Journal of Colloid and Interface Science 534 (2019) 672–682

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

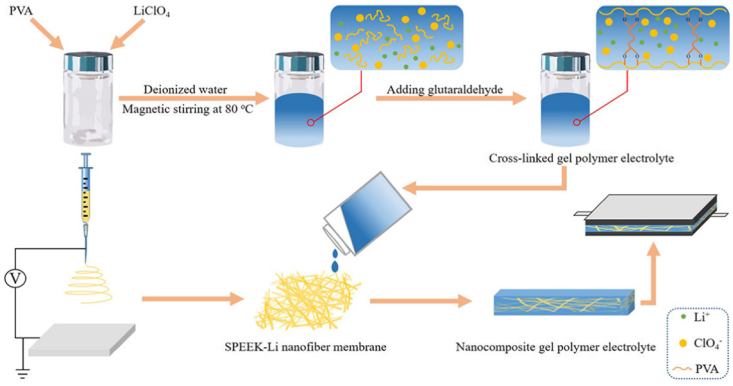
journal homepage: www.elsevier.com/locate/jcis

High performance electrospun Li^+-functionalized sulfonated poly(ether ether ketone)/PVA based nanocomposite gel polymer electrolyte for solid-state electric double layer capacitors

Nan Lu [a], Xi Zhang [b,c], Ruiqi Na [a], Wendi Ma [a], Chongyang Zhang [a], Yuchao Luo [a], Yongfeng Mu [a], Shuling Zhang [a], Guibin Wang [a,*]

[a] College of Chemistry, Key Laboratory of High Performance Plastics, Ministry of Education, Jilin University, Changchun 130012, PR China
[b] Department of Hand Surgery, The Second Hospital of Jilin University, Changchun 130041, PR China
[c] Department of Burn Surgery, The First Hospital of Jilin University, Changchun 130021, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 August 2018
Revised 6 September 2018
Accepted 10 September 2018
Available online 22 September 2018

Keywords:
SPEEK(Li)
Electrospinning
Nanocomposite gel polymer electrolytes
Cross-linked PVA/$LiClO_4$

ABSTRACT

The synthesis of a nanocomposite gel polymer electrolytes (NGPEs) using Li^+-functionalized SPEEK (SPEEK(Li)) nanofiber membrane as a matrix, cross-linked PVA as a gelled agent and $LiClO_4$ as an electrolytic salt for electric double layer capacitors (EDLCs) were reported in this work. Compared with conventional PVA based gel electrolyte, the "$SO_3^-Li^+$" functional groups and the pores structure of the SPEEK (Li) nanofiber membrane improves the ionic conductivity as well as mechanical stability, which made the prepared NGPEs exhibited a high ionic conductivity of 8.9×10^{-3} S cm^{-1} at ambient temperature and a large voltage stability window range from 0 to 2.0 V. The fabricated symmetric EDLCs showed a specific capacitance of 146.96 F g^{-1} at a current density of 0.5 A g^{-1}, with a maximum energy density of 18.26 W h kg^{-1}. Meanwhile, the EDLCs showed outstanding cyclical stability of 98% specific capacitance retention after 3000 cycles GCD testing, all of these results indicated that the NGPEs should be appropriate to EDLCs and next-generation energy storage systems.

* Corresponding author.
E-mail address: wgb@jlu.edu.cn (G. Wang).

https://doi.org/10.1016/j.jcis.2018.09.027
0021-9797/

1. Introduction

Technology has advanced at a breathless pace, meanwhile, the world's population also proliferates, which has led to the fast consumption of fossil fuels, leading to global challenges in serious environmental problems and energy crisis [1–6]. These problems are likely to become steadily exacerbate. Consequently, considerable explorations are urgent needed to development sustainably and renewable clean energy sources [6]. In fact, electrochemical energy storage (referred as EES) is playing an important role in the post-fossil fuel era [7]. Among the various EES systems, electric double layer capacitors (EDLCs) have been regarded as one of the most promising energy storage devices in recent years, as they exhibit favorable features of high energy density (compared with conventional capacitors), superior power density (compared with batteries), fast charging-discharging rates, long cycling stability, and environmental friendly [7–11], which make the EDLCs possible to yield unusually brilliant results in the next-generation energy storage systems.

The electrochemical performances of EDLCs are usually determined by the electrode materials, electrolytes and their interactions [12]. Notably, the electrolytes used in EDLCs often play an important part to determine the maximum operating voltage and safety of them [13,14]. The conventional electrolytes used in EDLCs, such as aqueous electrolytes, organic electrolytes etc., exhibit high ionic conductivities and widely used in commercial EDLCs [15–18]. However, these electrolytes may leak during packaging and lead to safety issues. In recent years, polymer electrolytes have obtained more attention and are considered to be potential substitutions of conventional electrolytes, because they showed excellent properties of safety and flexibility [19,20]. Gel polymer electrolytes (GPEs) [21] and micro-porous polymer electrolytes (MPEs) [22] have recently attracted much attention due to the high ionic conductivity (compared with solid state electrolytes) and favorable safety (effective to prevent leakage compared with liquid electrolytes) [23–26], and considerable efforts have been devoted to various GPEs for EDLCs systems, such as polyacrylamide (PAAM) [27,28], polyethylene oxide (PEO) [29–31] and polyvinyl alcohol (PVA)-based [32–34] GPEs. Among them, PVA-based GPEs are considered to be prospective GPEs owing to the favorable features of excellent hydrophilicity, price moderate and toxicity free, but the conventional PVA-based gel electrolytes usually showed weak mechanical strength, and the mechanical properties deteriorate during the usage leading to deteriorative electrochemical performance of the EDLCs. Notably, the PVA-based gel electrolytes with cross-linked polymer networks exhibit reinforced mechanical strength and high liquid uptake, which are suitable to supersede conventional weak gel electrolytes and could be used for EDLCs [35].

Poly(arylene ether)s (PAEs), a kind of high performance engineering thermoplastics, have been widely probed in fiber reinforced composites, proton/anion exchange membranes, and low dielectric constant materials owing to its outstanding thermal stability and mechanical properties. Very recently, we reported a series of functionalized PAEs based separators and polymer electrolytes for supercapacitors. Huo. et al. [9,10] reported a quaternary ammonium functionalized poly(aryl ether sulfone)s as separators with excellent mechanical property for EDLCs, but the cell performance was unsatisfying because the membrane with dense structure cannot provide enough ionic transport channels for the electrolyte [36]. Na. et al. [11] prepared MPEs by synthesizing a PAEK-g-PEG polymer as the matrix for the MPEs, however the membrane matrix restricted by porosity (with porosity of only 58.8%) also showed relatively poor cell performance [37]. Sulfonated poly(ether ether ketone) (SPEEK) is a typical kind of PAE with a rigid polymer main chain and many sulfonic acid groups (—SO_3H) side chains, and is considered to be a promising material for EDLCs owing to its excellent ionic conductivity, high thermal stability and mechanical strength [38,39]. In addition, the —SO_3H can easily convert into "—$SO_3^+Li^-$" by immersing the SPEEK into LiOH solution for proper times at ambient temperature, the introduction of Li^+ ions can effectively increase the ionic conductivity of the GPEs using SPEEK(Li) membranes as the matrix [40,41].

Electrospinning has been proven to be a simple but effective method to prepare nanofiber membranes with high porosity, large specific surface area and controllable fiber diameter [42,43]. Recently, a certain amount of works have been reported about the application of nanofiber membranes in direct methanol fuel cells (DMFCs) and lithium-ion batteries (LIBs). Sara Cavaliere et al. [44] reported a sulfonated poly (ether ether ketone) (SPEEK)/Aquivion® nanocomposite membrane for fuel cell, which was demonstrated have outstanding cell performance. Kang et al. [45] used PAN-based nanofiber membrane as the matrix of the SN-based all solid electrolyte, which showed favorable mechanical strength, excellent safety, high ionic conductivity and outstanding electrochemical battery performance. However, there have been no reports on EDLCs prepared with nanocomposite gel polymer electrolytes.

Herein, with the purpose of preparing high performance nanocomposite gel electrolytes for EDLCs, the SPEEK(Li) nanofiber membrane was prepared via electrospinning as the matrix, the pores of the SPEEK(Li) nanofiber membrane were filled with cross-linked PVA/$LiClO_4$ (20 wt%) gel electrolyte, resulting in NGPE. The prepared NGPE was used to fabricate an EDLC. And the fabricated EDLC was demonstrated to possess outstanding electrochemical performance with a specific capacitance of 146.96 F g^{-1} at a current density of 0.5 A g^{-1} and a maximum energy density of 18.26 W h kg^{-1}. Meanwhile, the EDLC showed outstanding cyclical stability of 98% specific capacitance retention after 3000 cycles GCD testing. As a contrast, an EDLC assembled with commercial separator and uncrosslinked PVA/$LiClO_4$ (20 wt%) gel electrolyte was also prepared, which exhibited unsatisfying cell performance compared to the EDLC assembled with NGPE. The results indicated that the prepared NGPE is appropriate to EDLCs, and even next-generation energy storage systems.

2. Experiment

2.1. Materials

Poly (ether ether ketone) (012PF-100) was provided by Jilin University Super Engineering Plastics Research Co. Ltd., China., and dried under vacuum at 80 °C for 24 h prior to use. Concentrated sulfuric acid (98 wt%) was purchased from Beijing chemical works. Lithium perchlorate ($LiClO_4$, purity of 99.9%), lithium hydroxide (LiOH, purity of 99.9%), polyving akohol (PVA, M_w ~67,000), dimethylacetamide (DMAc), glutaraldehyde (GA, AR, 50% in H_2O) and polytetrafluoroethylene (PTFE) preparation (60 wt% dispersion) were all purchased from Aladdin Reagent Co. Ltd. Shanghai, China. The commercial cellulose separator (thickness of 30–35 μm, porosity of 54.0% and defined as CS) was obtained from Lizhiyuan Sales Dept. of Batteries, Taiyuan, China. The activated carbon (AC) powder (surface area of 1600 m^2 g^{-1}, porous volume of 0.7 mL g^{-1}) and Ketjen black were provided by SCM Industrial Chemical Co. Ltd. Shanghai, China.

2.2. Preparation of Li^+-functionalized SPEEK

SPEEK was prepared by sulfonating PEEK with concentrated sulfuric acid. Briefly, PEEK (10 g) and 200 mL concentrated sulfuric acid (98 wt%) were added into a 500 mL two-neck flask equipped