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Achieving simultaneously high energy and power densities in an asymmetric supercapacitor with the fe₃o₄/gns electrode combination

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Abstract. With our growing need for highly efficient energy supplies, a demand for new devices with better energy conversion and storage capabilities arises. Asymmetric supercapacitors combining a pseudocapacitive and an EDLC electrode show great potential as a prospective energy storage device. The relatively broad voltage window and low cost of iron (II, III) oxide and the eminent properties of graphene nanosheets (high electrical conductivity, large surface area, etc.) make them ideal candidates for the electrode materials of supercapacitors. An asymmetric supercapacitor using iron (II, III) oxide as the anode and graphene nanosheets the cathode with an aqueous electrolyte of 3 M potassium hydroxide was proposed here. Iron (II, III) oxide nanoparticles were synthesized from $FeCl_3 \cdot 6H_2O$ using a hydrothermal approach. Graphene nanosheets were prepared from fine-grained graphite raw materials via Hummer’s method. The electrochemical performance of the device was characterized using a triple-electrode setup, with the electrodes being submerged in a medium of 6 M KOH. This specific asymmetrical supercapacitor shows promise as a practical foundation towards a future of more effective energy transformation and storage, such as line-filtering and signal selection, particularly due to the relative abundance and environmentally-friendly nature of its electrode materials.

Keywords: asymmetric supercapacitor, iron (II, III) oxide, graphene nanosheets, energy storage, EDLC, pseudocapacitance, hybrid capacitor.

1. Introduction

With the fast development of technologies that transform our civilization and lifestyle, our need for highly efficient energy supplies grows while Earth's stock of fossil fuels declines. Therefore, we need to look for alternative clean sources of energy meanwhile paying attention to constructing new devices with better energy conversion performance and highly-efficient storage mechanisms than what we currently have available [1]. The typical ways to convert and store energy are through batteries, fuel cells, and supercapacitors, all of which are electrochemical energy storage devices [1]. Despite having their advantages, each of these devices has limitations that prevent them from satisfying our rising energy demand.

Due to the redox reactions within its electrodes, a battery typically has a relatively high energy density. They are capable of storing a comparatively good amount of energy. However, repetitive and irreversible charging/discharging tend to lower their cycle life. During charging/discharging, ions within the battery are driven out of and embedded back into the electrodes of the device, which, along with the possibility of side reactions, could eventually lead to permanent deformations in the crystal structures of the electrodes and interfere with the battery's ability to function correctly. Furthermore, an unstable solid electrolyte interface (SEI) would gradually consume the electrodes' active materials and thus giving rise to a decrease in capacity over numerous cycles.

Supercapacitors (SCs), on the other hand, excel at charging/discharging efficiency and cycle life compared to batteries. Traditional electric double-layer capacitors (EDLCs), in particular, are devices in which charges redistribute electrostatically on the surface of two conducting plates when an external electric field is applied. Unlike batteries, no redox reactions occur within them. As a result, EDLCs charge and discharge almost instantly, leading to high power density, which means they can supply energy faster than batteries. In addition, because charge exchange takes place at or near the surface of the electrodes, leading to virtually no phase transition of the materials within EDLCs, they tend to have a longer life cycle than batteries. The downside, however, is that EDLCs are not as impressive as batteries when it comes to energy storage. The energy density of EDLCs is far from most secondary batteries.

To avoid these limitations and utilize the strengths of both devices, considerable attention has been given to various combinations of batteries and supercapacitors to build pieces of equipment having competitive energy and power densities. Such devices are collectively known as pseudocapacitors. By having redox reactions occurring at or near the surfaces of the electrodes, pseudocapacitors have excellent capability to store and quickly supply energy. Moreover, there are also combinations of pseudocapacitors and EDLCs, such as asymmetric supercapacitors and hybrid capacitors [2].

Asymmetric supercapacitors refer to devices involving two different electrode materials, either from the perspectives of potential windows or charge-storage mechanisms [2]. The main advantage of asymmetric supercapacitors is the possibility of broader potential windows [2]. According to the equation below,

$$E = \frac{1}{2}CV^2 \tag{1}$$

The specific energy (E) forms a parabolic relationship with the potential (V), where the proportionality constant is $\frac{1}{2}C$ [2]. Thus, doubling the voltage window would lead to an energy density four times greater, suggesting that using electrodes working under different potential intervals significantly improves the energy densities of asymmetric supercapacitors. Additionally, the overall capacitances (C_T) for asymmetric supercapacitors are calculated with the following equation,

$$\frac{1}{C_T} = \frac{1}{C_P} + \frac{1}{C_n} \tag{2}$$

where C_P and C_n represent the capacitances, in this case, for the electrodes constructed from iron (II, III) oxide and GNS, respectively [2]. This relationship implies that the capacitance of a supercapacitor is restricted by the electrode having a lower capacitance [2]. To this end, replacing a supercapacitive electrode with a Faradaic structure possessing a higher specific capacitance might be a compelling method to enhance the energy storage capacity of supercapacitors.

Consequently, a highly efficient asymmetric device could be a robust solution to achieving capacitive electricity storage mechanisms possessing at the same time large capacity and fast charging/discharging rates.

Hybrid capacitors, as a specific category of asymmetric supercapacitors, describe particularly the situation where the device's electrodes have different charge-storage mechanisms, with one being capacitive while the other Faradaic, which include supercapacitors employing both battery and EDLC electrodes, or ones containing distinct redox-active electrolytes, or having identical EDLC carbon materials with different faradaic active functional groups on the surface [2]. Besides maintaining superior rate performance and persistent stability, these devices have increased capacitance compared with traditional EDLCs.

Here, we intend to build an asymmetric hybrid supercapacitor using Fe_3O_4 nanoparticles as the anode and graphene nanosheets (GNS) as the cathode. The widespread potential window and environmentally-friendly nature of iron (II, III) oxide, and its low cost, make it an ideal candidate for electrode materials of supercapacitors [3,4]. For example,

Wang et al., using an ultrasonic-assisted approach, synthesized Fe_3O_4 nanoparticles with diameters strictly constrained between 5 to 10 nanometers, and a relatively enormous specific surface area (165.05 m^2/g). They reported a capacitance density of 207.7 F/g at 0.4 A/g. Additionally, a supercapacitive device made from such iron (II, III) oxide nanoparticles was reported as having no capacitance loss after 2000 cycles [4].

Zeng et al. fabricated homogeneous Fe_3O_4 sub-micron spherical shells (also known as HFOS) having diameters in between 350-450 nm via a controlled solvothermal method. When used to construct the anode for a supercapacitor, the authors found that these Fe_3O_4 sub-micron spheres enhance the device's electrochemical properties [5]. The HFOS have a high stationary magnetization value of 80.2 $A/m^2/kg$ under the influence of an external magnetic field and low coercive force of 7.3 Oe because of their high purity and spherical shapes [5]. These materials have a capacitance density of 294 F/g at 0.5 A/g with a 90.8% maintenance of original capacitance after 500 charging/discharging cycles [5]. Therefore, Fe_3O_4 anode materials are capable of serving as a high-capacitance Faradaic electrode in asymmetric supercapacitors.

On the other hand, graphene nanosheets have gained much attention as an electrode material for supercapacitors due to their incredible efficiency at storing and releasing energy, large theoretical surface area, and outstanding cycle stability [6]. In addition, numerous studies demonstrate desirable EDLC performances for graphene nanosheets in aqueous electrolytes.

Liu et al. synthesized porous graphene nanosheets and mono-mural carbon nanotubes composite film (also called GNCF) as the cathodic ingredients for supercapacitors. They assembled a symmetric all-solid-state supercapacitor using GNCF and found that the instrument maintains a specific capacitance of 202.5 F/g at 10 mV/s, with a capacitance retention level of 91.2% after 10,000 charging/discharging cycles [6].

Ali et al. prepared graphene oxide via Hummer's method and reduced it to obtain GNS. The electrochemical studies show that GNS has a specific capacitance of 140 F/g at 0.05 A/g, with cyclic stability of approximately 86% over 1100 cycles at 1 A/g [7]. Furthermore, the material's large chemical active surface area means that a significant portion of the GNS would be available for ion adsorptions in the electrolyte system [7].

2. Experimental

2.1. Hydrothermal preparation of fe3o4-nanoparticle anode

Iron (II, III) oxide nanoparticles were synthesized using a hydrothermal approach, with iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) being the starting material [8]. One millimole (27.03 mg) of $FeCl_3 \cdot 6H_2O$ was first dissolved in 10 mL of ethylene glycol and to this solution 0.25 mmol CH_3COONa was added [8]. The mixture was stirred at 25 °C for 30 minutes. Next, 0.01 mol of poly(vinyl)pyrrolidone (molecular weight 10 kDa), which acted as a surfactant layer, was combined with the resultant mixture [8]. The precursor solution was obtained by stirring vigorously for an hour, also at room temperature [8]. After this, the solution was enclosed in a 20-mL Teflon-lined stainless steel hydrothermal reactor. The reaction proceeded at 200 ºC for 8 hours [8]. Once the process was done, the temperature of the system was slowly brought down to 25 degrees Celsius. The sediment was collected and rinsed five rounds using ethyl alcohol and deionized water. The sample was subsequently dried overnight at 60 ºC under vacuum. The electrode was forged by mixing 80% (by weight) of the Fe_3O_4 synthesized previously, 15% (by weight) of acetylene black (AB), and 5%

polytetrafluoroethylene (PTFE) by weight in DMF to produce a slurry, which was coated onto a nickel grid (the current collector for the anode) at a loading mass of 5 mg/cm^2 using the doctor blade-coating technique. Finally, the electrode was dried overnight at 160 ºC in a vacuum oven.

2.2. *Ultrasound-assisted synthesis of graphene-nanosheet (GNS) cathode*

Graphene nanosheets (GNS) for the cathode were prepared by reducing the graphene oxide obtained using graphite as the reactant via a modified Hummer's reaction [9]. First, graphene oxide was added to deionized water, followed by subjection to ultrasound to obtain a suspension, which was stirred at 95 ºC for 16 hrs [10]. Then, the suspension was cooled in air to roughly 25 degrees Celsius, at which point vacuum filtration was performed in an effort to collect the dark solid [10]. The product was rinsed five times using deionized water and absolute ethanol, and was subsequently left in a vacuum oven at 80 ºC for 12 hours in order to remove the remnant moisture [10]. The electrode was constructed by mixing GNS, AB, and PTFE based on a mass ratio of 80:15:5, with 80% GNS, 15% AB, and 5% PTFE by weight. The fabricated material was then attached to a piece of copper foil, which served as the current collector for the cathode [11]. The loading mass was 1 mg/cm^2. A few drops of ethanol were mixed with the electrode material to form a more consistent slurry. Lastly, the GNS cathode was kept in a vacuum oven at 80 ºC for 12h.

2.3. *Electrochemical characterization of Fe3O4 nanoparticles/KOH/GNS asymmetric supercapacitor*

Electrochemical characterizations were performed in a classic triple-electrode configuration with the application of a 6 M KOH aqueous electrolyte. A piece of platinum foil served as the counter electrode, whereas an Hg/HgO standard electrode took the place of the reference. Bio-logic electrochemical workstations were used to conduct relevant electrochemical analyses. The CV diagram within a voltage span of -0.3 to 0.7 V was acquired at the twelfth round of charging and discharging. The potential range of the GCD curves was set to be 0 ~ 0.45 V. Impedance spectra were obtained with frequencies spanning from 0.01 Hz to 100 kHz at the open circuit potential, to which was assigned a perturbation bias of 5 mV. Equations (3) and (4), as presented below, illustrate the calculations of the specific capacitance (C_s) and coulomb efficiency (η),

$$C_s(C\,g^{-1}) = \frac{i\Delta t}{m} \tag{3}$$

$$\eta(\%) = \frac{\Delta t_D}{\Delta t_C} \times 100\% \tag{4}$$

where C_s has the unit $\frac{C}{g}$, i is the discharging current (A), m is the mass of the active material (g), and Δt is the discharging time (s). Δt_C and Δt_D refer to charging and discharging time (s) measured under a constant current (A), respectively.

The iron (II, III) oxide and AC previously synthesized played correspondingly the roles of positive and negative electrodes in the asymmetric supercapacitor, whose electrolyte was a 3 M KOH aqueous solution. Equations (5) and (6), as shown below, demonstrate individually the calculations of energy (E, Wh/kg) and power densities (P, W/Kg).

$$E = \frac{C_s(\Delta V)}{7.2} \tag{5}$$

$$P = \frac{3600E}{\Delta t} \tag{6}$$

where ΔV represents the potential range, measured in volts (V).

The optimum positive- and negative-electrode mass ratios for the maximum potential window achievable were determined to be about 0.35 using the electrode mass-balancing principle shown in equation (7) below,

$$\frac{m_+}{m_-} = \frac{C_{s-} \times \Delta V_-}{C_{s+} \times \Delta V_+} \tag{7}$$

where m represents the electrode mass `measured in grams (g). The "$+$" and "$-$" subscripts in equation (7) are used to indicate a particular quantity for positive or negative electrodes. For example, ΔV_{+} and ΔV_{-} represent the potential ranges of the anode and cathode of the supercapacitor, respectively.

Scanning electron microscopy images were applied to analyze the nano-configurations of the electrode constituents (SEM, JEOL JSM-6700F). Additional details of nanoscale features and elemental compositions were obtained from transmission electron microscopy (TEM JEM2100) and energy-dispersive X-ray spectroscopy (EDS). A characterization of the crystal frameworks of the Fe_3O_4 and GNS electrodes was carried out through powder X-ray diffraction (XRD, Rigaku D/max-2550PC, Cu Kα radiation, λ = 1.5406 Å). Perkin-Elmer Spectrum One B instrument was used to collect the Fourier transform infrared spectra (FT-IR) via the KBr pellet technique. Moreover, the chemical states and supplemental compositional information of the materials were characterized with/using X-ray photoelectron spectroscopy (XPS, PHI X-tool). A reference of exogenous carbon was used to calibrate the C_{1s} peak at a binding energy of 284.8 eV. A NOVA-2200e instrument (Quantachrome, USA) was used to gather the data on the N_2 sorptometry at a temperature of -196 °C.

3. Conclusion

An asymmetric hybrid supercapacitor was constructed using Fe_3O_4 anodic nanoparticle materials and cathodic graphene-nanosheet (GNS) materials, with a 3 M aqueous KOH solution being the electrolyte. The iron (II, III) oxide was synthesized from an ethylene glycol solution of $FeCl_3 \cdot 6H_2O$ by adding sodium acetate and poly(vinyl)pyrrolidone to the system and then heating the mixture obtained to 200 ºC for 8 hours. The actual anode was prepared by blending 80% Fe_3O_4, 15% acetylene black, and 5% PTFE by weight in DMF. Next, the resulting material was coated onto a nickel grid, which acted as a current collector for the negative electrode. Using Hummer's method, oxidized graphene derived from natural graphite powder was reduced to GNS [10]. The reduced graphene oxide was then deposited onto a copper foil, which serves as the current collector for the positive electrode [11].

The combination of Fe_3O_4 anode (the pseudocapacitive electrode) and GNS cathode (the capacitive electrode) allows this particular asymmetric supercapacitor to have a relatively wide potential window, leading to high energy and power densities for the equipment. Such a mix of electrodes also shows promises toward a longer cycle life for the device. In addition, the abundance and low costs of the electrode materials provide a potentially affordable solution to the energy storage problem, creating more possibilities for the further use of the apparatus.

Supercapacitors exhibit great prospects as a potential energy supply for the future. They could serve to compensate for the relatively low power densities of lithium-ion batteries and enhance charging/discharging rates while maintaining the superior energy storage capability of a battery. For instance, supercapacitors can act as a buffer during the charging process by charging quickly and slowly releasing the stored charges to a lithium-ion battery, allowing the battery to take the charges in at an even higher energy density.

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