Journal of Power Sources 282 (2015) 394–400

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Micro Li-ion capacitor with activated carbon/graphite configuration for energy storage

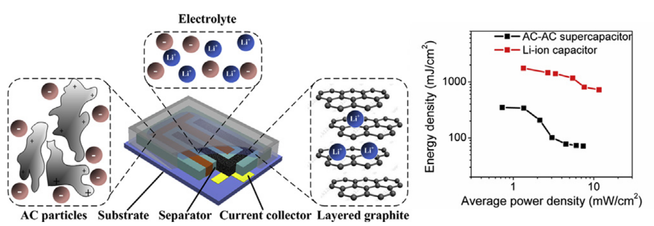
Siwei Li [a], Xiaohong Wang [a, b, *]

[a] Tsinghua National Laboratory for Information Science and Technology, Institute of Microelectronics, Tsinghua University, Beijing, PR China
[b] State Key Laboratories of Transducer Technology, Chinese Academy of Sciences, PR China

HIGHLIGHTS

- Asymmetric micro Li-ion capacitor with AC/graphite configuration is presented.
- Electrodes in 3D structure contain different materials are designed and constructed.
- Pre-lithiation of graphite electrode improves the performance.
- The device shows higher energy density over symmetric AC supercapacitor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 November 2014
Received in revised form
13 January 2015
Accepted 5 February 2015
Available online 7 February 2015

Keywords:
Micro Li-ion capacitor
Activated carbon
Graphite
Asymmetric configuration
Three-dimensional electrode

ABSTRACT

This paper presents an asymmetric micro Li-ion capacitor which is the integration of a supercapacitor electrode and a Li-ion battery electrode. It exploits the power of supercapacitor and the capacity of Li-ion battery, together with an extended cell potential. Activated carbon (AC) of the supercapacitor material is used to construct the positive electrode, graphite of the anode material in Li-ion battery is adopted in the negative electrode, and an electrolyte used in Li-ion battery, 1 M $LiPF_6$ in organic solvent serves as the electrolyte in the device. The micro three-dimensional (3D) electrodes with separator are fabricated by using micro electro mechanical systems (MEMS) fabrication technology. A pre-lithiation of graphite electrode is then carried out to reduce the electrolyte needed when packaging the prototype and improve its performance. Measurements show that the Li-ion capacitor prototype with 100-μm-thick interdigital electrodes has a capacity of 180 μA h/cm^2 and an energy density of about 1750 mJ/cm^2 at a charge/discharge current of 0.5 mA/cm^2. The energy density is much higher than the symmetric AC supercapacitor at the same size.

1. Introduction

The rapid growth of portable electronic equipment and wireless sensor networks is driving an increasing demand for better power supply systems under various environments and conditions. With the development of low power technologies and miniaturization of sensors, circuits and communication modules in sensor nodes [1], it is a promising way to provide long-term, stable and environment-friendly power supply by building power systems at comparable scale containing harvesters, rechargeable energy storage devices and management components [2]. In such power systems, energy storage devices serve as buffers to collect unstable discontinuous outputs of harvesters and export usable power to other

* Corresponding author. Tsinghua National Laboratory for Information Science and Technology, Institute of Microelectronics, Tsinghua University, Beijing, 100084, PR China.
E-mail address: wxh-ime@tsinghua.edu.cn (X. Wang).

http://dx.doi.org/10.1016/j.jpowsour.2015.02.026
0378-7753/

components. Rechargeable Li-ion batteries and supercapacitors are currently two types of important energy storage devices [3,4].

Li-ion batteries store charge by bulk Faradaic reactions taking place within the cathodes and anodes. The mechanism enables batteries large capacity but hinders their power capability and cycle life. Intensive work focusing on advanced electrode materials with high power and stable structure has improved the performance of Li-ion batteries [5,6], while materials with even higher specific capacity are being developed, such as silicon or alloy [7,8]. Micro batteries for miniaturized systems are fabricated by either scaling down from layer-by-layer macro scale ones, or building three-dimensional (3D) structure to ensure the loading mass of material and high capacity in limited footprint [9]. Currently, though full cells of 3D micro Li-ion battery have been presented [10–12], the majority of work has been still limited in half cells with only cathode or anode fabricated and tested.

Supercapacitors utilize electric double layer (EDL) capacitance and/or pseudocapacitance at the interface of electrode/electrolyte [13]. They are featured by high power density, long cycle life and high charge/discharge efficiency, but suffer low energy density due to limited capacity and generally low cell potential. Supercapacitors complement batteries to afford peak power and frequently charge/discharge. Work on advanced electrode materials of supercapacitors has been focusing on increasing the specific capacitance mainly by nanomaterials with high specific surface area and/or pseudocapacitance [14,15]. 3D electrode architecture has also been proposed in micro supercapacitors to load more electrode material. Most of the micro supercapacitor prototypes applied symmetric configuration and store energy with identical principle in two electrodes. Though developed with various types of materials including carbon with EDL capacitance [16–21], conducting polymer films with pseudocapacitance covered on 3D electrode architecture [22,23], and composite electrode materials incorporating the synergistic effect of both types [24], the energy density of the micro supercapacitors is still not satisfying.

Asymmetric design with different types of electrodes in one cell takes advantages from various mechanisms. EDL and pseudocapacitance electrodes are combined in aqueous electrolyte as the asymmetric supercapacitor. The pseudocapacitance electrode provides higher capacitance than the EDL one, and the cell potential can be expended to 1.5–2.0 V by utilizing respective potential ranges of two types of electrode materials [25–27]. Beyond supercapacitors, battery electrodes have also been introduced in the asymmetric cells [28,29]. The Li-ion capacitor is a hybrid cell showing capacitive behavior, with EDL material in positive electrode and anode material of Li-ion battery in negative electrode [29]. The anode of battery provides even higher capacity than supercapacitor electrode and produces wider cell potential, results in increased energy density. Developed negative electrode materials in Li-ion capacitors include titanium-based compounds as $Li_4Ti_5O_{12}$ (LTO) [29,30] and TiO_2 [31,32], as well as carbonaceous materials represented by hard carbon [33] and graphite [34]. The positive electrode materials are dominated by porous carbons and the most common one is activated carbon (AC) [29–36]. Recently, graphene-based materials become alternatives with the advanced properties in both specific capacitance and power capability [37–40]. Micro asymmetric supercapacitor with manganese dioxide (MnO_2)/AC configuration has been reported [41]. Though provides advanced performance over symmetric one, the asymmetric supercapacitor is still limited in energy density.

In this work, a micro Li-ion capacitor is designed and demonstrated with the AC/graphite configuration for higher energy density [42]. The prototype contains supported 3D interdigital electrodes fabricated with the assistant of micro-fabrication technology. Pre-lithiation of the graphite electrode is adopted to reduce the electrolyte used and improve the performance of the prototype. The prototype is then encapsulated and characterized with galvanostatic charge/discharge. Compared with symmetric AC supercapacitor at similar dimensions, higher energy density with moderate power is achieved.

2. Design and materials

The diagram of the proposed micro Li-ion capacitor is illustrated in Fig. 1. A pair of 3D interdigital electrodes consisting of EDL material in the positive one and anode material of Li-ion battery in the negative one are separated and supported by an insulated serpentine high separator layer. The structure allows thick electrodes with high loading mass of active material. Commonly used EDL materials are diverse porous carbons. The intensively studied and commercialized AC serves as the positive electrode material in the work taking the relative high specific capacitance and facile fabrication into account. While titanium-based compounds generally show better cycle stability compared with graphite as anode material of Li-ion battery, the later one has higher capacity and lower Li^+ intercalation/deintercalation potential, capable of providing higher energy density. Therefore, graphite is taken as negative electrode material in the micro Li-ion capacitor cell. The electrodes are immersed in the ionic electrolyte of Li-ion battery, 1 M $LiPF_6$ in 1:1 (w:w) ethylene carbonate (EC)/dimethyl carbonate (DMC) solvent to form the asymmetric cell.

The capacities of electrode materials were examined with galvanostatic charge/discharge at different current densities in a two-electrode configuration with Al foil carried material as working electrode, a Li foil as counter and reference electrode, immersed in the electrolyte to form a button-type cell. Both AC and graphite were mixed with acetylene black (AB) as conductive agent and carboxymethylcellulose (CMC) as polymer binder to form composites with the same mass ratio of 87:10:3, respectively. The composites were dispersed in water as slurries that were then pasted on the Al foils, followed by drying to prepare the working electrodes. The discharge curves of AC- and graphite-based composites are shown in Fig. 2(a) and (b), and the applied current density ranges from 100 mA/g to 500 mA/g (normalized by the total weight of the each composite). The potential range of AC as shown in Fig. 2(a) is 2.3–4.3 V vs. Li/Li^+, and the range of graphite is 0.1–1.5 V vs. Li/Li^+ with a Li^+ intercalation/deintercalation plateau at around 0.4–0.5 V vs. Li/Li^+ in Fig. 2(b).

The calculated specific capacities of AC and graphite are summarized in Fig. 2(c). The different trends indicate the properties of two materials: at low current density of 100 mA/g, the capacity of graphite, 249.9 mA h/g is about 4.3 times of AC, 57.6 mA h/g (in the situation, the charge/discharge rate of graphite is lower than 1 C).

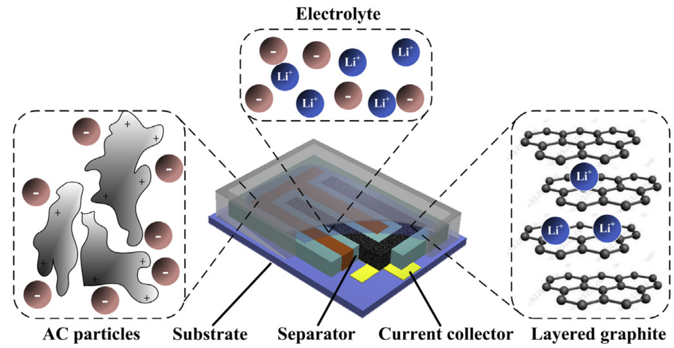


Fig. 1. Schematic of the on-chip prototype with AC/graphite configuration and interdigital 3D electrode structure supported by the separator.