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A high-capacitance solid-state supercapacitor based on free-standing film of polyaniline and carbon particles ☆

A. Khosrozadeh [a], M. Xing [a,b,c,*], Q. Wang [a]

[a] *Department of Mechanical Engineering, University of Manitoba, Winnipeg, MB, Canada*
[b] *Department of Biochemistry and Medical Genetics, University of Manitoba, Winnipeg, MB, Canada*
[c] *Manitoba Institute of Child Health, Winnipeg, MB, Canada*

HIGHLIGHTS

- The solid-state supercapacitor has high energy density and good cyclic stability.
- The electrode is a freestanding composite film of polyaniline and carbon particles.
- The impregnation of electrodes with gel electrolyte facilitates high capacitance.
- The supercapacitor is lightweight, thin, flexible, and environmental friendly.

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ABSTRACT

Polyaniline tends to degrade with cycling in aqueous electrolytes and it can be alleviated using gel electrolytes. A low-cost solid-state supercapacitor of high energy density and good cyclic stability is fabricated with a facile method. The electrodes of the supercapacitor are made of a freestanding composite film of polyaniline and acid-treated carbon particles using phytic acid as a crosslinker, and the gel electrolyte is composed of sulfuric acid and polyvinyl alcohol. The electrochemical performances of the as-fabricated supercapacitor are investigated with cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. Our results show that a maximum capacitance of 272.6 F/g (3.63 F/cm^2) at a current density of 0.63 A/g can be achieved by the supercapacitor, which is significantly higher than most solid-state ones reported in the literature. The ability to achieve a high-capacitance supercapacitor with good cyclic stability is mainly attributed to excellent infiltration of the gel electrolyte into the electrodes. The developed lightweight, thin, flexible, and environmental friendly supercapacitor would have potential applications in various energy storage devices, such as wearable electronics and hybrid electric vehicles.

1. Introduction

Clean energy technologies play an important role in overcoming fossil fuel exhaustion and global pollution for the sustainable development of human society. Among clean energy technologies, electrochemical energy storage and conversion, such as batteries, fuel cells and supercapacitors (SCs), are considered the most feasible, environmentally friendly, and sustainable [1]. SCs, an important class of energy storage devices, have attracted lots of attention in recent years owing to their fast charge-discharge rate, high power density, low maintenance, and long cycle life [2,3]. SCs have several applications in areas including power electronics, memory protection, battery enhancement, portable energy sources, power quality improvement, adjust able speed drives, high power actuators, hybrid electric vehicles, renewable and off-peak energy storage, and military and aerospace applications [1].

Electrode materials are usually considered to play the most important role in designing SCs. SCs store energy using either ion adsorption (electrical double-layer capacitors, EDLCs) or fast and reversible redox reactions (pseudocapacitors) [3]. The former uses carbonaceous materials with a large specific surface area, such as porous carbons, carbon fibers, carbon nanotubes, and graphene. The latter uses transition metal oxides or conducting polymers as

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* Corresponding author at: Department of Mechanical Engineering, University of Manitoba, Winnipeg, MB, Canada. Tel.: +1 204 474 6301.

E-mail address: malcolm.xing@umanitoba.ca (M. Xing).

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electrode materials [4]. Two mechanisms can function simultaneously depending on the nature of the electrode materials. Pseudocapacitors can provide higher specific capacitance and energy density than EDLCs, although their power density and cycle life are generally slightly inferior [5,6]. Improved energy storage could be achieved by designing electrode materials to combine double layer capacitance together with fast and reversible pseudocapacitance. In such a composite electrode, pseudocapacitance materials provides the source of high specific capacitance and high energy density, while the carbon nanostructures ensure good rate capability, cyclic stability and high power density at a large current [7]. A number of recent reviews and books have extensively discussed scientific and technological aspects of SCs and electrode materials [1,3,5–13].

Among pseudocapacitance materials, polyaniline (PANI) has been considered as one of the most promising electrode materials owing to its low cost, ease of synthesis, relatively good conductivity, good environmental stability, and color change corresponding to diverse redox states. However, PANI tends to be a brittle material with poor ductility. Although films of PANI nanofibers can be cast onto substrates, it is not possible to produce films, mechanically robust enough to be freestanding [14].

To achieve synergistic performances of composite electrodes, carbonaceous materials with their characteristics of high surface area, tunable surface functionalities, dimensional stability, and transport property can be combined with tunable redox state, and environmental stability of PANI [15,16]. To date, extensive efforts and many approaches have been developed to prepare PANI-based composites. Long et al. [17], for the first time, synthesized a carbon nanotube (CNT)/PANI composite showing enhanced electrical properties. Zhou et al. [18] showed that a composite electrode made of CNTs/PANI exhibited much higher specific capacitance and better power characteristics than a pure PANI electrode in an aqueous electrolyte. Yan et al. [19] synthesized a graphene nanosheet (GNS)/PANI composite using in situ polymerization. They concluded that the enhanced specific capacitance of the composite was due to the synergistic effect between GNS and PANI. Later on, several researches have been focused on developing composite electrodes based on CNTs/PANI [20–23] and graphene/PANI [24–28]. Jang et al. [15] successfully coated PANI on carbon nanofibers (CNFs) using one-step vapor deposition polymerization technique. They investigated the feasibility of PANI coated CNFs as electrode materials for SCs. A freestanding, flexible CNF/PANI composite paper was fabricated via in situ polymerization of aniline on an electrospun CNF paper as substrate [29]. The resulting composite paper displayed enhanced electrochemical capacitance in an aqueous electrolyte compared with a CNF paper. Nevertheless, a lot of researches are still going on to produce composite electrodes having good cyclic stability, high energy density, and high power density.

So far, most of SCs have been fabricated by means of liquid electrolytes, which are usually hazardous to the environment. Therefore, sealing of the electrolyte and housing of the devices are inevitable, making them unsuitable for thin and lightweight applications [30]. In contrast, Gel and solid polymer electrolytes combine the function of an electrolyte and a separator into a single component to reduce the number of parts and increase the potential window through the higher stability offered by a polymer matrix. Gel electrolytes offer a slightly lower conductance than liquid ones, but they provide more efficient mechanisms of ion transport and better cycle life [1]. In addition, electrodes containing PANI tend to degrade in aqueous acidic electrolytes resulting in a poor cyclic stability and a lower capacitance performance. This finding justifies the usage of gel electrolytes for PANI-based electrodes to achieve higher stability. Hence, developing solid-state PANI-based SCs is highly desired for flexible, wearable and miniaturized electronics. Meng et al. [22] reported an ultrathin all-solid-state SC with composite electrodes produced by coating PANI on CNT films. Although the developed flexible SC showed a good cyclic stability and specific capacitance as high as 175 F/g, designing a solid-state SC showing better performance in capacitance is still a need. Even though electrodes show good electrochemical performances in aqueous electrolytes, there are different design factors that should be considered in fabricating a solid-state SC, such as making good penetrations of an gel electrolyte into electrodes, optimizing an amount of gel electrolyte provided to electrodes, adjusting the thickness of electrodes, selecting suitable and flexible charge collectors, and a proper assembling.

Here we report a fabrication of a low-cost high-capacitance solid-state SC based on a composite film of acid-treated carbon particles (TCPs)/PANI with a well-impregnated sulfuric acid/polyvinyl alcohol (PVA) gel as the electrolyte. The fabrication process is pretty simple and the materials are low-cost and environmental friendly. In addition, the degradation problem of PANI or its poor cyclic stability is addressed herein. In a typical synthesis process, a composite consist of nano-sized TCPs and PANI nanofibers is prepared by in situ polymerization of aniline in the presence of hydrochloric acid and phytic acid. Then a freestanding thin film of TCPs/PANI is formed by vacuum-filtering of the as-prepared mixture (Fig. 1a). In addition to doping of PANI, phytic acid acts as a cross-linker of PANI nanofibers [31], which facilitates fabrication of a freestanding composite film. Finally, two TCPs/PANI electrodes are assembled into a solid-state SC by using sulfuric acid/PVA gel electrolyte and stainless-steel charge collectors as shown in Fig. 1b. The electrochemical performances of the solid-state SC are analyzed by means of cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS). In addition, effects of different parameters on the design and performance of the device are studied in details.

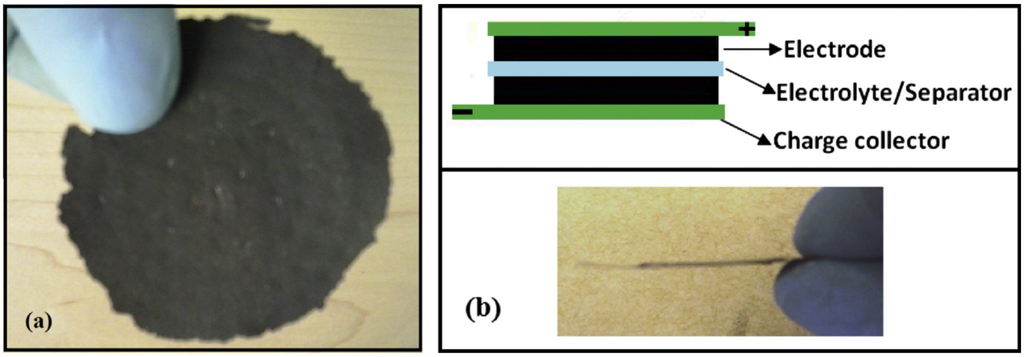

Fig. 1. (a) Photograph of the freestanding TCPs/PANI film, (b) side-view photograph of the fabricated SC (bottom) and its schematic diagram (top).