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Capacitive Performance of Graphene-based Asymmetric Supercapacitor

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ABSTRACT

A two-electrode asymmetric supercapacitor with positive and negative electrodes was developed. The positive electrode was composed of reduced graphene oxide/zinc oxide/cobalt oxide nanostructures (RZCo) that were prepared using a one-pot hydrothermal process. Meanwhile, polypyrrole/reduced graphene oxide (PyR) was electrodeposited on a graphite sheet as the negative electrode. These electrodes were separated by a 1.0 M Na_2SO_4 filter membrane. The synergistic effect between the positive and negative electrode materials widened the potential window to 1.6 V, thus contributing a high energy density of 41.8 Wh/kg at 2 mV/s, which was better than that of the KEMET commercial supercapacitor (17.7 Wh/kg). At room temperature (30 °C), the RZCo//PyR asymmetric supercapacitor exhibited a retention of 87% after 800 cycles compared to a retention of only 49% at 0 °C. Although the asymmetric supercapacitor retained 86% of its original capacitance at 60 °C, it possessed a lower specific capacitance than the asymmetric supercapacitor measured at room temperature. The RZCo//PyR asymmetric supercapacitor had a larger specific capacitance and smaller IR drop (0.09 V) than the KEMET commercial supercapacitor, which has a huge IR drop (0.22 V), providing a specific capacitance of 77.7 F/g.

1. Introduction

Supercapacitors, which are electrochemical devices that bridge the difference between batteries and conventional capacitors, have been given considerable attention because of their high power density (2–10 kW/kg), fast charging/discharging, and longer lifespans (10^4–10^6 cycles) [1–3]. Supercapacitors are classified into two classes, namely the electric double layer capacitor (EDLC) and pseudo-capacitor. The distinctive differences between EDLCs and pseudo-capacitors are solely related to their charging mechanisms. An EDLC's electrode materials are electrochemically inactive and depend on its accumulation of charges at the electrode/electrolyte interface, whereas the occurrence of a faradaic reaction on a pseudo-capacitor enables the storage of charges during the charging and discharging process [4–8]. The materials used for an EDLC, such as carbonaceous materials, have a profound effect on the establishment of its cyclic stability, whereas the materials for a pseudo-capacitor are transition metal oxides with multi-oxidative transition states and conducting polymer, which have high capacitive values in the energy storage family. Transition metal oxides have excellent oxidation and reduction reversibility characteristics over a wider potential range, which are favorable in supercapacitor applications.

Recently, there have been persistent efforts to maximize the performances of supercapacitors. The limitations of symmetric supercapacitors such as their low overall power and energy density, which have been ascribed to their narrow potential range, have prompted a switch from the symmetric configuration for a supercapacitor to an asymmetric configuration [4]. An asymmetric supercapacitor is made up of a combination of a battery-type faradaic cathode and a capacitor-type anode. These can increase the potential window range, which maximizes the operating voltage of an asymmetric supercapacitor [9,10] and increases the energy density of the energy storage device [11,12]. The occurrence of a redox reaction with or without a non-faradaic reaction and EDL (electrostatic adsorption/desorption) on either of the electrodes

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clearly distinguishes the asymmetric and symmetric configurations for a supercapacitor [13].

The negative electrodes or anodic materials of an asymmetric supercapacitor are mainly composed of carbonaceous materials such as carbon nanotubes (CNTs), activated carbon (AC), and graphene. A typical AC-based energy storage device with a specific surface area in the range of 1000–2000 m^2/g records a gravimetric capacitance of 100–120 F/g in an organic electrolyte and energy density of 4–5 Wh/kg [14], whereas a multiwalled CNT device with a specific area of 430 m^2/g has a specific capacitance and energy density of 113 F/g and 0.56 Wh/kg, respectively, in a 38 wt% H_2SO_4 electrolyte [15]. The exceptionally high specific area of graphene (2630 m^2/g) provides fertile ground for implementation in supercapacitor applications [14,16,17]. In addition, a graphene-based supercapacitor with a high specific capacitance of 154.1 F/g and high energy density of 85.6 Wh/kg in an ionic liquid electrolyte at a current density of 1 A/g has been reported [17–20]. Although monolayer graphene possesses a large specific surface area with excellent conductivity, and mechanical and electrical properties, graphene is inherently hydrophobic in nature, which leads to the non-dispersion of graphene in most aqueous solvents [21–26]. The agglomeration of graphene hinders the ionic accessibility of an asymmetric supercapacitor [13], but could be solved through the use of reduced graphene oxide (rGO), which has an excellent electrical conductivity of up to 1.28 S/m at 6 wt% [27]. In addition, the remnant oxygen groups of rGO could prevent the restacking of graphitic sheets as a result of the strong Van de Waals forces. Occasionally, compositing rGO with electrochemically active materials is necessary to leverage the supercapacitor performances. Conducting polymers are capable of storing more capacitance per gram, and thereby contribute to a higher energy density and faradaic capacitance [28–30]. One of the most-sought after conducting polymers, polypyrrole (PPy), is highly conductive, has ultrahigh-flexibility, and has been reported to display a high capacitance value [31]. A hybrid of PPy and rGO significantly improved the capacitive performance of supercapacitors [28,32,33].

Meanwhile, the positive electrodes or cathodic materials of asymmetrical supercapacitors include oxides such as cobalt oxides (Co_3O_4), nickel hydroxide ($Ni(OH)_2$), manganese dioxide (MnO_2), and ruthenium oxide (RuO_2). Cobalt oxide (Co_3O_4) is a pseudo-capacitive material with high electro-activity and multi-capacitance storage ability, where Co_3O_4 nanostructures are able to store a charge via the double layer and pseudo-capacitive reaction. Co_3O_4 could theoretically deliver a specific capacitance of ~3650 F/g [2]. On the other hand, zinc oxide (ZnO) has a good carrier mobility and provides a high energy density [34,35], A one-dimensional ZnO nanostructure possesses excellent electron transport properties [36], which can enhance the capacitive performances. A composite of Co_3O_4@graphene nanosheet prepared using a microwave-assisted method could homogenously distribute Co_3O_4 nanoparticles (3–5 nm in size) on a graphene sheet [13]. The inclusion of conductive graphene sheets provided an opened pathway for rapid charge storage and delivery, which resulted in a high electronic conductivity and capacitance performance, and an improved cyclic life for the device [16,17]. Thus, when transition metal oxides are included, which in our work refer to the ZnO/Co_3O_4 nanostructures, they behave as intercalating agents and intercalate the rGO layers to prevent the restacking of rGO sheets. This phenomenon is expected to be able to enhance the inflow and outflow of electrolyte ions, resulting in excellent electrochemical performances, in addition to increasing the porosity of the graphite sheet. The inclusion of rGO could produce better wettability and thus induce the good dispersion in water ascribed to the presence of the remaining oxygen groups, in line with the aromatic rings, which offer active sites for the π-π interaction [37]. The synergetic effects of the ternary materials (ZnO/Co_3O_4/rGO) hence produce excellent electrical conductivity and better porosity.

Tailoring the nanostructure of the electrode is essential to increase the surface area of the active materials, because it produces a shorter ion insertion/desertion diffusion path and enables efficient charge and mass transfer without compromising the double layer capacitance [10]. In addition, the merit of a binderless electrode is its excellent charge transportation [10], in order to minimize the supercapacitive resistance and "dead volumes" in the electrode materials [11,38]. We here present our work on the fabrication of an RZCo//PyR asymmetric supercapacitor on a graphite sheet via a one-step facile hydrothermal and electrodeposition process. The graphite sheet was chosen as the current collector and treated with nitric acid prior to the deposition of the active materials. This was expected to improve the functionalization between the functional groups of the active materials and the carbon surface, which would lead to an excellent electro-catalytic activity performance [39,40]. To date, only a few temperature dependent studies have been reported, whereas most supercapacitor application studies have focused on the performances at room temperature. The supercapacitive performances of an asymmetric supercapacitor at different temperatures were also investigated in this study.

2. Experimental

2.1. Materials

Graphite powder was obtained from Ashbury Graphite Mills Inc. (code no. 3061). Potassium permanganate ($KMnO_4$, 99.9%), sulphuric acid (H_2SO_4, 95%–98%), phosphoric acid (H_3PO_4, 85%), and hydrogen peroxide (H_2O_2, 30%) were purchased from Systerm, Malaysia. Hydrogen chloride (HCl, 37%), sodium sulphate anhydrous (Na_2SO_4, 70%), and a toluene-4-sulfonic acid sodium salt (NapTS, 98%) were purchased from Merck. Pyrrole (99%) was purchased from Across Organic, stored at 0 °C, and distilled prior to use. The graphite sheet (natural graphite >99.5%) was purchased from Latech Singapore. The nylon membrane filter was purchased from Membrane Solutions, LLC, US. Zinc nitrate hexahydrate, ($Zn(NO_3)_2.6H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) were purchased from Bendosen and R&M Chemicals, respectively. Nitric acid ACS reagent ($\geq$65%) was obtained from Sigma-Aldrich. Urea was purchased from AnalaR, BDH laboratory supplies from England, and ammonium chloride (NH_4Cl) was obtained from Merck.

2.2. Preparation of graphene oxide (GO)

GO was prepared through the simplified Hummer's method, where the oxidation reaction was carried out by mixing H_2SO_4:H_3PO_4 (360 ml:40 ml), graphite flakes, and $KMnO_4$ using a magnetic stirrer at room temperature. The mixture was then left stirring for three days to allow the complete oxidation of the graphite. Subsequently, the H_2O_2 solution was added to the mixture to stop the oxidation process, and the color of the mixture turned bright yellow. Next, the graphite oxide was washed with a 1 M HCl aqueous solution three times and with deionized water ten times using the centrifugation technique until the pH reached a value of approximately 4–5 and GO was formed. The concentration of GO was 6.3 mg/ml.

2.3. Preparation of rGO/ZnO/Co_3O_4 (RZCo) positive electrode

First, 2 mmol $Co(NO_3)_2.6H_2O$, 1 mmol $Zn(NO_3)_2.6H_2O$, 4 mmol NH_4Cl, and 0.02 mg/ml GO precursors were dissolved in 30 ml of