

High performance battery–supercapacitor hybrid energy storage system based on self-doped polyaniline nanofibers

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ABSTRACT

Nanostructured self-doped polyaniline (SDPA) is prepared from an aqueous solution of aniline and *m*-aminobenzoic acid using an electrochemical method onto a stainless steel electrode. This electrode employed as a positive shared electrode in the construction of a hybrid battery–supercapacitor energy storage system AC/SDPA/Zn. This hybrid system is constructed using a parallel combination of an asymmetric supercapacitor (AC/SDPA) and a secondary battery (Zn/SDPA) in a single cell configuration and same electrolyte. Different electrochemical methods including cyclic voltammetry, galvanostatic charge–discharge and rate charge–discharge studies are carried out to characterize electrochemical performances of the hybrid system. Based on the obtained results, the hybrid system shows specific capacity, specific energy, specific power and maximum power values of 215 Ah kg⁻¹, 204 Wh kg⁻¹, 863 W kg⁻¹ and 8909 W kg⁻¹, respectively, at a current density of 2.5 mA cm⁻².

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1. Introduction

Nanoscale materials have opened a new rich world of possibilities for science and engineering and widely used in many fields [1,2]. The electroactive nanomaterials can improve the performance of electrochemical energy storage systems such as batteries and supercapacitors [3]. It is due to more efficient electrochemical reactions of nanomaterials in these two energy storage systems as compared to micromaterials [4,5]. So, using electroactive nanomaterials, the performance of such systems is extremely improved and specific capacity of batteries and supercapacitors get close to the theoretical values.

The ability to store transiently and redeliver high energy and high power electric energy in the modern energy storage systems is an essential component of today's hybrid electric devices. In such electric systems, performance requirements are high energy density, high rate charge acceptance-delivery and long cycle life [6–9]. Supercapacitors and secondary batteries are energy storage systems; however, in practical applications, none of them can be properly used as a single power supply for hybrid electric devices due to low energy and low power characteristics of supercapacitors and secondary batteries, respectively [10–13]. A parallel combination of these two energy storage systems provides a high power

hybrid energy storage system which simultaneously shows high energy and high power characteristics of batteries and supercapacitors, respectively [14,15]. They could be used in parallel (separated cells) and/or shared electroactive materials and electrolytes (single unit cell). However, it does not mean that the hybrid energy storage systems can be easily achieved by combining any supercapacitor with any secondary battery because of their difference in the operational voltage range [16]. If the operational voltage range of supercapacitor is not equal to the secondary battery, one of them is always at the overcharge state and undergoes irreversible reactions and the other is always at the discharge state. So the hybrid energy storage system works with poor performance. Moreover, the simple parallel design of any supercapacitor with any secondary battery with the same working voltage cannot reach hybrid power source; it is due to the difference in charging/discharging slope of these two systems. So, it is necessary to use a DC–DC converter because charging or discharging of the supercapacitor is done up or down to the secondary battery voltage level. The single cell configuration of hybrid energy storage systems is more interesting than separated cell configuration because in these systems, the DC–DC converter does not need and has a higher specific gravimetric/volumetric energy and power due to use of shared electroactive material and the same electrolyte [17]. With this design, the total charge and discharge currents of the hybrid energy storage systems are composed of both supercapacitor and secondary battery current.

Among the wide variety of electrically conducting polymers (ECPs) polyaniline (PAN) nanostructures as an advanced materials

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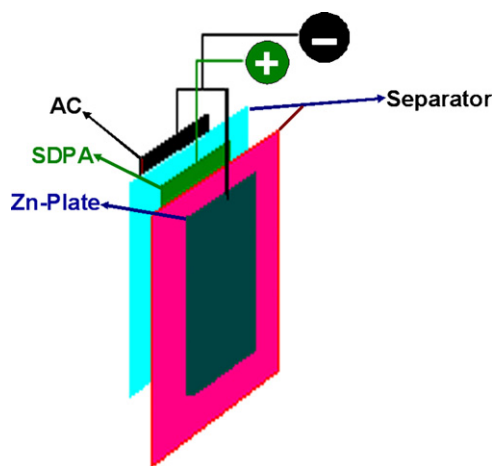


Fig. 1. Schematic view of AC/SDPA/Zn hybrid cell: SDPA as positive shared electrode, electrodeposited on a stainless steel current collector, cellulose acetate separator and activated carbon (AC), pressed on a stainless steel current collector, and Zn plates as negative electrodes.

with high surface area and high porosity give the best performances in the PAN–Zn secondary batteries with aqueous electrolytes [18]. A difficulty arises when Zinc is the counter electrode, since Zinc undergoes spontaneous dissolution in acidic media, while PAN is electroactive only in acidic media [19–22]. The other difficulty is PAN degradation in the aqueous medium [23] which causes lowering the OCV of PAN–Zn battery [24]. Studies show that some steric reagents reduce the rate of PAN degradation [25]. Unlike PAN, its derivatives, e.g. SDPA exhibit better chemical stability due to steric protection by the carboxylic and sulfonic group [26]. In addition, the SDPA does not lose its electrochemical activity in low acidic solutions. Because in the charge–discharge cycles of energy storage systems, the reversible exchanging of anions among ECP and electrolyte limits very important characteristics such as available power that slakes due to limited rate of anions mobility [27–29]. However, SDPA excludes the participation of functional groups with negative charge (like COO^- and SO_3^-), which eliminates the ion mobility problem. So, by employing SDPA, the carboxylic group of the *m*-aminobenzoic acid can locally provide both necessary proton and anionic dopants in the polymer's network. So, polymer electroactivity does not need the external protons in the solution. In other words, SDPA enables one to work in mild pH which provides the following advantages: (i) retain the polymer electroactivity, (ii) decrease polymer degradation and (iii) decrease spontaneous Zn dissolution. So, SDPAs are expected to be promising electroactive materials for the positive electrodes in Zinc and Lithium secondary batteries [30–33].

In previous reports, we constructed a secondary battery [21] and a symmetric supercapacitor [34] using SDPA and Platinum as electroactive material and current collector, respectively. Although this system shows a high specific capacitance 480 F g^{-1} , the limited application of the symmetric supercapacitor SDPA/SDPA due to its low working voltage does not let it parallel with the secondary battery Zn/SDPA. It should be noted that the symmetric supercapacitors are constructed with two similar electroactive materials which reach maximum 1.2V in the aqueous electrolyte solutions. Whereas, the asymmetric supercapacitors are assembled using a positive electrode with the large positive cutoff potential and a negative electrode with high hydrogen overpotential, which results in a significant increase in the overall cell operating voltage in the aqueous solutions. Therefore, by employing asymmetric supercapacitor configuration, one can extend the operational cell voltage as reported by Park and Park [35] as 1.6V

and by Wang et al. [36] as 1.4V for asymmetric supercapacitor AC/PAN.

Following our recent works on improving the performance of lead acid [37,38], dry and wet Zn–PAN batteries [39–42], and more recent studies on using SDPA nanofibers as a new material for symmetric redox supercapacitor [34]. Herein, we introduce a new high power–energy hybrid power source using a parallel combination of high operational voltage aqueous asymmetric supercapacitor with a secondary battery in a mild pH. In this system, to improve the performance, the working voltage of the symmetric supercapacitor SDPA/SDPA was increased by replacing of SDPA negative electrode with activated carbon (AC). So, the operational working voltage of this asymmetric configuration (AC/SDPA) was tuned to match with the secondary battery Zn/SDPA. This is an essential requirement for construction of a hybrid battery–supercapacitor. Different electrochemical methods including cyclic voltammetry, galvanostatic charge–discharge and rate charge–discharge studies are carried out to characterize electrochemical performances of the AC/SDPA/Zn hybrid energy storage system.

2. Experimental

2.1. Chemicals

AC, reagent grade *m*-aminobenzoic acid and aniline were obtained from Merck and Fluka. Aniline was doubly distilled and kept under argon in darkness at 5°C . HCl, NH_4Cl and ZnCl_2 were prepared from Merck as analytical grade chemicals. Doubly distilled water was used to prepare all solutions.

2.2. Methods

An Autolab PGSTAT 30 instrument (Eco-Chemie, The Netherlands) was used for electrochemical depositions and measurements. Electrodeposition of SDPA was carried out in a conventional three electrode cell. The stainless steel (SS, grade 304, 0.5 mm thickness) plate ($2 \text{ cm} \times 2 \text{ cm}$) was used as the working electrode, a Pt plate and Ag/AgCl (KCl, saturated) were utilized as counter and reference electrodes, respectively.

Electrochemical studies on the hybrid system were performed using a lab-made three electrode configuration cell that is shown in Fig. 1. In this cell, a shared SDPA acts as the positive pole of Zn-secondary battery and asymmetric supercapacitor. Zn plate and AC were used as negative poles in the Zn-secondary battery and asymmetric supercapacitor. Positive plate was separated from negative plates using cellulose acetate as a separator. The AC was coated on SS plate ($2 \text{ cm} \times 2 \text{ cm}$) by mixing 90 wt% of AC powder with 10 wt% of poly(tetrafluoroethylene) (PTFE). This resulted in a rubber-like paste that was rolled in a film (about 2 mm thick) on a flat SS surface and dried 12 h at 60°C . Then to assure a good electrical contact, electrode was hot-pressed under a pressure of 15 MPa at 110°C for 3 min. Before the electrochemical measurements, the AC electrode must be activated by immersing it into 1.0 M ZnCl_2 and 0.5 M NH_4Cl mixed electrolyte solution for 24 h. Scanning electron microscopy (SEM) was performed with a Philips instruments, Model X-30. All experiments were carried out at 25°C in an air-conditioned room.

2.3. Electrodeposition of SDPA

SDPA nanofibers were potentiostatically deposited on the SS plate at the potential of 0.85 V vs. Ag/AgCl in an electrolyte solution of 1 M HCl + 0.05 M aniline + 0.05 M *m*-aminobenzoic acid. Before electrodeposition of SDPA, SS electrodes were polished using slurry (particle size $0.5 \mu\text{m}$), washed in water and ethanol. Then the modified electrodes were washed with 1.0 M HCl solution to perform

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