Journal of Power Sources 270 (2014) 318–325

Contents lists available at ScienceDirect

Journal of Power Sources

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

High performance lithium-ion hybrid capacitors with pre-lithiated hard carbon anodes and bifunctional cathode electrodes

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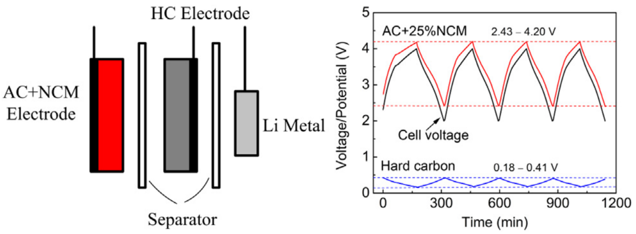
HIGHLIGHTS

- Hard carbon, graphite and mesocarbon microbeads were investigated for Lithium-ion hybrid capacitors.
- A facile approach to achieve the pre-lithiation of carbonaceous anode was developed.
- Electrode potentials of hybrid capacitors were monitored during the galvanostatic charge–discharge processes.
- Hybrid capacitor shows high energy density, high power density and superior cycleability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form
26 June 2014
Accepted 22 July 2014
Available online 30 July 2014

Keywords:
Lithium ion hybrid capacitor
Pre-lithiation
Hard carbon
Activated carbon

ABSTRACT

Lithium-ion hybrid capacitor is a type of energy storage device that bridge the gap between lithium-ion battery and electrical double layer capacitor. We have developed a facile approach to achieve the pre-lithiation of carbonaceous anode, and then fabricated lithium-ion hybrid capacitors with bifunctional cathode containing capacitor material (activated carbon) and battery material ($LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$). The hybrid capacitor with 25 wt.% $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ addition in bifunctional cathode (denoted as LAN25) exhibits excellent rate capability and high energy density. The rate capability of LAN25 is comparable to that with pure AC cathode (denoted as LAC), while the volumetric energy density is 1.36 times higher than the latter one. The continuous galvanostatic charge–discharge cycling tests reveal that the lithium-ion hybrid capacitor remains more than 98% capacity after 20,000 cycles, and nearly 100% coulombic efficiency over entire cycles. The superior performance is ascribed to the synergy effect of the active components in bifunctional cathode and the effective pre-lithiation of hard carbon anode. The present work makes the study of lithium-ion hybrid capacitor easily accessible and broadens roads to hybrid devices with high energy density, high power density and long cycle life.

1. Introduction

Lithium-ion battery (LIB) and electrochemical capacitor (EC) are two important types of electrochemical energy storage devices that can be used in hybrid renewable energy power generation/energy storage systems, electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1]. LIB displays relatively high energy density but limited power density and cycle life. EC possesses high power capability and superior cycleability, however, the specific energy is much lower than that of LIB [2,3]. The internal hybrid systems can be designed to combine the advantages of both LIB and EC by the synergetic hybridization of the battery and capacitor components [4].

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http://dx.doi.org/10.1016/j.jpowsour.2014.07.146

The internal serial/parallel hybridization approaches can be achieved employing the lithium-ion intercalation materials and the electrical double layer capacitive materials within one device [5]. Generally, these kinds of hybridizations are called lithium-ion capacitors or lithium-ion hybrid capacitors (LICs). Amatucci and Du Pasquier et al. [6,7] firstly reported the internal serial hybridization system using activated carbon (AC) as capacitive component (cathode), and $Li_4Ti_5O_{12}$, graphite, or WO_2 as battery component (anode). After that, carbonaceous materials for LICs, e.g., graphite [8–10], soft carbon [11,12], hard carbon [13], graphene nanosheets [14], carbon nanofiber [15], amorphous carbon [16], and the internal serial hybridization systems [17–22] were extensively investigated and even successfully commercialized by some Japanese companies including JM Energy, FDK, ACT, etc. On the other side, the internal parallel hybridization system within one device can be prepared by using at least one bifunctional electrode including both capacitive material and lithium-ion intercalation material, e.g., ($LiCoO_2$-AC)/$Li_4Ti_5O_{12}$ [3], ($LiFePO_4$-AC)/$Li_4Ti_5O_{12}$ [23–25], ($LiMn_2O_4$-AC)/$Li_4Ti_5O_{12}$ [26], and ($LiMn_2O_4$-AC)/($Li_4Ti_5O_{12}$-AC) [5,27,28].

In our previous work [29], the internal hybrid energy storage devices have been prepared by employing (AC + $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM)) bifunctional electrode as cathode and graphite electrode as anode. The hybrid device with a (25 wt.% AC+75 wt.% NCM) cathode possesses a specific energy 5.7 times higher than that of electrical double layer capacitor (EDLC) with nonaqueous electrolyte of tetraethyl ammonium tetrafluoroborate (Et_4NBF_4) in acetonitrile (AN). At the same time, the hybrid device delivers 62.6% and 42.1% of its maximum capacity at the rate of 30C and 50C, respectively. Besides, it shows stable capacity retention and high coulombic efficiency over 2000 electrochemical cycles. However, it is found that the experimental specific capacities of the composite cathodes are much smaller than the theoretical capacities. From the CV curves of the (AC + NCM)/graphite hybrid devices, no obvious peaks corresponding to the sequential phase transition processes ($Ni^{2+} \leftrightarrow Ni^{3+} \leftrightarrow Ni^{4+}$) appear when the relative amount of NCM in the total active materials is not larger than 0.5, i.e., $r = m_{NCM}/(m_{AC} + m_{NCM}) \leq 0.5$. It implies that most of Li ions deintercalated from NCM in the initial charge process did not insert back. These Li ions were consumed when the solid electrolyte interphase (SEI) films formed on graphite electrode surface [30,31]. The competing relationship exists between the ionic adsorption of electrical double layer contributed by AC and the faradaic electrochemical process (redox reaction) caused by Li ion intercalation in composite cathode. In general, the surface adsorption/desorption process is much faster than the Li ion intercalation/de-intercalation reaction, thus the faradaic process is suppressed. In the subsequent charge–discharge cycles, the cathode cannot be fully discharged, leading to the low capacity and low energy density. Therefore, it is necessary to pre-dope Li ions into carbonaceous anode to reduce the irreversible capacity loss.

Generally, the pre-lithiation of carbon anode is carried out using the following methods [16,32]: (1) the lithium foil and the carbon electrode are separated by a separator in a Li-to-carbon arrangement, and then the cell is externally shorted or electrochemically discharged; (2) the carbon electrode directly contacts with the lithium foil in electrolyte without electronic charger or external electric circuit; (3) the special aluminum/copper foils with through holes are employed as current collectors of cathode and anode, a lithium foil is used as a lithium source. This configuration allows Li ions to transport through the holes of current collector. For the former two methods, the cells would be disassembled after the lithiation process completed, and the full cell with cathode and lithiated anode is rearranged in an operating configuration. By the latter method, the rearrangement step can be eliminated. Furthermore, in this work, we found that the carbon electrode could be well lithiated by using ordinary Al/Cu foils instead of expensive through-hole Al/Cu foils.

To date, graphite is the most widely used anode material in commercial LIBs and LICs due to its low negative redox potential (~0.1 V vs. Li^+/Li), high theoretical capacity (372 mAh g^{-1} for LiC_6 stoichiometry) and relatively low cost. However, the power capabilities of devices are restricted by the poor charge rate (Li ion intercalation) capability of graphite electrode due to the limitations of Li ion diffusion into the bulk structure [10]. In addition, the potential plateau of graphite anode electrode is so close to the potential of metal lithium plating, which increases the risk of lithium dendrites formation and growth on the surface of anode at high charge current, causing the internal short-circuits failure of a cell.

In the present work, we proposed a novel LIC structure using a hard carbon anode and a bifunctional cathode (AC + NCM). The hybrid capacitor can be regarded as an internal parallel combination of one LIC (AC/hard carbon) and one LIB (NCM/hard carbon). In order to pre-dope lithium ions into the anode electrode and monitor the potential changes of cathode and anode electrodes, a three-electrode cell with flexible package was introduced, in which a metal lithium foil was used as both a lithium source and a reference electrode. On this basis, the electrochemical performances of the hybrid capacitors were studied.

2. Experimental

$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ powders (NCM) were provided by Hebei Strong-Power Li-ion Battery Technology Corporation, China. AC powders (YP50F) was purchased from Kuraray Chemicals, Japan. Hard carbon (HC) was purchased from ATEC, Japan. The electrolyte is 1 M lithium hexafluorophate ($LiPF_6$) in the mixture solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) in a volume ratio of 1:1:1, provided by Beijing Institute of Chemical Research, China. The separator is 25-μm-thick Celgard 2400 (Celgard company, USA). All the chemicals were used as received without any further treatment.

All the electrodes were prepared by a doctor-blade casting process. The composite electrodes consist of 80 wt.% active materials (AC and NCM), 10 wt.% Super C45, 2 wt.% KS-6, and 8 wt.% poly(vinylidene fluoride) (PVdF). The graphite electrode contains 90 wt.% HC, 5 wt.% Super C45, 2 wt.% styrene-butadiene rubber (CMC), and 3 wt.% styrene-butadiene rubber (SBR). The current collectors for cathode and anode electrodes are 20-μm-thick aluminum foil and 12-μm-thick copper foil, respectively. The electrodes were dried thoroughly and punched into suitable sizes: 13-mm-diameter circular discs for CR2032 coin cells, and 35 mm × 40 mm squares for three-electrode full cells.

The schematic structure of a three-electrode pouch cell is depicted in Fig. 1. The cell was prepared according to the following steps: firstly, cathode electrode, separator and anode electrode were stacked together with a sandwich structure (cathode–separator–anode), which was then inserted into an aluminum-plastic bag by following an overnight drying process under heating and vacuum. After excess electrolyte was added in a glove box (MBRAUN, $H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm), a lithium foil was placed near the anode, separated by a separator. Finally, the flexible aluminum-plastic package was heat-sealed. The lithium pre-doping was accomplished by electrochemical discharge process (lithium intercalation) of HC anode using the lithium metal foil as counter electrode. The current density for pre-lithiation is 6 mA g^{-1}, and the discharge specific capacity is about 120 mAh g^{-1} (based on HC mass). The typical voltage profile of pre-lithiation process for HC anode is depicted in Fig. 2.