



Capacitive performance of a heteroatom-enriched activated carbon in concentrated sulfuric acid



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HIGHLIGHTS

- A heteroatom-enriched activated carbon (N-ASC) was prepared from PET.
- N-ASC showed an interesting electrochemical activation phenomenon.
- The maximum specific capacitance of N-ASC is 201 F g⁻¹ in 5.3 M sulfuric acid.
- N-ASC exhibits excellent long-term electrochemical stability.

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ABSTRACT

A heteroatom-enriched activated carbon with low surface area is prepared from poly(ethyleneterephthalate) and is used as an active electrode material for supercapacitor in 1.28 g cm⁻³ H₂SO₄ solution. Thus prepared heteroatom-enriched activated carbon is characterized by nitrogen adsorption/desorption at 77 K, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The electrochemical characterizations are performed by cyclic voltammetry and galvanostatic charge/discharge in a three-electrode system. The prepared heteroatom-enriched activated carbon shows an interesting electrochemical activation phenomenon because of which the specific capacitance is significantly increased by charge at high potentials. The activation process involves the insertion of ions into the narrow enclosed free space inside the carbon material to generate new pores. The final results show that the heteroatom-enriched activated carbon electrode has a better discharge rate capability than the commercial activated carbon (Norit AZO) over a wide range of loading current (1–20 A g⁻¹). The highest specific capacitance (201 F g⁻¹) is obtained at 5 mV s⁻¹, which is two fold greater than the one before electrochemical activation. In addition, the specific capacitance of the heteroatom-enriched activated carbon is retained approximately 92% of the initial value after 20,000 cycles, indicating its excellent cycle stability.

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1. Introduction

Transport is one of the largest sources of human-induced greenhouse gas emissions and fossil-fuels consumption. Thus,

there is a strong push for automobiles with reduced CO₂ emissions and improved fuel economy.

Hybrid-electric vehicles (HEVs) are developed due to the environmental concerns to reduce vehicle emissions. However, energy storage in HEVs operates continuously at high-rate partial-state-of-charge (HRPSoC) mode. Therefore, batteries used in HEVs should possess improved charge acceptance as well as longer life under HRPSoC working conditions. Lead-acid batteries are the most widely used batteries in hybrid vehicles and are highly reliable and cost-effective. However, traditional valve-regulated lead-acid (VRLA) battery can't satisfy the need of HEVs as it can't deliver the

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required cranking current when the state-of-charge (SoC) is below 30% and can't accept charge efficiently when SoC is above 70% [1]. In addition, under HRPSoC duty, the VRLA battery suffers from a progressive build-up of 'hard' lead sulfate and is difficult to recharge. This effect can impair battery performance and reduce charge-acceptance during regenerative braking. Moreover, high-rate discharge can make sulfation layer more compact, and the problem of over-sulfation is exacerbated during prolonged parking of the vehicle.

To address above-mentioned problems, more attention has been focused on improving the cycleability of the VRLA batteries under HRPSoC duty. Some researchers [2–4] observed that high proportion of carbon added to the negative plate of lead-acid battery can suppress the sulphation phenomenon efficiently. This way the carbon in battery can form a supercapacitor built-in, which can increase the specific power of battery. At the same time, a new technology was developed by the Commonwealth Scientific and Industrial Research Organization in Australia. This new technology on battery combined an asymmetric supercapacitor (an enhanced-power negative electrode) and a lead acid battery in a single unit, creating a hybrid car battery (UltraBattery). The UltraBattery has the advantage of being long lasting, cost effective and more powerful than past technologies used in HEVs [1]. The supercapacitor, by acting as a buffer during high-rate discharge and charge, enhances the power and lifespan of the lead-acid battery. Thus, the UltraBattery in HEVs is able to deliver and absorb charge rapidly during vehicle acceleration and regenerative braking, respectively. These favorable parameters of this technology have been described in literature in detail [5,6].

One of the key issues in new hybrid technology is to select a suitable activated carbon as a capacitive electrode material. Activated carbon is known to be the most widely used double layer electrode material and it has excellent capacitive performance in dilute sulfuric acid ($0.5\text{--}2\text{ mol L}^{-1}$). However, it has also been shown that common activated carbon can be oxidized and the specific capacitance rapidly decreases when the acid concentration increases to a certain value [7]. In fact, the environment of the UltraBattery is very harsh due to concentrated sulfuric acid electrolyte (about 5.3 mol L^{-1}). Therefore, the purpose of our research was to find a suitable activated carbon with excellent electrochemical stability, highly specific capacitance, and satisfactory rate performance in concentrated sulfuric acid.

Recently, more attention has been focused on certain non-porous graphitizable carbon (so-called soft-carbon) pre-treated with alkali. These carbons, activated with alkaline solutions such as KOH and NaOH at $600\text{--}1000\text{ }^\circ\text{C}$, exhibit high volumetric capacitance of $20\text{--}40\text{ F cm}^{-3}$ and wide working voltage of $3\text{--}3.5\text{ V}$ in organic electrolyte. Takeuchi et al. [8,9] first reported the KOH-activated soft carbon and found an electrochemical activation phenomenon in this material. This carbon had quite a low specific capacitance at the outset due to its relatively low specific surface area. However, its capacitance increased significantly by the first charging process, and exceeded the capacitance of activated carbon. A similar electrochemical activation phenomenon was also observed for alkali-treated soft carbon by Aida et al. [10], and showed that it is applicable to the positive electrode of a hybrid electrochemical capacitor (HEC) with a combination of hard carbon as the negative electrode. The resulting advanced HEC had much higher power and energy densities than the conventional electrical double-layer capacitors (EDLCs). Recently, Ruch et al. [11] studied the mechanism of electrochemical activation by nitrogen adsorption, electrochemical dilatometry, and in situ small-angle X-ray scattering. Their results showed that KOH activated carbon had a specific capacitance of 121 F g^{-1} after electrochemical

activation and exhibited an irreversible volume expansion of 24% during activation. It has been shown that the electrochemical activation played an important role in yielding high specific capacitance, which referred to the co-intercalation of ions and solvent into electrode materials during electrochemical activation process.

Heteroatom-enriched activated carbon has been widely investigated in recent years due to the synergetic effects of electrical double-layer and Faradaic redox reaction [12–15]. It has been generally accepted that functional groups or heteroatoms such as nitrogen and oxygen, which are present on the surface of the carbon electrode material, can not only considerably enhance the capacitance through additional faradaic reactions, but also enhance the wettability between the electrode and electrolyte. In this sense, some nitrogen-rich and oxygen-rich carbons with a small specific surface area show capacitance values comparable to the best activated carbons [16–18].

Here, we report a new type of oxygen and nitrogen-enriched activated carbon that shows an interesting electrochemical activation phenomenon in concentrated sulfuric acid. The heteroatom-enriched activated carbon is prepared from homogeneous poly(ethylene terephthalate) (PET) and is modified by NaOH activation. In fact, the nitrogen heteroatoms are introduced to the carbon framework by an ammoxidation method. The electrochemical activation behavior is investigated by cyclic voltammetry (CV) using a three-electrode system and the activation mechanism is discussed in detail in this article. Heteroatom-enriched activated carbon in our study exhibits excellent capacitive performance as an electrode material in $5.3\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$ solution.

2. Experimental

2.1. Materials and procedures

2.1.1. Carbonization

Homogeneous PET was used as precursor. PET was put into a horizontal furnace, pyrolyzed at $500\text{ }^\circ\text{C}$ for 2 h under a N_2 flow (200 mL min^{-1}). Thus prepared sample was immersed in 0.5 M HCl at room temperature for 24 h, and then the acid-treated char was thoroughly rinsed with distilled water and dried in an oven. The final product was labeled SC.

2.1.2. Activation

NaOH was mixed with SC at room temperature by a weight ratio of 3:1. After the physical mixing, the sample was activated at $850\text{ }^\circ\text{C}$ in a N_2 flow (200 mL min^{-1}) for 2 h. The obtained product was washed in diluted HCl, rinsed with distilled water, and dried at $100\text{ }^\circ\text{C}$ for 24 h. This product was named as ASC.

2.1.3. Ammoxidation

Ammoxidation of ASC was performed under NH_3 atmosphere at $350\text{ }^\circ\text{C}$ for 5 h. The product was named as N-ASC.

2.2. Material characterization

The specific surface area and pore size distribution of the samples were analyzed using the Brunauer–Emmet–Teller (BET, ASAP-2020, Micromeritics, USA). X-ray diffraction (XRD) analysis was carried out between 5° and 90° by using $\text{Cu-K}\alpha$ radiation on a Y-2000 X-ray generator. The morphologies of the samples were observed under a high-resolution scanning electron microscope (SEM, JSM-6380). Transmission electron microscopy (TEM) images were investigated by JEOL JSM 2010. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 250 X-ray photoelectron spectrometer.

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