Electrochimica Acta 187 (2016) 134–142

Contents lists available at ScienceDirect

Electrochimica Acta

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

Different types of pre-lithiated hard carbon as negative electrode material for lithium-ion capacitors

Jin Zhang[a], Xifeng Liu[b], Jing Wang[a], Jingli Shi[a], Zhiqiang Shi[a,*]

[a] Laboratory of Fiber modification and Functional Fiber, College of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China
[b] China Blue Chemical Ltd., Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 16 September 2015
Received in revised form 5 November 2015
Accepted 9 November 2015
Available online 12 November 2015

Keywords:
Lithium-ion capacitors
Hard carbon
Pre-lithiation
Plateau
Potential range

ABSTRACT

Lithium-ion capacitors (LICs) are assembled with activated carbon (AC) cathode and pre-lithiated hard carbon (HC) anode. Two kinds of HC materials with different physical and electrochemical behaviors have been investigated as the negative electrodes for LIC. Compared with spherical HC, the irregular HC shows a distinct lithium ion intercalation plateau in the charge–discharge process. The existence of lithium ion intercalation plateau for irregular HC greatly affects the electrochemical behavior of HC negative electrode and AC positive electrode. The effect of working potential range on the electrochemical performance of LIC-SH and LIC-IH is investigated by the galvanostatic charging–discharging, electrochemical impedance tests and cycle performance testing. The charge–discharge potential range of the irregular HC negative electrode is lower than the spherical HC electrode due to the existence of lithium ion intercalation plateau, which is conducive to the sufficient utilization of the AC positive electrode. The working potential range of LIC should be controlled to realize the optimization of electrochemical performance of LIC. LIC-IH at the working potential range of 2.0-4.0 V exhibits the optimal electrochemical performance, high energy density up to 85.7 Wh kg^{-1} and power density as high as 7.6 kW kg^{-1} (based on active material mass of two electrodes), excellent capacity retention about 96.0% after 5000 cycles.

1. Introduction

In the recent past, research focus is directed towards the development of advanced electrochemical devices which can display high energy and power density as well as high cycling stability at the same time. The conventional electrochemical double-layer capacitor (EDLC) contains two symmetrical activated carbon electrodes with high surface area, which stores the energy in the double layer formed at the activated carbon porous electrode and electrolyte interface [1–4]. EDLC possesses high power density and superior cycle performance, however, the limited energy density restricts its application in many fields including electric vehicles (EVs), hybrid electric vehicles (HEVs) and other large-scale energy storage systems. Compared with EDLC, lithium ion battery (LIB) displays relatively high energy density, but it can't satisfy the need of high power capability and long cycle life [5–8]. In general, EDLC and LIB can't independently meet the requirement of such advanced electrochemical storage devices. Therefore, lithium ion capacitor (LIC) combining the lithium ion battery electrode and electrochemical double-layer capacitor electrode has emerged as one of the most promising alternatives [9–19].

Generally, LIC contains an EDLC cathode material, a pre-lithiated LIB anode material and an organic electrolyte containing lithium salt. Due to this combination, LIC displays a higher power density and longer cycle life than lithium ion batteries and a higher energy density than EDLC. Some factors will affect the electrochemical performance of LIC, such as the pre-lithiation process of anode, types of active materials of cathode and anode, the safe operational limit of the conventional electrolytes and configuration of the electrodes [20]. The pre-lithiation process has important influence on the electrochemical performance of LIC. The pre-lithiation can improve the working potential, energy density and cycle stability, reduce the irreversible capacity loss and electrode resistance. Therefore, some researches about the pre-lithiation of anode have been reported [21,22].

In a LIC, during the charge–discharge process, the positive electrode undergoes anion adsorption/desorption on the activated carbon material with high surface area, whereas, lithium ion intercalation/de-intercalation occurs within the bulk of the negative electrode. The intercalation/de-intercalation reaction of lithium ion at the negative electrode is much slower than the

* Corresponding author. Tel.: +86 22 83955816; fax: +86 22 83955055
E-mail address: shizhiqiang@tjpu.edu.cn (Z. Shi).

http://dx.doi.org/10.1016/j.electacta.2015.11.055
0013-4686/

adsorption/desorption reaction on the surface of the positive electrode, so the power performance of LIC is determined by the negative electrode [23,24]. To date, graphite is widely used in commercial LIB and LIC due to its high theoretical capacity (372 mAh g^{-1}), low and stable charge–discharge platform, natural abundance and relatively low cost. However, the low lithium ion solid phase diffusion rate at the graphite layer restricts its application as a power device. Hard carbon (HC) is an attractive material for the features of rapid kinetics and larger space gap between the carbon layers than graphite [25]. These advantages of HC are beneficial for the lithium ion intercalation/de-intercalation, which is particularly desirable for power sources. Recently, Kim et al. proved that LIC with HC anode showed higher power density and cycle stability in comparison with the LIC using graphite as negative electrode [26]. The LIC also exhibited the excellent cycle performance of about 83% retention at 10C rate after 10,000 cycles. Sun et al. fabricated LIC with a HC anode and a bifunctional cathode containing capacitor material and battery material [27]. The LIC with 25 wt.% battery material addition in bifunctional cathode remained more than 98% capacity after 20,000 cycles, and nearly 100% coulombic efficiency over entire cycles. Cao et al. did a series of research works about the LIC assembling with activated carbon cathode and hard carbon/lithium stabilized metal powder anode,

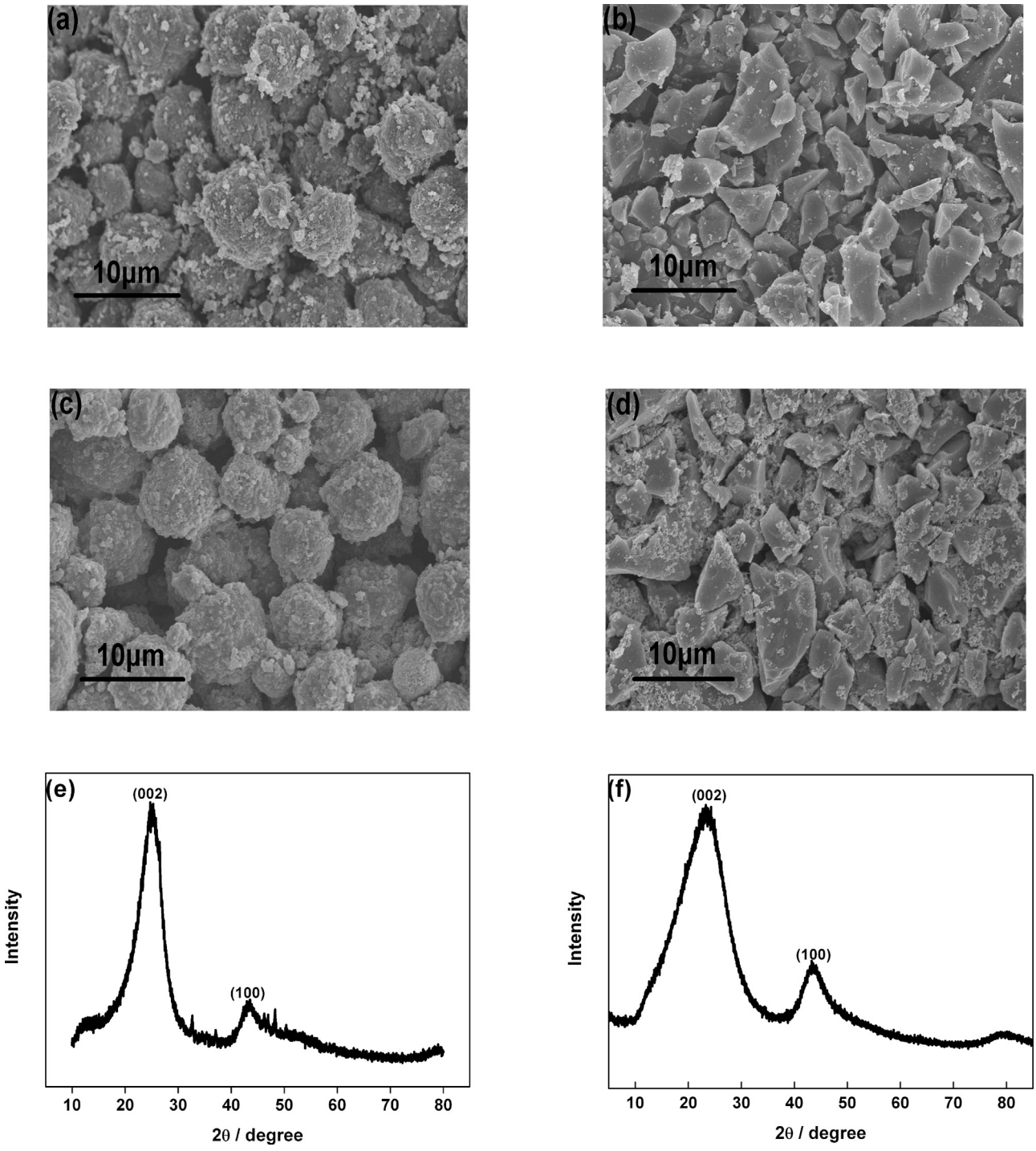

Fig. 1. FE-SEM images of the (a) spherical HC, (b) irregular HC, (c) spherical HC electrode, (d) irregular HC electrode. XRD pattern of the (e) spherical HC, (f) irregular HC.