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Regular Article

Nitrogen-doped carbon spheres: A new high-energy-density and long-life pseudo-capacitive electrode material for electrochemical flow capacitor

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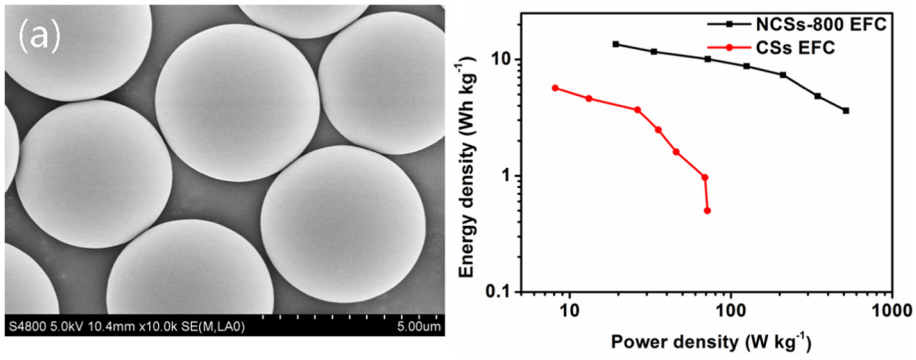
GRAPHICAL ABSTRACT



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ABSTRACT

One of the most challenging issues in developing electrochemical flow capacitor (EFC) technology is the design and synthesis of active electrode materials with high energy density and long cycle life. However, in practical cases, the energy density and cycle ability obtained currently cannot meet the practical need. In this work, we propose a new active material, nitrogen-doped carbon spheres (NCSs), as flowable electrodes for EFC application. The NCSs were prepared via one-pot hydrothermal synthesis in the presence of resorcinol/formaldehyde as carbon precursors and melamine as nitrogen precursor, followed by carbonization in nitrogen flow at various temperatures. The results of EFC experiments demonstrate that NCSs obtained at 800 °C exhibit a high energy density of 13.5 Wh kg^{-1} and an excellent cycle ability, indicating the superiority of NCSs for EFC application.

1. Introduction

In recent years, supercapacitors (SCs) have attracted increasing attention as an alternative energy-storage system to deliver fast charge/discharge with a long cycle life [1–7]. However, current applications for SCs are limited because of their low energy density and high cost [8,9]. To solve this problem, a new dynamic energy storage concept, namely electrochemical flow capacitor (EFC), was first developed by Gogosti et al. in 2012 [10]. The EFC is based on the similar charge storage mechanism as SCs, whereas the film electrodes are replaced by flowable electrodes [11,12]. Analogical to film electrodes, flowable electrodes are traditionally composed of porous carbons with high specific surface area [13,14]. Specially,

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porous carbons with spherical geometry/shape (denoted as carbon spheres, CSs) have been demonstrated to be a promising electrode material for EFC due to their minimized viscosity and energy required to pump and transport the flowable electrode [13,15,16]. Despite the progress achieved to date, the transfer of science into a realistic technology has yet to be completed due to the unsatisfied EFC performance of CSs. Moreover, it is extremely difficult to improve the EFC performance of CSs because of their limited specific surface area [17]. Therefore, it should be an urgent need to find an effective strategy to improve the EFC performance of CSs for further development of EFC.

Recently, two strategies have been developed and adopted by Gogosti's group for improving the EFC performance of CSs. On one hand, by decorating CSs with graphene sheets, the obtained graphene-containing flowable electrodes exhibited an improved EFC performance compared with pure CSs [12]. There's no denying that decorating CSs with high-conductivity graphene sheets can not only endow the obtained hybrid with improved conductivity, but also enhance the connectivity of hybrid particles, which thus improve the EFC performance of the obtained graphene-containing flowable electrodes. However, due to the limitation of the specific surface area, the obtained energy density is very low ($\sim$7 Wh kg^{-1}), which cannot meet the demand of practical application of EFC.

On the other hand, the EFC performance of CSs can be enhanced by depositing different amounts of hydroquinone (HQ) on CSs via a self-assembly approach [17]. In this approach, HQ was used as redox-active mediator, which can improve the EFC performance of CSs by contributing pseudo-capacitance via faradaic reactions between HQ molecules and electrolyte [18]. Compared with pure CSs flowable electrode, both the capacitance and the energy density of CSs/HQ flowable electrode were enhanced obviously. In detail, the capacitance increased from 160 F g^{-1} for CSs to 342 F g^{-1} for CSs/HQ, and meanwhile the energy density increased from 5.6 Wh kg^{-1} for CSs to $\sim$12 Wh kg^{-1} for CSs/HQ. However, the poor cycle life of CSs/HQ flowable electrode restricted its further application.

Taking these points into consideration, a superior electrode material for EFC should not only possess a high energy density, but also exhibit a long cycle life. However, to the best of our knowledge, such an EFC electrode material has rarely been reported up to date. Herein we propose a new strategy to improve the EFC performance by utilizing nitrogen-doped CSs (NCSs) as flowable electrodes. The nitrogen atoms in carbon matrix are not only favourable for improving the electrical conductivity and wettability of carbon matrix [19–21], but also beneficial for enhancing the EFC performance by pseudo-capacitance contribution via faradaic reactions between nitrogen atoms and electrolyte [22–24]. The NCSs flowable electrodes exhibit good capacitive performance including a high energy density of 13.5 Wh kg^{-1} and stable cycle ability.

2. Experimental

2.1. Material synthesis

All chemicals were purchased from Sinopharm without any further purification. The precursors for NCSs were synthesized by a reported method [25,26]. Typically, 3.87 g resorcinol (R) and 5.70 g formaldehyde (F) were dissolved and stirred in 30 mL deionized (DI) water at room temperature, and the obtained solution was labelled as solution A. Meanwhile, solution B was composed of 4.43 g melamine (M) and 8.56 g F dissolved in 30 mL DI water under stirring at 70 °C. After cooled down to room temperature, solution B was added into solution A and stirred for 0.5 h. The mixed solution was then transferred into a Teflon-lined autoclave and heated at 100 °C for 24 h. The products were obtained by filtration and air-dried at 80 °C overnight. Then the NCSs were obtained via carbonization at various temperatures for 2 h in N_2, and denoted as NCSs-x, where x represents the temperature. Fig. 1 exhibits the preparation route of NCSs. For comparison, CSs were prepared by using a similar synthesis process with NCSs without using melamine as nitrogen source.

2.2. Characterizations

The morphologies of the as-synthesized carbon spheres were characterized using a field emission scanning electron microscopy (FESEM, JEOL JSM-LV5610). The nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP 2020 Accelerated Surface Area and Porosimetry System (Micrometritics, Norcross, GA) to obtain pore properties, including specific surface area, total pore volume, and pore size distribution. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an Imaging Spectrometer (Axis Ultra, Kratos Analytical Ltd) with a monochromatic Al Kα X-ray source.

2.3. Electrode preparation

Film electrodes were fabricated by mixing NCSs-x, carbon black (CB) and polyvinylidene fluoride with a mass ratio of 80:10:10 in N-methyl-2-pyrrolidone to get carbon slurries. Then, the carbon slurries were uniformly casted on graphite substrates. Finally, the film electrodes were obtained after dried at 80 °C under vacuum condition overnight.

Flowable electrodes with 16 wt% solid were prepared by adding the mixture (NCSs-x:CB = 7:3) into 1 M H_2SO_4 solution.

2.4. Electrochemical measurements

The electrochemical testing including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS, 10 mHz-100 kHz, 10 mV AC amplitude) of the film electrodes were carried out in 1 M H_2SO_4 solution using an Autolab PGSTAT 302 N electrochemical station in a three-electrode mode with Ag/AgCl as reference electrode and platinum foil as counter electrode. The CV test was performed at scan rates between 2 and 100 mV s^{-1}. The specific capacitance (C_s, F g^{-1}) was calculated from the CV curves according to the following equation:

$$C_S = \frac{\int idV}{2 \times m \times \Delta V \times S} \quad (1)$$

where $\int idV$ is the integrated area of the CV curve (W), m is the active material mass of one electrode (g), ΔV is the window voltage (V), and S is the scan rate (mV s^{-1}).

All electrochemical testing of the flowable electrodes was performed in symmetric two-electrode model with graphite current collectors by Autolab PGSTAT 302N electrochemical station. The specific capacitance (C_t, F g^{-1}) was calculated from the CV curves based on the equation:

$$C_t = \frac{\int idV}{m \times \Delta V \times S} \quad (2)$$

In all measurements of flowable electrodes the weight of NCSs was $\sim$56 mg.

The energy density and power density were calculated using following equations:

$$E_S = 0.5 C_t V^2 \quad (3)$$

$$P_S = E_S / t \quad (4)$$

where t is the discharge time.