



Full paper

The use of an electrocatalytic redox electrolyte for pushing the energy density boundary of a flexible polyaniline electrode to a new limit

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ARTICLE INFO

Keywords:

Rectangular-nanotube polyaniline
Carbon cloth
Electrocatalysis
Flexible supercapacitor
1,4-naphthoquinone

ABSTRACT

While the market for supercapacitors is rapidly growing due to their high power density, their low energy density compared to batteries represents a great barrier for the future of this technology. The poorly understood chemistry of electrode-electrolyte interfaces implies that there is substantial room for improvement through a careful design of the materials involved. Here we present a unique approach for improving the energy density of supercapacitors through redox additive-assisted electrocatalytic in situ regeneration of the electrode active materials. By utilizing a quinone-based redox electrolyte and a nanostructured conjugated polyaniline electrode, we continually regenerate the reactants, resulting in a redox supercapacitor having an extremely high energy density of 1091 Wh kg⁻¹ (based on the total mass of the electrode active materials and the redox additive) and a high power density up to 196 kW kg⁻¹. Considering the other outstanding properties of the polyaniline-naphthoquinone system, such as extreme flexibility (96% capacity retention after bending at an angle of 180° for 1000 cycles), non-flammability, and excellent cycling stability (84% capacity retention after 7000 cycles at 35 A g⁻¹), such a well designed in situ regeneration of the electrode active materials makes this method a very promising approach towards the development of state-of-the-art energy storage devices.

1. Introduction

Supercapacitors represent a well-established energy storage technology that is currently in use in regenerative braking systems, voltage stabilization, hybrid buses and electronic devices [1,2]. Reducing the size, increasing the flexibility, and achieving battery-level energy density, integrated with the intrinsic high power density and cyclability of supercapacitors would constitute a major step forward toward a more sustainable and efficient energy storage system. Supercapacitors store energy via three main mechanisms: (i) electric double-layer capacitance (EDLC) [2], (ii) Faradaic capacitance [3], and (iii) capacitance directly from redox active electrolytes [4]. Via the first two mechanisms, only solid-phase electrode materials contribute to charge storage, while the other cell components, including electrodes and electrolyte, are electrochemically inert. Recently, it was found that the addition of redox active species to the electrolyte could enhance the cell capacitance through electrochemical

reactions at the electrode/electrolyte interface [5–7]. However, although promising, the energy density of such devices is still far from being able to compete with batteries. This deficiency originates mainly from the limited mass loading of the electrode active materials. The aforementioned mechanisms of charge storage are often revisited when new knowledge is obtained with the hope of eventually finding solutions to one of the most complicated challenges facing supercapacitors. Moreover, with a growing market for printed and wearable electronics, the need to create similarly flexible power sources has become urgent [8,9]. The field of electrocatalysis has seen much progress in recent years and shown great potential in different clean energy conversion reactions, such as oxygen reduction/evolution, hydrogen oxidation/evolution, and CO₂ and N₂ reduction reactions [10]. In an excellent review, Jaramillo and coworkers have combined theory and experiment to clarify key limitations of the catalysts in energy conversion reactions, and proposed that a new paradigm for catalyst design is needed to circumvent the current limitations [11].

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<https://doi.org/10.1016/j.nanoen.2017.11.058>

Received 2 August 2017; Received in revised form 12 October 2017; Accepted 27 November 2017

Available online 12 December 2017

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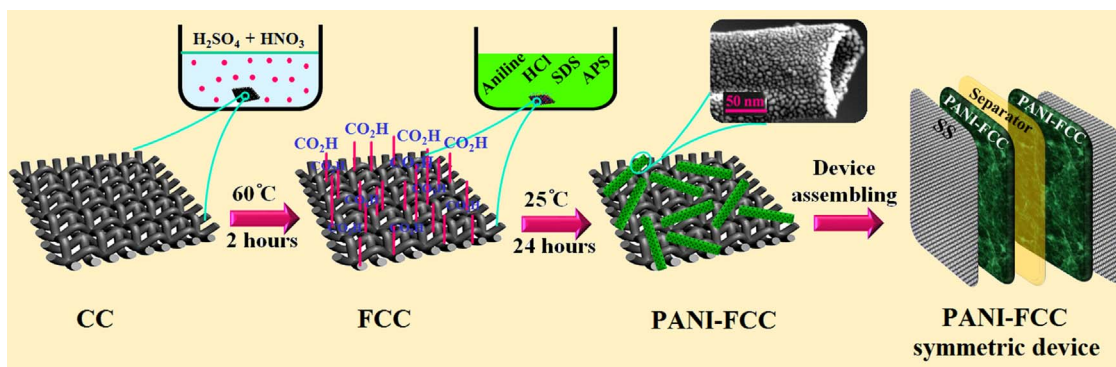


Fig. 1. Schematic illustration of the fabrication process of a polyaniline-functionalized carbon cloth (PANI-FCC) device. CC: carbon cloth.

Herein, we introduce redox additive-assisted electrocatalytic in situ regeneration of the electrode active materials as a new paradigm for developing high-performance supercapacitors. Thus, although current paradigms for the development of energy storage devices have been helpful to date, there remains substantial room for improvements to develop higher-performance energy storage devices. Therein lies the need to make progress in the chemistry of electrode-electrolyte interfaces, many details of which have remained poorly understood to date [11]. We have progressed from a trial-and-error approach to a pre-planned process and deliberately designed all three essential components of a supercapacitor to work synergistically: the active material, the substrate and the electrolyte to achieve the best possible supercapacitive performance that circumvents the current limits of electric double layer capacitors and approaches the upper boundary of the desired characteristics. This is made possible through the direct synthesis of the conjugated polymer polyaniline, in tubular form with rectangular pores, on chemically functionalized carbon cloth (Fig. 1). The addition of 1,4-naphthoquinone (NQ) as a redox additive to the electrolyte not only provides Faradaic capacitance with direct redox reactions on the electrode surfaces, but also serves as the basis for a

regenerative pathway towards long-term utilization of the electrode active materials, thus considerably enhancing the overall performance of the device. The combination of this electrode with activated carbon in an asymmetric configuration results in a supercapacitor with an outstanding specific capacitance (4007 F g^{-1} based on the mass of electrode active materials and NQ at 1.4 A g^{-1} , 1.14 F cm^{-2}) and 84% cycling stability after 7000 cycles at 35 A g^{-1} .

2. Experimental

2.1. Materials

Aniline was purified by water steam distillation before use. All other chemicals were of analytical grade, purchased from Sigma-Aldrich (USA) or Merck (Germany), and used without further purification.

2.2. Apparatus

The structure and morphology of the different electrode materials were examined using field-emission scanning electron microscopy

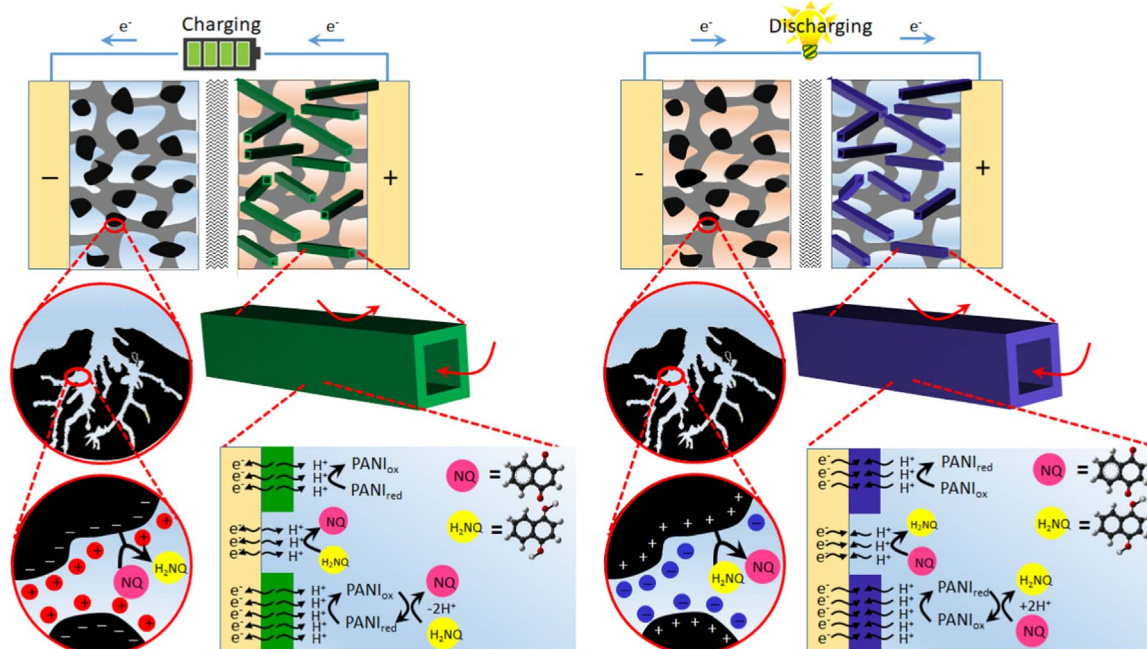


Fig. 2. Schematic representation of an asymmetric activated carbon on functionalized carbon cloth (AC-FCC)/polyaniline-FCC device showing different charge storage mechanisms. During charge and discharge operations the activated carbon undergoes electric double layer capacitor (EDLC) charge storage as the 1st mechanism. Polyaniline undergoes not only direct redox processes (upper route, the 2nd mechanism, positive pole) but also exhibits electrocatalytic behavior in the presence of a deliberately selected additive, i.e. 1,4-naphthoquinone (the 3rd mechanism) using a gelled H_2SO_4 supporting electrolyte, at the electrode-electrolyte interface (lower route, the 4th mechanism, positive pole), and consequently capacitance is dramatically increased.

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