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Short communication

Pre-lithiated graphene nanosheets as negative electrode materials for Li-ion capacitors with high power and energy density

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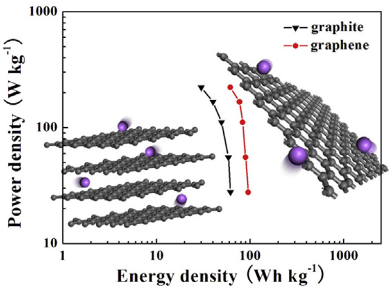
HIGHLIGHTS

- Pre-lithiated graphene nanosheets are explored for Li-ion capacitors.
- The Li-ion capacitors exhibit high energy and power density at high voltages.
- Pre-lithiated graphene nanosheets are promising for high power Li-ion capacitors.

GRAPHICAL ABSTRACT



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ABSTRACT

A Li-ion capacitor (LIC), typically composed of a pre-lithiated negative electrode and an activated-carbon positive electrode, can provide high energy and power density. In this work, we compare the electrochemical performances of pre-lithiated graphene nanosheets and conventional graphite as negative electrode materials for LICs. The LICs employing pre-lithiated graphene nanosheets show a specific capacitance of 168.5 F g^{-1} with 74% capacitance retention at 400 mA g^{-1} after 300 cycles. Moreover, the capacitors deliver a maximum power density of 222.2 W kg^{-1} at an energy density of 61.7 Wh kg^{-1}, operated in the voltage range of 2.0–4.0 V. Therefore, pre-lithiated graphene nanosheets are promising negative electrode materials for high power LICs.

1. Introduction

With dramatically increasing demand for electric vehicles (EVs) and hybrid EVs in recent years, discovering novel electrochemical energy storage devices with both high power and energy density is a huge challenge. Traditional secondary batteries cannot meet the requirement of high power density [1,2], while electrochemical double-layer capacitors (EDLCs) with high power density and long cycle life can only provide low energy density [3–5]. Under the circumstances, lithium-ion capacitors (LICs) have emerged and attracted considerable attention. LICs generally utilize pre-lithiated lamellar materials as negative electrodes and high-surface area activated carbon (AC) as positive electrodes [6–9]. In principle, when LICs work in a limited voltage range, anions adsorb/desorb onto/from the positive electrode surface, and simultaneously Li ions intercalate/de-intercalate into/from the bulk of the negative electrode. Therefore, LICs are amazing energy-storage devices combining the strong points of both EDLCs and secondary batteries

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[10]. Unlike EDLCs, the negative electrodes in LICs involve electrochemical reactions of pre-lithiated materials, and then their energy densities are much higher than those of EDLCs. Also, unlike secondary batteries, the positive electrodes of LICs only undergo anion ad/de-sorption on high-surface-area carbon materials and facilitate fast kinetics for charge/discharge processes, which enables higher power densities than those of secondary batteries.

As the Li^+ intercalation/de-intercalation reaction at the negative electrode is much slower than the ad/de-sorption reaction on the surface of the positive electrode, the general performance of LICs will be determined by the negative electrodes [11,12]. Therefore, it is crucial to find an ideal negative electrode material. A variety of materials including graphite, hard carbon and $Li_4Ti_5O_{12}$ (LTO) have been developed as LIC negative electrode materials [13–16], and so far graphite is the most widely used one for LICs. Graphite can offer a relatively flat lithium intercalation/de-intercalation potential between 0.1 and 0.2 V vs. Li/Li^+ and a theoretical capacity of 372 mAh g^{-1}. However, the layered structure of graphite with high crystallinity and anisotropy must impact the rate performance of capacitors under high current densities [13,17]. Similarly, hard carbon was also explored as the negative electrode materials for LICs, and showed good rate capability, which is ascribed to the microstructure of hard carbon. Hard carbon is composed of smaller pieces of graphene layers than graphite, which can contribute to faster ionic diffusion [8]. The good electrochemical performance of hard carbon ultimately comes from the existence of graphene nanosheets (GNSs). Thus, adopting graphene nanosheets to the negative electrode of LICs is highly attractive.

With respect to graphite and hard carbon, graphene possesses some advantages. Graphene, the single layer of carbon atoms in a honeycomb lattice, has high specific surface area, high carrier mobility and outstanding electrical conductivity, providing an ideal platform for the storage and transportation of lithium ions and electrons [18]. As a result, it is a promising material for wide applications, particularly in electronic devices [19–21]. More importantly, the three-dimensional interconnected porous graphene network makes it an ideal material for hybrid capacitors [22,23]. However, graphene, considered as the most potential EDLC material, has scarcely been reported as the negative electrode material for LICs.

As LICs primarily served as power devices, the major criteria for LIC negative electrodes include high capacity, low operation potential and fast charge/discharge capability. Graphene meets these requirements basically. Although the charge/discharge plateaus of graphene are not as flat and low as graphite, which is the problem for graphene's applications as Li ion battery and capacitor electrodes. Fortunately, graphene could supply much larger capacity and boost the energy density of LICs [24–27]. Most importantly, the porous structure and large surface area can afford fast ion transport and rich space for surface/interface electrochemical reactions, which are favorable for supercapacitors.

Herein, we pre-lithiated GNSs and graphite as negative electrode materials for LICs, and compared their performances in cyclic performance, rate capability, as well as energy and power density.

2. Experimental

2.1. Preparation of electrodes

Commercial graphite (Nanshu Hongda, Qingdao) and active carbon (Maxsorb) were used as received. Few-layered GNSs were prepared through exfoliation and chemical reduction of graphite oxide with the assistance of CuBr [25,26,28,29]. The graphite and GNSs were characterized by scanning electron microscope (SEM, FEI Nanosem 430 field-emission gun SEM). The positive electrode (PE) was composed of AC, acetylene black (AB), and polyvinylidene difluoride (PVDF) with a weight ratio of 80:10:10. Aluminum foil was used as the current collector. For the negative electrode (NE), graphite and graphene were used as the active material, respectively. Negative electrodes were prepared through the same method above except for the ratio of active material, AB, and PVDF (70:20:10). Copper foil was used as the current collector. The average weight of the working electrodes was approximately 3 mg. The electrolyte was 1 mol L^{-1} $LiPF_6$ dissolved in a 1:1:1 mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC). Under the consideration of operating voltage of LICs (2.0–4.0 V), the mass ratio of NE and PE was tailored at 1:2.

2.2. Pre-lithiation of negative electrodes

Pre-lithiated carbon materials can provide low potentials to negative electrodes, increase the open circuit voltage (OCV), and thus enhance the energy density of LICs accordingly [24,27]. As a result, the pre-lithiation is a critical step for LICs. In this work, the pre-lithiation involves the following procedures. Before cycling, the OCV of the cells was about 3.1 V. At first, the cells were discharged (Li^+ intercalation) from its OCV to 0.01 V in Li/carbon cells at a constant current density of 400 mA g^{-1}. In this procedure, graphitic carbon materials tend to form solid electrolyte interface (SEI) films. Therefore, the electrochemical capacity is much higher than that of the following cycles. Next, the cells were charged to OCV at 400 mA g^{-1} and then discharged/charged in the same way for another two cycles. Fig. 1 shows the charge/discharge curves for the initial three cycles. The capacities became stable in the second and third cycles, and then we set these values as the maximum Li intercalation capacities. Finally, we discharged the electrodes again and controlled the discharge time to insure that 70% of the maximum Li ions were intercalated into the electrodes. The remaining capacity provides the space to Li intercalation/de-intercalation during LIC operation. Therefore, pre-lithiation was successfully accomplished within three discharge/charge cycles and a discharge process in total.

2.3. Electrochemical tests

After pre-lithiation, LICs were assembled in a glove box filled with high-purity argon (H_2O and O_2 < 1 ppm). Galvanostatic charge/discharge tests were performed in the voltage range of 2.0–4.0 V under a LAND-CT2001A instrument at room temperature. The capacitance was calculated according to the corresponding total weight of the active material in both electrodes. Cyclic voltammetry (CV) was performed at a scanning rate of 0.1 mV s^{-1} between 2.0 and 4.0 V. Electrochemical impedance spectroscopy (EIS) was performed by using an IM6e electrochemical workstation at 25 °C with a frequency range from 10 kHz to 100 mHz and an alternating current signal with an amplitude of 5 mV as the perturbation.

3. Results and discussion

3.1. Microstructure characterizations

The SEM images of graphite and graphene are displayed in Fig. 2. The graphite sample has thick and lamellar morphology while the graphene sample shows an irregular shape with cross-linked nanosheets.

Since the intercalation/de-intercalation of Li ions is strongly affected by pore size distribution [30–32], we compared the pore size distributions of graphite and GNSs (Fig. 3). There is significant difference between those two curves. GNSs present a unimodal