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A high-performance asymmetric supercapacitor based on $Co(OH)_2$/graphene and activated carbon electrodes

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ABSTRACT

A high-performance asymmetric supercapacitor has been fabricated using graphene supported $Co(OH)_2$ nanosheet ($Co(OH)_2$/GNS) as the positive electrode and carbon fiber paper supported activated carbon (AC/CFP) as the negative electrode in KOH aqueous electrolyte, respectively. The asymmetric supercapacitor exhibits a significantly improved capacitive performance in comparison with that of the symmetric supercapacitors fabricated with $Co(OH)_2$/GNS or AC/CFP as the electrodes. The improvement is attributed a high conductivity and reversibility of electrode materials, leading to the large specific capacitance and broadened potential window, resulting in a high energy density (19.3 Wh kg^{-1} at a power density of 187.5 W kg^{-1}), excellent power density (3000 W kg^{-1} at an energy density of 16.7 Wh kg^{-1}) and long-term cycling stability (after 20000 cycles, initial capacitance remains well). These encouraging results make these low-cost and eco-friendly materials promising for applications in asymmetric supercapacitors with high energy density, power delivery and cycling stability.

1. Introduction

The global energy crisis, climate change, and environmental pollution have accelerated the development in not only the clean and renewable energy sources but also advanced energy conversion/storage systems. Supercapacitors, also known as electrochemical capacitors, with high power density and cycle life, have attracted growing attention as important energy storage devices for potential applications in hybrid electric vehicles and mobile electronic devices. However, the current commercial supercapacitors are symmetric electric double layer capacitors (EDLCs), which are based on high surface area carbon materials in the two electrodes in aqueous or organic electrolytes. With the virtue of large surface, high conductibility and large EDL formation, these commercial supercapacitors possess high power density but low energy density (less than 10 Wh kg^{-1}) due to the limited specific capacitance and operation voltage [1–5]. Therefore, it is necessary to develop high-performance supercapacitors with high energy density without forfeiting the power delivery and cycling stability. Asymmetric supercapacitors (ASC), employing electrochemical active materials different in two electrodes (electric double layer anode and redox reaction cathode) in aqueous electrolytes, show notable improvement in energy density by the increscent specific capacitance and comprehensive operation voltage, such as activated carbon (AC)//$LiMn_2O_4$ [6,7], AC//M_xO_y (M = Fe, Co, Ni, Mn, V, etc.) [8–11], AC//$Ni(OH)_2$ [12,13], and so on. These redox active materials provide a pronounced improvement in energy density of ASC by giving a specific capacitance about 2–10 times as large as that of carbon materials as well as a cell voltage higher than ~ 1 V of EDLCs in aqueous electrolytes [3,13]. In addition, compared to organic electrolyte, the aqueous electrolytes have the advantages of high ionic conductivity, low cost, non-toxic, safety, non-corrosiveness and convenient assembly in air [14,15].

However, these devices with metal oxides as the positive electrode material, AC as negative electrode material, still have restricted performance of relatively low energy density (10–30 Wh kg^{-1}), power density and cycling stability [6–8]. For one thing, among the redox pseudocapacitance active materials, the low conductivity of cheap metal oxide/hydroxide (such as NiO_x, CoO_x, and MnO_2) greatly undermines their overall effectiveness for ASC. For another, AC has a high hydrogen evolution potential leading to large negative potential range with low average capacitance resulting in imbalanced synergism [16–18]. Recently, partially due to the discovery of new electrode materials and new synthesis methodology, advanced supercapacitors with high performance have been developed. Asymmetric supercapacitors with high-performance electrode materials show a significant superiority in energy density, power density and cycling stability [19,20]. For example, Wang et al. [19] have grown $Ni(OH)_2$ or RuO_2 nanoparticles on high quality graphene sheets in order to improve capacitive performance of these materials, and prepared a high performance asymmetrical

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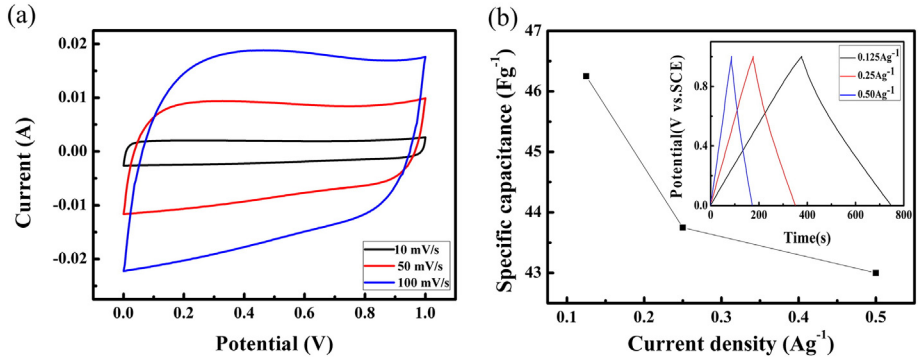

Fig. 1. (a) CV curves of AC/CFP//AC/CFP symmetric supercapacitor measured at various scan rates of 10, 50, and 100 mV s^{-1}, (b) specific capacitance of the AC/CFP//AC/CFP symmetric supercapacitor at different current densities based on GCD curves. Inset: GCD curves of the device measured at current densities of 0.125, 0.25 and 0.50 Ag^{-1}.

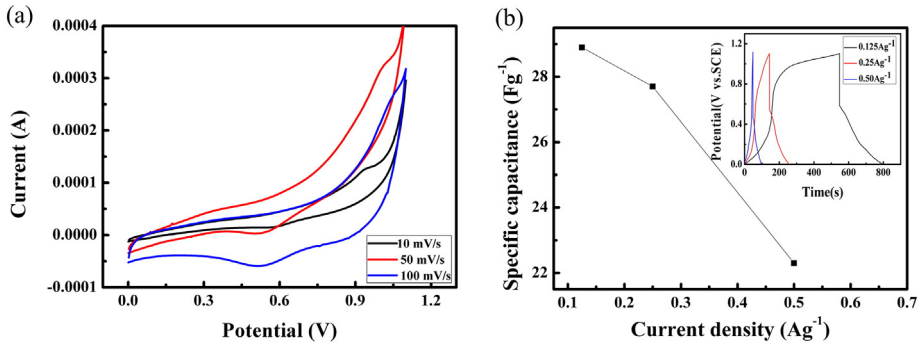

Fig. 2. (a) CV curves of $Co(OH)_2$/GNS//$Co(OH)_2$/GNS symmetric supercapacitor measured at various scan rates of 10, 50, and 100 mV s^{-1}, (b) specific capacitance of $Co(OH)_2$/GNS//$Co(OH)_2$/GNS symmetric supercapacitor at different current densities based on GCD curves. Inset: GCD curves of the device measured at current densities of 0.125, 0.25 and 0.50 Ag^{-1}.

supercapacitor with $Ni(OH)_2$/graphene positive electrode and RuO_2/graphene negative electrode in aqueous solutions. A high energy density of 48 Wh kg^{-1} at a power density of 0.23 kW kg^{-1} with a voltage of 1.5 V has been achieved. And the asymmetrical supercapacitor also exhibited good cycling stability (92% of the original capacitance after 5000 cycles at a current density of 10 Ag^{-1}). Asymmetric supercapacitors with high energy and power densities were also fabricated using the MnO_2/rGO hydrogel as the positive electrode and a pure rGO hydrogel as the negative electrode in a Na_2SO_4 electrolyte. The asymmetric supercapacitor exhibited a high performance with an energy density of 21.2 Wh kg^{-1} at a power density of 0.82 kW kg^{-1}, and the asymmetric supercapacitor exhibited stable cycling performance with 89.6% original capacitance after 1000 cycles at a current density of 1 Ag^{-1} [20].

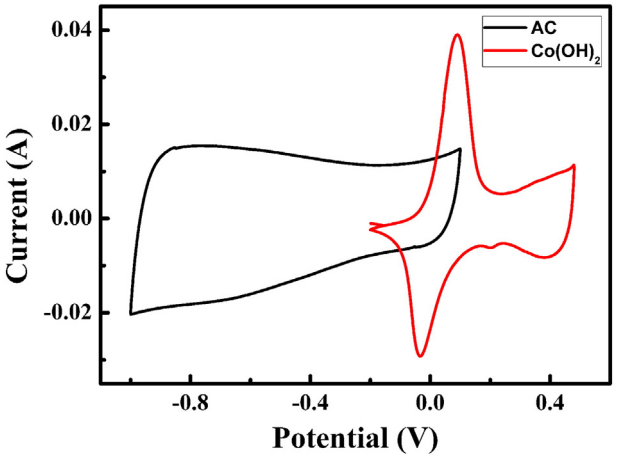

Fig. 3. CV curves of AC/CFP and $Co(OH)_2$/GNS electrode collected at a scan rate of 10 mV s^{-1} in a three-electrode system.

However, so far, since most of the reported hydroxide/carbon materials have been prepared by the chemical precipitation process, some problems exist, for example, the particles during synthesis are agglomerated easily, and a binder is often required, that will reduce the electrochemical activity [21].

Considering the fabrication cost and the environmental pollution, a promising direction is to design environmental friendly materials that have high electrochemical properties in aqueous electrolytes. In our previous work, we obtained binder-free graphene nanosheet supported $Co(OH)_2 \cdot (Co(OH)_2$/GNS) electrode material with high electrochemical performance [21]. In this work, we prepared $Co(OH)_2$/GNS and AC/carbon fiber paper (CFP) electrodes and fabricated symmetric and asymmetric supercapacitors. We aimed at developing a new supercapacitor with high energy density, power density and cycling stability.

2. Experimental

2.1. Preparation of $Co(OH)_2$/GNS/Ni foam electrode

Our previous work demonstrated that the combination of plasma-enhanced chemical vapour deposition (PECVD) and electrochemical deposition is a simple and reliable technique to obtain high-performance $Co(OH)_2$/GNS hybrid electrode material. Vertically oriented GNS were synthesized by PECVD on Ni foam used as substrates for cathodic electrodeposition of $Co(OH)_2$ nanosheets in $Co(NO_3)_2$ aqueous solution, the detailed description about the preparation can be found in ref. [21].

2.2. Preparation of AC/CFP electrode

The influence of activated carbon on the performance of capacitor is very important, therefore high-quality commercial AC (TF-02) with a surface area of 2000 m^2 g^{-1} and average particle size of 8 μm was chosen. The AC electrode was prepared by a simple and low-cost spray