



# Composite of mesocarbon microbeads/hard carbon as anode material for lithium ion capacitor with high electrochemical performance



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## ABSTRACT

Lithium-ion capacitor (LIC) is fabricated using activated carbon (AC) as the positive electrode and a mixture of mesocarbon microbeads (MCMB) and hard carbon (HC) as the negative electrode (denoted as MH). The structure characterization of carbon materials are investigated by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and nitrogen adsorption apparatus. The electrochemical performances of LIC with different HC content are characterized by the charge–discharge measurements of three-electrode cell, electrochemical impedance tests and cycle performance testing. The addition of HC material greatly affects the charge–discharge process and behavior, which impacts on the comprehensive electrochemical performance of LIC. The power density and cycle stability of LIC are improved with little sacrifice of energy density. LIC with 30 wt.% HC was found to have the optimal electrochemical performance, high energy density up to 89.3 Wh kg<sup>-1</sup> and power density as high as 7.1 kW kg<sup>-1</sup> (based on active material mass of two electrodes), excellent capacity retention of 93.9% after 5000 cycles at 10 C rate. The power density and cycle performance of LIC can be further improved by increasing the HC content. The present work indicates such electrodes as promising candidates for the realization of LIC with high energy density, high power density and long cycle life.

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## 1. Introduction

Electrochemical double-layer capacitor (EDLC) and lithium-ion battery (LIB) are two important types of electrochemical energy storage devices that can be used in wind-generated electrical power storage systems, electric vehicles and hybrid electric vehicles. Lithium ion battery (LIB) is usually assembled with Li-intercalation compounds cathode (LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFePO<sub>4</sub>, etc.), carbonaceous anode (graphite, hard carbon, etc.) and lithium-based organic electrolyte as electrolyte [1–4]. EDLC contains two symmetrical high surface area activated carbon porous electrodes in contact with ammonium salts electrolyte, and stores the energy in the double layer formed at the activated carbon electrode and electrolyte interface [5–7]. However, both LIB and EDLC have limitations that hinder their way of popularization. LIB has limited power density although it shows relatively high working voltage and energy density. Compared with LIB, EDLC displays high power density, high cycle performance but relatively low energy density. Therefore, considerable attention has been focused on how to

develop an electrochemical energy storage device, which combines the advantages of the LIB and EDLC.

Recently, lithium ion capacitor (LIC) has been proposed as an advanced capacitor [8–15]. LIC consists of a lithium-doped carbon negative electrode, an activated carbon (AC) positive electrode and an organic electrolyte containing lithium salt. Namely, the LIC is the combination of lithium ion battery anode material and electrochemical capacitor cathode material. Due to this combination, LIC demonstrates better power density than LIB and higher energy density than EDLC, as well being capable of long cycle life [16–18].

Although many material combinations are possible for the realization of LIC, the use of activated carbon positive electrode together with lithium intercalation negative electrode appears the most convenient till now [19–21]. Currently, graphite is the most commonly used negative electrode material in LIB due to its high theoretical capacity, low and stable charge–discharge platform, natural abundance and relatively low cost, which also has certain research in LIC. Sivakkumar researched the effect of ball-milling on the rate and cycle life performance of graphite negative electrode and compared the rate capability of different type graphite materials as negative electrode in LIC [22,23]. Khomenko et al. introduced a LIC using activated carbon as cathode and graphite as anode, the as-assembled LIC exhibited high energy density and cycle stability in the voltage range of 1.5–4.5 V [24]. The effect

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of the ways and degrees of pre-lithiation of the graphite negative on the LIC's electrochemical performance has also been investigated [25,26]. Their research work proved that the pre-lithiation of graphite anode had important influence on the electrochemical performance of LIC.

In LIC assembling with graphite anode and activated carbon cathode in organic  $\text{Li}^+$  electrolyte, anion adsorption/desorption occurs on the surface of activated carbon positive electrode, whereas, lithium ion intercalation/de-intercalation occurs within the bulk of the graphite negative electrode during the charge-discharge process. Compared with the lithium ion intercalation/de-intercalation process at the graphite electrode, the reaction rate of AC positive electrode with a non-Faradaic process is relatively fast. Therefore, the power performance of LIC is determined by the rate capability of the negative electrode [9,22]. The slower diffusion kinetics of lithium ion in the graphite structure directly affected the power capability of LIC. In addition, the lithium ion intercalation/de-intercalation will lead to the expansion and contraction of graphite layer, which likely gives rise to the collapse and destruction of graphite structure during the cycle process at high current density, causing capacity attenuation of the LIC.

Considering that LIC is preferred to use as a power device, so the LIC should show high power density and excellent cycle performance at high current density. Although graphite as negative electrode material is widely used in commercial LIB and LIC, the power capability is restricted by the diffusion kinetics of lithium ion into the bulk structure. To replace the graphite material with low lithium ion solid phase diffusion rate between the graphite layers, a series of anode materials have been proposed. Among them, hard carbon (HC) becomes attractive due to the feature of rapid kinetics. HC is a kind of carbon materials that is difficult to be graphitized, showing highly irregular and disordered structure. Besides, the space gap between the carbon layers is larger than graphite materials, which is beneficial for the lithium ion intercalation/de-intercalation [27–29]. As a result, it is considered that HC is suitable for the high power devices. Recently, Kim et al. proved that LIC with HC anode showed higher power density and cycle stability at large charge-discharge rate in comparison with the LIC using graphite as negative electrode [9]. The LIC also exhibited excellent cycle life performance of about 83% retention at 10 C rate after 10,000 cycles. Cao et al. assembled the LIC pouch cell with activated carbon cathode and hard carbon/lithium stabilized metal powder anode, and it delivered over 50% of the maximum stored energy at a discharge rate over 100 C rate [30]. The LIC punch cell still has 80% of the initial capacitance after 10,000 cycles.

Previously, we have reported a LIC with activated carbon cathode and graphitized mesocarbon microbeads anode, showing good energy density, power density and cycle stability [25]. In consideration of the structure characteristic and the feature of rapid kinetics of hard carbon, in this work, we proposed a novel LIC structure using an activated carbon positive electrode and a composite negative electrode (MCMB + HC) to improve the LIC's power density and cycle performance at high charge-discharge rate, and undertake a more detailed evaluation of the electrochemical performance of LIC with different hard carbon contents.

## 2. Experimental

### 2.1. Materials structure characterization

The positive electrode commercial activated carbon (AC, Kuraray Co. Ltd, Japan), negative electrode graphitized mesocarbon microbeads (MCMB, BTR New Energy Material Co. Ltd, China) and hard carbon (HC, Kureha Corp., Japan) were obtained directly from suppliers and used as received. Field-emission scanning electron

microscopy (FE-SEM) (Hitachi-S4800) was used to observe the morphological characterizations of the carbon materials. The crystal structure of the negative electrode material was analyzed by X-ray diffraction (XRD, D/MAX-2500) with  $\text{Cu K}\alpha$  radiation (40 kV, 100 mA,  $\lambda = 0.154056$  nm). The specific surface area and pore size distribution was measured with an Autosorb-iQ adsorption analyzer (Quantachrome).

### 2.2. The preparation of positive and negative electrode

The positive electrode was made with mixture of activated carbon (AC), conductive carbon black (CB) and polytetrafluoroethylene (PTFE) at a ratio of 85:7:8 and then pressed with roller press to control the thickness. The aluminum foil with conducting resin was used as current collector. The negative electrode was prepared by coating a mixture of composite active material (MCMB/HC), conductive carbon black (CB) and polyvinylidene fluoride (PVDF) dispersed in *N*-methylpyrrolidone (NMP) with a mass ratio of 89:3:8, and the copper foil was used as current collector. The positive and negative electrode were cut into a disk of 13 mm diameter and dried at 120 °C for 12 h in a vacuum oven. The HC content in composite active material was 0, 30, 50, 70 and 100 wt.%, respectively. Based on the content of HC, the composite negative electrode was signed as MH-0, MH-30, MH-50, MH-70, MH-100, the corresponding LICs were denoted as LIC-0, LIC-30, LIC-50, LIC-70, LIC-100.

### 2.3. Cell fabrication and electrochemical testing

The half cell performance of mesocarbon microbeads/hard carbon composite electrode (denoted as MH) was evaluated using lithium metal as counter electrode. Pre-lithiation process of MH composite electrode was carried out by galvanostatic charging in coin cell which assembled with MH working electrode and lithium countering electrode. Two-electrode LIC was assembled to evaluate the energy density, power density and cycle life. Three-electrode LIC was charged and discharged from 2.0 to 3.8 V, where the potentials of positive and negative electrode vs.  $\text{Li}/\text{Li}^+$  reference electrode were monitored to study the charge-discharge process and the variation of potential both the positive electrode and negative electrode. The mass ratio of positive to negative electrode was kept at 1. A microporous membrane (Celgard 2400, Celgard Company, USA) was used as the separator, and the electrolyte was  $1.2 \text{ mol L}^{-1}$   $\text{LiPF}_6$  in 1:1 EC/DEC (ethylene carbonate/diethyl carbonate). The charge-discharge tests for two-electrode LIC and three-electrode LIC were carried out using the battery test system (LAND CT2001, China and Arbin BT2000, USA). The cyclic voltammetry and electrochemical impedance spectra were recorded on an electrochemical workstation (Autolab PGSTAT128N, Switzerland). All cells were assembled in an Argon-filled glove box with oxygen and water contents lower than 1 ppm. The energy and power density were calculated per active materials mass of two electrodes. All potentials in this paper were presented vs.  $\text{Li}/\text{Li}^+$ , and the electrochemical tests were operated at room temperature.

## 3. Results and discussion

The structural characterization of AC, MCMB and HC materials are shown in Fig. 1. It is observed that the AC particles show irregular morphology, with some macropores dispersed on the surface of particles. The average size of the particles is about 10  $\mu\text{m}$ , interspersed with some 3–5  $\mu\text{m}$  ultra-fine powder. The BET specific surface area of AC is  $1604 \text{ m}^2 \text{ g}^{-1}$  and the micropore specific surface area is  $1360 \text{ m}^2 \text{ g}^{-1}$ . The FE-SEM image of MCMB shows that the particles are evenly distributed with a size of approximate 10  $\mu\text{m}$ .

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