Journal of Power Sources 393 (2018) 145–151

Contents lists available at ScienceDirect

Journal of Power Sources

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

Mesocarbon microbead based dual-carbon batteries towards low cost energy storage devices

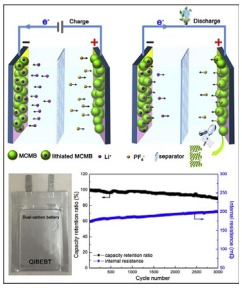
Pengxian Han[a,1], Xiaoqi Han[a,1], Jianhua Yao[a], Liping Yue[a], Jingwen Zhao[a], Xinhong Zhou[b], Guanglei Cui[a,*]

[a] Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China
[b] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China

HIGHLIGHTS

- A dual-carbon battery is developed with MCMB cathode and pre-lithiated MCMB anode.
- The PF_6^- can reversibly intercalate into MCMB in 1 M $LiPF_6$-EMC/SL electrolyte.
- An energy density of 47.9 Wh kg^{-1} at 583.6 W kg^{-1} was delivered.
- The dual-carbon battery retains 88.5% after 3000 cycles at a rate of 5 C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Dual-carbon
Mesocarbon microbead
Lithium ion battery
Pre-lithiation

ABSTRACT

Recently, the low cost energy devices with high energy density and high power density are becoming more and more important in the field of electric vehicles. In this work, the electrochemical intercalation/deintercalation behaviors of PF_6^- into graphitic mesocarbon microbead (MCMB) cathode are investigated in the electrolyte of 1 M $LiPF_6$ in the mixed solvent of ethylmethyl carbonate and sulfolane. The charge storage mechanisms related to surface-limited capacitive and diffusion-controlled intercalation capacity are also studied by cyclic voltammetry measurements, which indicates that both the intercalation reaction and the capacitive reaction contribute to the overall capacity. Furthermore, dual-carbon batteries comprising MCMB cathode and pre-lithiated MCMB anode are unprecedentedly demonstrated in the form of aluminum pouch cells with laminated structure and exhibit an encouraging energy density of 47.9 Wh kg^{-1} at the power density of 583.6 W kg^{-1} based on the overall mass of the battery. Finally, electrochemical impedance spectroscopy is used to differentiate the resistance variation of MCMB cathode and MCMB anode before and after 3000 cycles. The continuous intercalation/deintercalation of PF_6^- into MCMB cathode lead to the exfoliation of the active material and the increase of internal resistance.

1. Introduction

With the development of pure or hybrid electric vehicles, energy storage systems (ESSs) with low cost, energy and power coupling properties, as well as enhanced safety characteristic have become increasingly essential [1–3]. Lithium ion batteries (LIBs) are considered as one of the most promising power sources for EESs. In the past few years, tremendous efforts have been made on high-voltage LIBs (> 5 V)

* Corresponding author.
E-mail address: cuigl@qibebt.ac.cn (G. Cui).
[1] Pengxian Han and Xiaoqi Han contributed equally to this work.

https://doi.org/10.1016/j.jpowsour.2018.05.021
Received 7 January 2018; Received in revised form 28 April 2018; Accepted 5 May 2018
0378-7753/

based on $LiNi_{0.5}Mn_{1.5}O_4$, $LiNiPO_4$ and its element-doped ones [4–11], which exhibit excellent electrochemical performance. However, the tedious preparation process, high cost-effectiveness, and metal dissolution during long cycling become huge obstacles in practical application. Therefore, it is of great urgency to develop new high voltage battery systems to avoid these disadvantages.

Fortunately, the anion-intercalated reaction of graphite-based carbon materials can provide a voltage as high as 5 V *vs.* Li^+/Li, which shows a potential feasibility for high voltage LIBs [12]. Furthermore, it should be noted that graphite-based cathode can avoid the use of rare transition metals and significantly decrease the cost of LIBs. In 1994, Carlin et al. discovered a novel dual-ion battery which operated *via* intercalation/deintercalation of PF_6^- and EMI^+ into graphite electrodes [13]. Subsequently, a great deal of dedication in relation to anion-intercalation reactions was made towards such batteries in ionic liquid system [14–19], where the anodic instability of such batteries working at high voltage in conventional electrolyte solvents was well resolved. However, the high cost of ionic liquids restricted their further application. Recently, Wang et al. systematically studied the intercalation/deintercalaion of different anions, including PF_6^-, BF_4^- and ClO_4^-, into graphite cathode in various solvents [20–22]. They found that graphite anode could reversibly work at > 5.0 V *vs.* Li^+/Li in 1 M $LiPF_6$ dissolved in mixed solvents of sulfolane (SL) and ethylmethyl carbonate (EMC) [23]. To date, most of the studies on dual-ion batteries focused on carbon-based cathodes, lithium [24] or aluminum foil [25,26] based anodes. Their safety issues should be concerned for practical applications. In contrast, the so-called “dual-carbon” or “dual-graphite” systems based on the anion intercalation into the graphite cathode and cation intercalation into the pre-lithiated graphite anode simultaneously during charge may well resolve the safety risks by avoiding the direct application of metal lithium anode [27–29]. Moreover, the pre-lithiated graphite anode can provide a stable potential (~0.1 V *vs.* Li^+/Li) and may also decrease the electrolyte consumption during the long-term cycling at high rate, thus the cycle performance is guaranteed.

Mesocarbon microbead (MCMB) is known to be one of the most important carbonaceous anode materials in LIBs by virtue of its unique spherical profile and their good cycle ability [30]. In this paper, we present MCMB based “dual-carbon battery” using the EMC and SL

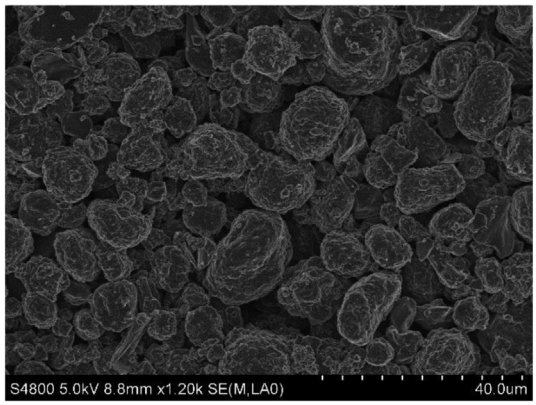


Fig. 2. Typical SEM images of graphitic MCMB.

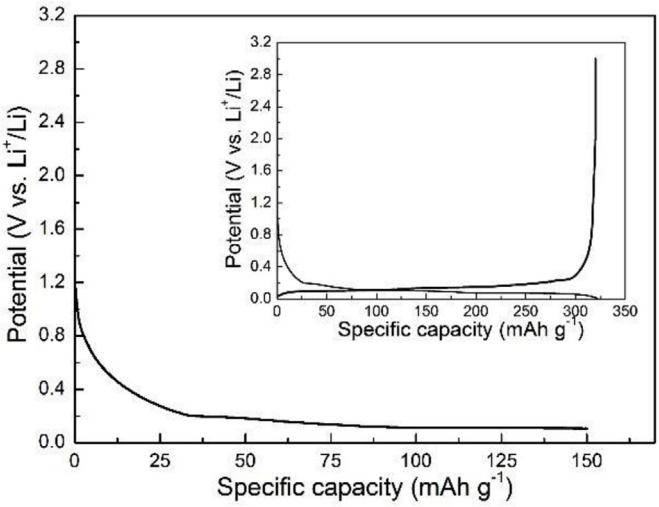


Fig. 3. The pre-lithiation curve of MCMB *vs.* Li half cell at 0.02 C (the inset is the charge/discharge curve of the half cell, 1 C equal to 320 mAh g^{-1}).

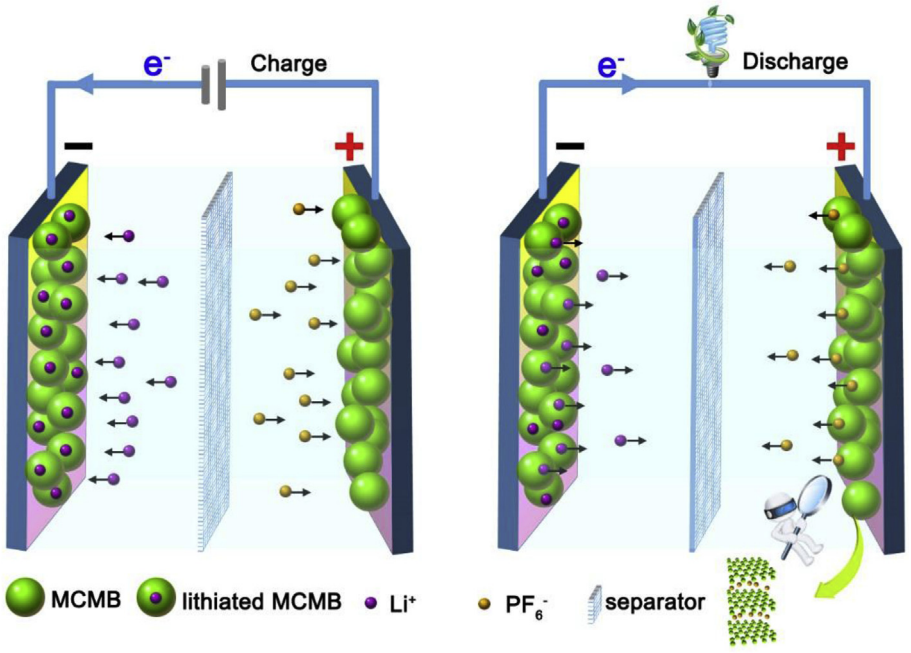


Fig. 1. Schematic illustration of charge/discharge processes of the dual-carbon battery using MCMB cathode and pre-lithiated MCMB anode in $LiPF_6$-EMC/SL electrolyte.