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Multifunctional structural supercapacitor based on graphene and geopolymer

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ABSTRACT

A novel multifunctional structural supercapacitor based on graphene and geopolymer infused with 2 M KOH electrolyte was fabricated. Metakaolin-based geopolymers, which were first applied as structural separators in this paper, were prepared with metakaolin and different moduli of alkaline activator solution. The widespread pores in geopolymer matrix provide enough channels for ion storage and motion. The effects of alkaline activator solution modulus and curing age on the electrochemical properties were analyzed. The results revealed the ideal capacitive behavior of structural supercapacitor. The samples with modulus of 2.0 exhibited the highest specific capacitance of 36.5 F g^{-1} at curing age of 28 days. A possible mechanism was proposed to explain the factors that influence the specific capacitance of geopolymer-based structural supercapacitor. The result of multifuncitonality analysis showed that samples with modulus of 1.6 exhibited the best level of multifunctionality, with compressive strength of 33.85 MPa and specific capacitance of 33.4 F g^{-1} at curing age of 28 days. It achieved a balance between mechanical property and electrochemical performance.

1. Introduction

In recent years, the developments of energy storage materials have played a crucial role in the innovation of emerging technologies such as aerospace, new energy vehicles and portable electronic products [1]. Despite great progress of energy storage system was obtained, there is a particular demand of multifunctional energy storage system which exhibits at least one additional function such as load-bearing capability, thermal and corrosion-proof properties [2,3].

Recently, a great deal of attention was paid to structural energy storage systems which simultaneously maintain structural strength and energy storage capability [4]. Conventional method to achieve structural energy storage systems involves physically embedding devices into structural composites to protect themselves [5,6]. A more potential and promising approach is to develop truly multifunctional materials which could increase electrochemical performance and reduce redundant elements in the system [7]. Different from traditional systems which consist of separate structural and energy storage components, multifunctional structural materials offer an opportunity to greatly reduce the weight of system, or to significantly improve the energy storage capability of system with the same weight. However, the focal points of earlier works remain to improve the electrochemical performance such as energy storage capacity, charge-discharge efficiency and cycle life [8]. With the advancement of energy storage system, multifunctional energy storage materials are appeared to enhance structural and electrochemical performance, as well as practicability [4].

As a potential energy storage device, supercapacitor gains great interest due to its high capacitance, large power density, great charge-discharge efficiency and long cycle life [9,10]. Compared to battery, it is easier for supercapacitor to maintain structural integrity because no physical destroying of electrode materials will appear in the charge-discharge process of supercapacitor. Compared to dielectric capacitor, supercapacitor has higher energy density. As a result, more and more researches have been focused on structural supercapacitor currently. Driven by the demand to bear mechanical loads in process of operation, structural supercapacitor must contain structural components: structural electrode and structural separator/electrolyte [11].

As a critical component of structural supercapacitor, electrodes must exhibit large surface area, high electrical conductivity and favorable stability during working. Among many possible materials, carbon materials remain the most common choice. In

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particular, structural carbon fiber-reinforced polymers are widely applied due to their excellent conductivity and good structural properties (strength and stiffness) [12,13]. To overcome the low surface areas of structural carbon fibers, activation becomes a common choice. Qian H et al. [14] proposed an effective way to activate structural carbon fibers with the aid of KOH. The activation of carbon fibers significantly increased the surface area and specific capacitance by 100 and 50 times, respectively. A novel method involves combining structural carbon fiber with carbon aerogel (CAG) through embedding [4]. CAG-modification significantly enhances the specific surface area, leading to a specific capacitance of 62 F g^{-1}, which is 100-fold higher than that without modification. Meanwhile, shear strength of electrode increases by 4.5 times. Recently, Deka B K et al. [15] fabricated structural supercapacitor with modified woven carbon fiber electrode. By growing CuO nanowires on woven carbon fiber, the specific capacitance increased to 2.48 F g^{-1}, compared to 0.16 F g^{-1} for the bare woven carbon fiber based supercapacitor. The growth of CuO nanowires also improved the combination of the carbon fiber with electrolyte, leading to an improvement of structural properties.

To combine excellent ionic conductivity with high structural strength into multifunctional electrolyte may be more challenging, since an enhancement in mechanical performance always leads to a reduction in ionic conductivity [16–19]. To date, the most widely accepted approach is to use solid polymer electrolytes [20–27], which is consisted of an ionic salt complex and polymer having electron donor atoms [3]. Among the many possible structural polymer matrix, structural epoxy resins which have compression modulus of up to 4 GPa have attracted great attention [19].

New opportunities are offered by graphene, a novel carbon-based material formed by a single layer of carbon atoms [28]. Due to its unique structure, graphene possesses many excellent properties including high mechanical strength, large surface area and great electrical conductivity, making it a potential electrode material for structural supercapacitor.

Synthesized by alkaline solution activating aluminosilicate source material, geopolymer possesses many excellent properties such as high compressive strength, good electrical insulation, excellent heat durability and resistance to chemical corrosion [29,30]. These characteristic make geopolymer a promising separator material for structural supercapacitor. Moreover, as a porous material, geopolymer is a good carrier of ionic liquid and the porous structure provides a great amount of channels for ion transmission.

This paper investigates on structural supercapacitors that are fabricated by graphene and geopolymer. Two highly conductive graphene electrodes were separated by a geopolymer paste that was infused with KOH electrolyte.

2. Experimental

2.1. Materials

Among various graphene-based materials, we chose high conductivity graphene as electrode materials. Since graphene oxide (GO) always exhibits poor electrical conductivity, the high resistance is not suitable for the fabrication of supercapacitor. As for reduced graphene oxide (rGO), different oxidation-reduction routes exert a considerable effect on the structure and chemistry of the final product, which always possesses oxygen-containing groups to some degree. In this paper, the choice of electrode focuses on the high conductivity of materials, so that we can efficiently eliminate the effect of electrode and concentrate on the property of geopolymer separator. Moreover, no doping or modification was applied to graphene-based electrode. Based on the above considerations, high conductivity graphene was used as electrode materials in this research, purchased from The Institute of Coal Chemistry CAS of China.

The metakaolin used to synthesize geopolymer separator was obtained from Guangdong Maoming company. The chemical composition of metakaolin, as measured by X-ray fluorescence (XRF) analysis, is shown in Table 1. Commercial sodium silicate solution (molar ratio SiO_2:Na_2O = 3.3, solid content = 34%) and sodium hydroxide (analytical grade) were used to prepare the alkaline activator solution.

2.2. Preparation of the structural supercapacitor

The alkaline activator solution was prepared by mixing commercial sodium silicate solution, sodium hydroxide and deionized water. The modulus of the mixed alkaline activator solution, with a fixed SiO_2 content of 20 wt%, was tuned to 1.4, 1.6, 1.8, 2.0 and 2.0 M ratios of SiO_2/Na_2O by adding various weight of sodium hydroxide. The solid-to-liquid ratio, which is defined as the weight ratio of aluminosilicate precursor to alkaline activator solution, was 0.77. The metakaolin-based geopolymer pastes were prepared by mixing metakaolin with alkaline activator solution. The mixture was stirred in a mortar mixer at low speed for 2 min. After a stop for 1 min to scrap down pastes on the sides of the bowl, the mixer was operated at high speed for 2 min. Directly after mixing, the geopolymer pastes were poured into cylindrical molds with inner diameter of 10 mm and height of 1 mm to shape geopolymer separator. And cubic molds (20 × 20 × 20 mm) were used to form samples for compressive strength test. The molded pastes were removed from the molds after 24 h, kept at 20 ± 1 °C and relative humidity exceeding 90% until tests.

Structural supercapacitor samples were prepared by two graphene electrodes sandwiched with one geopolymer separator, infused with 2 M KOH electrolyte. In order to measure the electrochemical characterization, nickel foam was applied to the graphene electrode as a current collector.

2.3. Testing methods

All of the electrochemical experiments were carried out on CHI 660E workstation at room temperature. Galvanostatic charge-discharge measurements were conducted at the current density of 1.0 A g^{-1}. Cyclic voltammetry (CV) experiments were carried out with working voltage range from −0.5 to 0.5 V, at a scan rate of 100 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) plots were measured with the frequency range from 0.1 Hz to 100 kHz, the initial voltage was set to open circuit potential. The specific capacitance was determined using the following equation

$$C = i\frac{\Delta t}{\Delta V} \quad (1)$$

where i is discharge current density, Δt is the discharge time, ΔV is the voltage change.

The measurements of compressive strength of geopolymer specimens were conducted on a JES-300 compressive strength tester (Wuxi, China). The loading rate was set to 2.4 kN s^{-1}, and each value of compressive strength was calculated by averaging values of six specimens.

The morphology of geopolymer was characterized by a FEI field emission environmental scanning electron microscopy (Quanta

Table 1
Chemical composition of metakaolin.

Component	Al_2O_3	SiO_2	Fe_2O_3	P_2O_5	K_2O	Na_2O	TiO_2	SO_3
Percentage (%)	38.1	55.3	0.73	0.72	0.56	0.34	0.33	0.20