degradation or bulk damage, such as the appearance of cracks or phase separation is detected. This is particularly favorable for continuous ion conduction and resultant device stability, also indicates that CS and PAADDA are combined well with



**Fig. 1.** (a) Chemical structures of CS, PAADDA and cross-linked CS/PAADDA- $OH^-$  alkaline membranes; (b) The SEM image of PAADDA33; (c) the actual appearance of PAADDA33; (d) the curved PAADDA33; (e) Elemental mapping of PAADDA33.

Download English Version:

<https://daneshyari.com/en/article/6602859>

Download Persian Version:

<https://daneshyari.com/article/6602859>

[Daneshyari.com](https://daneshyari.com)