Journal of Power Sources 382 (2018) 95–100

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Solvent evaporation induced graphene powder with high volumetric capacitance and outstanding rate capability for supercapacitors

Xiaozhe Zhang[a,b], Devaraj Vasanth Raj[a], Xufeng Zhou[a,*], Zhaoping Liu[a,**]

[a] *Key Laboratory of Graphene Technologies and Applications of Zhejiang Province and Advanced Li-ion Battery Engineering Laboratory, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Zhejiang 315201, PR China*

[b] *University of Science and Technology of China, Nanoscience and Technology Institution, Suzhou 215123, PR China*

## HIGHLIGHTS

- Graphene electrode material with high volumetric performance is developed.
- A simple method is proposed to regulate the pore size of graphene powder.
- The supercapacitor can keep 76% capacity retention at 100 A $g^{-1}$.

## ARTICLE INFO

*Keywords:*
Graphene
Solvent evaporation
Pore size
Volumetric performance
Supercapacitor

## ABSTRACT

Graphene-based electrode materials for supercapacitors usually suffer from poor volumetric performance due to the low density. The enhancement of volumetric capacitance by densification of graphene materials, however, is usually accompanied by deterioration of rate capability, as the huge contraction of pore size hinders rapid diffusion of electrolytes. Thus, it is important to develop suitable pore size in graphene materials, which can sustain fast ion diffusion and avoid excessive voids to acquire high density simultaneously for supercapacitor applications. Accordingly, we propose a simple solvent evaporation method to control the pore size of graphene powders by adjusting the surface tension of solvents. Ethanol is used instead of water to reduce the shrinkage degree of graphene powder during solvent evaporation process, due to its lower surface tension comparing with water. Followed by the assistance of mechanical compression, graphene powder having high compaction density of 1.30 g $cm^{-3}$ and a large proportion of mesopores in the pore size range of 2–30 nm is obtained, which delivers high volumetric capacitance of 162 F $cm^{-3}$ and exhibits outstanding rate performance of 76% capacity retention at a high current density of 100 A $g^{-1}$ simultaneously.

## 1. Introduction

Supercapacitor, also known as electrochemical capacitor or ultracapacitor, has attracted considerable attention due to its outstanding features, such as high power density, excellent stability, low maintenance and safe operation, and is considered as the next-generation energy-storage system for potential applications in the pervasive portal electronics, hybrid vehicles and power back-ups [1–5]. Although there are many types of supercapacitor devices with specific configurations, symmetrical supercapacitors using carbon-based electrode materials such as activated carbon (AC) is widely acknowledged due to the high specific surface area of AC. However, a large content of micropores in AC leads to relatively large inaccessible surface area for electrolyte ions, especially at high rates [6]. As a result, the AC-based supercapacitors usually have low specific capacitance, which has become a major bottleneck in the application. Therefore, the development of the next generation carbon-based electrode materials with higher capacitance than AC has become an important research direction.

As a new type of carbon material, graphene has received increasing attention and been used as a new supercapacitor electrode material due to its high specific surface area, high intrinsic electrical conductivity and excellent mechanical flexibility [7]. Moreover, it can be regarded as an ideal building block to assemble various porous materials [8], which shows great potential in constructing more efficient pore structure for supercapacitive energy storage than AC. However, the pursuit of increasing the accessible surface area of graphene materials usually causes a large proportion of macropores, which leads to a large amount of redundant space for supercapacitor application, thus, most of the

---

[*] Corresponding author.
[**] Corresponding author.
*E-mail addresses:* zhouxf@nimte.ac.cn (X. Zhou), liuzp@nimte.ac.cn (Z. Liu).

https://doi.org/10.1016/j.jpowsour.2018.02.032
Received 9 December 2017; Received in revised form 8 February 2018; Accepted 12 February 2018

reported graphene-based electrode materials suffer from low volumetric performance due to the low density of graphene samples [9–11]. It is important to design and synthesize graphene-based electrode materials with high density, as the volumetric performance is always critical in practical applications due to limited space of supercapacitor devices. Recently, means to shrink the distance among graphene sheets by capillary force of liquids to effectively increase the density of graphene materials has been proposed. For instance, Li and co-workers have made a great breakthrough in controlling mesopore size of graphene hydrogel films by a liquid-mediated method. Graphene aerogel film with a high density of 1.33 g $cm^{-3}$ was prepared through capillary force induced volume shrinkage [12]. Yang and co-workers also used solvent evaporation method to shrink the graphene hydrogel to form dense graphene monoliths with very high volumetric capacitance [13].

Considering the compression process in electrode fabrication for supercapacitors, volumetric capacitance ($C_{vol}$) based on compressed electrode is of great importance for practical applications [14,15], however, it is widely acknowledged that excellent volumetric performance required by supercapacitor applications not only includes a large $C_{vol}$, but also an outstanding rate performance which strongly depends on the diffusion rate of electrolyte ions in the electrode materials, especially at high current densities. There lies a contradiction between these two indexes. The former one requires high density and low porosity of the electrode material, which can be easily achieved by compressing, however the compression has an adverse impact on the latter one which demands abundant pore volume and relatively large pore size. Consequently, it is important to design an appropriate pore structure that can achieve optimal balance between these two critical indexes. Unfortunately, most of the current studies fail to cope with the demands of enough pore channels in compact structure. The process of densifying the graphene-based electrode materials is usually accompanied with poor rate performance, even though a high $C_{vol}$ can be reached. For example, the specific capacity of densified graphene monoliths rapidly dropped to ~70% of its initial capacity when the current density was elevated to 15 A $g^{-1}$ in Yang's work [13]. Consequently, it is important to find a suitable pore structure that can provide enough pores suitable for ion diffusion while removing excessive voids to acquire high density. Recent progresses indicate that macropores in graphene powders can be effectively removed to attain a high density by mechanical compressing, while the mesopores are preserved to a large extent [14]. Such mesopores remained in a relatively compact structure can provide channels for rapid diffusion of electrolyte ions. Therefore, high content of mesopores in the graphene-based electrode material needs to be achieved to obtain excellent volumetric performance.

In our present work, graphene powder with outstanding volumetric performance, including both high $C_{vol}$ and excellent rate capability are prepared by selecting solvents that generate different capillary force to control its pore structure and pore size [16]. Ethanol has been used as a solvent instead of common water solvent to reduce the shrinkage degree of graphene powder during solvent evaporation due to its lower surface tension and wettability on graphene surface comparing with water [17]. With the assistance of mechanical compression, the graphene powder derived from ethanol solution possesses a major pore size distribution in the range of 2–30 nm and a high compaction density of 1.30 g $cm^{-3}$. The sample from aqueous solution has a similar density, however a mesopore volume ~40% lower than that of the former one. As a result, the graphene powder prepared from ethanol evaporation shows a high $C_{vol}$ of 162 F $cm^{-3}$, and outstanding rate performance of 76% capacity retention at a high current density of 100 A $g^{-1}$, which exhibits great potential for application in commercial supercapacitors.

## 2. Experimental section

### 2.1. Preparation of graphene oxide (GO)

Graphene oxide (GO) was synthesized from natural graphite flakes with a mean lateral size of 80 μm by Hummers method [18]. The as-synthesized GO was dispersed in water to form a 0.5 wt% brown suspension, and sonicated by a cell disruptor with the power of 500 W.

### 2.2. Preparation of reduced graphene oxide (rGO) powder

The GO suspension was placed in the oil bath at a temperature of 80°C with constant stirring, and hydrazine hydrate was added to the GO suspension slowly (the weight ratio of GO/hydrazine hydrate = 3). The reduction reaction was carried out for 5 h and finally the brown GO suspension was turned into a black turbid solution which indicated that the GO had been transformed to rGO. The rGO particles were collected from the above solution by vacuum filtration and washed with de-ionized water several times without drying. Equal amount of rGO was re-dispersed in water and ethanol, respectively, and kept steady for 12 h for thorough infiltration of the solvents in the rGO particles. Then the re-dispersed rGO suspensions were dried at 80°C in air atmosphere to acquire rGO powder. The rGO powder obtained from ethanol solution was named as ET-rGO, while that from aqueous solution was named as WA-rGO.

### 2.3. Materials characterization

The morphologies of the samples were examined using field emission scanning electron microscope (FESEM, Hitachi S4800) and transmission electron microscope (TEM, FEI Tecnai G2F20) operated at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was performed on a TGA50 analyzer (Shimadzu) under air atmosphere in the temperature range of 30°C to 850°C and a ramp rate of 10°C $min^{-1}$. The nitrogen adsorption/desorption isotherms were recorded by Micromeritics ASAP-2020M nitrogen adsorption apparatus, and the pore size distribution and pore volume were obtained from the adsorption branch using the Barrett, Johner and Halenda (BJH) method. Powder X-ray diffraction (XRD) measurements were performed using an AXS D8 Advance diffractometer equipped with Cu Kα radiation. Raman analysis was carried out by Renishaw in Via Reflex Raman spectrometer with excitation wavelength of 532 nm laser. X-ray photoelectron spectroscopy (XPS) measurement was carried out with an X-ray photoelectron spectrometer (Kratos AXIS Ultra DLD) using focused monochromatic Al Kα radiation (1486.6 eV).

### 2.4. Electrochemical measurements

A symmetrical two-electrode system (CR2032-type coin cells) was used to test the electrochemical performance of ET-rGO and WA-rGO. The electrolyte solutions were 6M KOH or ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4). The mass of a single electrode was 4–5 mg. The cycle performance was tested on a LAND-CT2001A battery test system (Jinnuo Wuhan Corp., China) under the current density at 1 A $g^{-1}$, and the charge-discharge tests were carried out in the voltage range of 0–0.9 V. Cyclic voltammetry tests were conducted at scan rates between 5 mV $s^{-1}$ and 800 mV $s^{-1}$ using an Autolab 83 710 electrochemical work station. A sine wave with the amplitude of 10.0 mV and frequency range of 100–0.01 kHz was applied in the impedance spectra test.

## 3. Results and discussion

### 3.1. Structure and morphology

Fig. 1a describes the entire procedure for preparing ET-rGO. The