



Nitrogen-doped carbonized polyimide microsphere as a novel anode material for high performance lithium ion capacitors



Xiaoqi Han^{a,1}, Pengxian Han^{b,1}, Jianhua Yao^b, Shu Zhang^b, Xiaoyan Cao^{a,*}, Junwei Xiong^c, Junnan Zhang^d, Guanglei Cui^{b,*}

^a College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

^b Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, 266101 Qingdao, China

^c Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, China

^d Shandong Wina Green Power Technology Co., Ltd, Taiqi New Power Industry Park, 262700 Shouguang, Shandong, China

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ABSTRACT

Lithium ion capacitors (LICs), which bridge the gap between lithium ion battery and electric double layer capacitor, have recently attracted considerable attention. Herein, we first propose the possible utilization of nitrogen-doped carbonized polyimide microsphere (CPIMS) as a novel anode material of LICs. The structures and lithium intercalation properties of CPIMS treated at different temperatures are investigated. It is demonstrated that some of nitrogen atoms are kept in the CPIMS, which is helpful for improving the electrochemical performances. The CPIMS900 (900 is the carbonization temperature) can deliver specific capacities of 328.3 and 48.2 mAh g⁻¹ at 10 mA g⁻¹ and 10 A g⁻¹, respectively. When the pre-lithiated CPIMS900 is coupled with an activated carbon cathode, an energy density of 28.5 Wh kg⁻¹ at 348 W kg⁻¹ is obtained based on the weight of both electrode materials. Even at 6940 W kg⁻¹, the energy density still remains 13.1 Wh kg⁻¹. After 5000 cycles at 500 mA g⁻¹, the capacity retention ratio is as high as 97.1%. The present work offers an opportunity to utilize the CPIMS material in LIC with high energy density, high power density and promising cycle life.

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1. Introduction

The demand for electrochemical devices with relatively high energy and power as well as long calendar life has continuously increased in the last few years [1–4]. Lithium ion capacitors (LICs), as a new class of advanced energy storage devices, have attracted extensive attention, due to its higher power densities compared to lithium ion batteries and higher energy densities compared to conventional electric double layer capacitors (EDLCs) [5–7]. In a typical LIC, a high surface area activated carbon (AC) and a lithium ion intercalation compound such as Li₄Ti₅O₁₂ [8,9], graphite [10–12], soft carbon [13,14], hard carbon [15,16], and graphene [17,18], etc., are usually used as the cathode and anode materials, respectively. Among the numerous anode materials, carbonaceous material is the most popular one by virtue of its low redox reaction potential (~0.1 V vs. Li⁺/Li). Besides, the electrochemical properties of the LIC are mainly determined by the carbon anode [19].

Therefore, it is important to improve the capacity and rate capability of carbon anode to boost the development of LICs.

Many researches have demonstrated that nitrogen-doping is an effective method to improve the electrochemical properties of carbon anode because nitrogen doping could modulate the band structure for a metal-semiconductor transition [20,21]. The well-bonded nitrogen atoms could increase the electronic conductivity, offer extra active sites and enhance the interaction between the carbon structure and lithium [22,23], thus it is effective to improve the capacity and kinetics of lithium storage. Ammonia annealing is an efficient method for nitrogen-doping [24], but ammonia emissions will pollute the environment. Alternatively, carbonizing a carbonaceous precursor under inert atmosphere could insert some nitrogen atoms in carbon material, which enhances its electrochemical properties as well [25,26].

Aromatic polyimides are often employed as carbon precursors in various morphologies, such as graphite membranes, nanoporous carbon membranes, carbon foams, carbon nanofibers and carbon nanoparticles [27–30]. In the imide part of polyimides, there exists abundant of nitrogen atoms. These nitrogen atoms are partially remained after carbonizing at high temperature, which is

* Corresponding authors. Tel.: +86 532 80662746; fax: +86 532 80662744.

E-mail addresses: caoxy@ouc.edu.cn (X. Cao), cuiql@qibebt.ac.cn (G. Cui).

¹ Xiaoqi Han and Pengxian Han contributed equally to this work.

beneficial for the enhancement of lithium storage capacity and related kinetics [31,32]. Furthermore, by solvothermal method, polyimide microsphere (PIMS) in 6~8 μm diameter could be synthesized. The small size PIMS with spherical structure is favorable for fast intercalation/deintercalation of lithium ions. Herein, we explored the carbonized polyimide microsphere (CPIMS) as the anode material of LICs for the first time. Initially, CPIMS was synthesized through solvothermal method followed by carbonization under argon atmosphere. Then the lithium storage behaviors of the negative electrode were deeply investigated. Finally, energy density, power density as well as cycling stability of the CPIMS-based LICs were also evaluated for exploring the advantages over other materials. The present work indicates that CPIMS can be served as a promising candidate for the realization of LIC with high energy density, high power density and promising cycle life.

2. Experimental

2.1. Preparation of PIMS

A solution of 4.0031 g 4,4'-oxydianiline (ODA, Aldrich) and 113.2 g dimethylformamide (DMF, Aldrich) was stirred for 15 min at 80 °C under Argon gas atmosphere. Then 4.2108 g polyvinyl pyrrolidone (PVP, Mw.: 40000) was dissolved in the solution and stirred for another 30 min. After that, 4.3642 g pyromellitic dianhydride (PMDA, Aldrich) was slowly added to vigorously stirred solution, and the mixture was continuously stirred for 5 hrs. Then the mixture was transferred into an autoclave with Teflon lining and heated at 180 °C for 10 hrs. Finally, the precipitate was collected by filtration and washed with water and ethanol. After

drying at 120 °C for 6 hrs in a vacuum, yellow powder was collected.

2.2. Carbonization of PIMS

The PIMS was carbonized at 5 °C min⁻¹ to 350 °C under nitrogen, then 1 °C min⁻¹ to 450 °C, then maintained at 450 °C for 30 min. Subsequently, it was further heated at 1.25 °C min⁻¹ to 550 °C, and maintained at 550 °C for another 30 min. Finally, it was continuously heated at 5 °C min⁻¹ to 900 °C, and carbonized at 900 °C for 60 min. Another two samples were prepared for comparison by carbonization at 700 and 800 °C, respectively. The carbonized PIMS at 700, 800 and 900 °C were denoted as CPIMS700, CPIMS800 and CPIMS900, respectively.

2.3. Fabrication of LIC

The anode slurry was prepared by mixing 80 wt.% CPIMS with 10 wt.% carbon black (Super P) as a conductive agent and 10 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) as a binder. The specific surface area of AC was 1600 m² g⁻¹ (Kurary Chemical Co., Ltd., Japan). The cathode slurry was made by a mixture of AC, Super-P and PVDF at a weight ratio of 82:8:10. The obtained slurries were spread onto the current collectors by a doctor blade technique. The copper foil and aluminum foil were served as the anode current collector and cathode current collector, respectively. The thicknesses of the composite electrode on copper foil and aluminum foil are 75 and 100 μm , respectively. After drying at 60 °C for 30 min, the electrodes were pressed and dried again at 120 °C for 6 hrs under vacuum before assembling the cell.

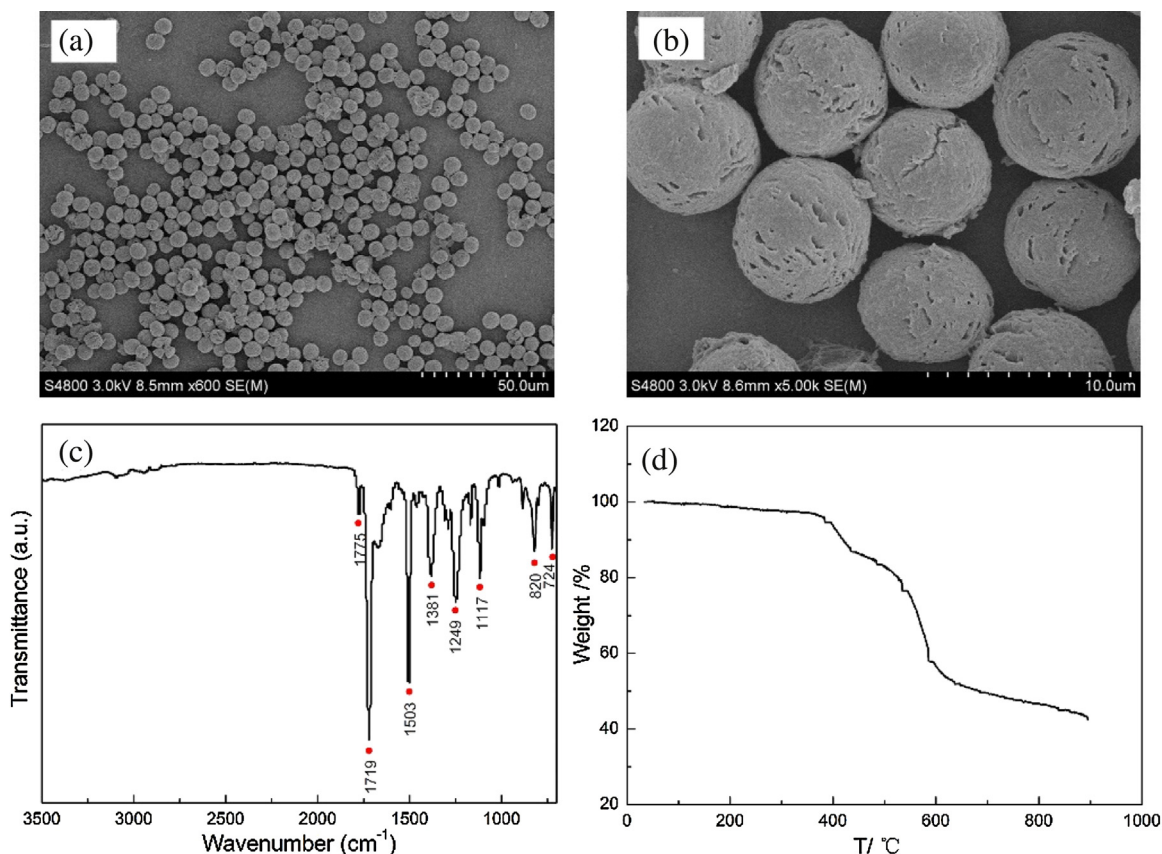


Fig. 1. (a,b) SEM images, (c) FTIR spectrum and (d) TGA curves of PIMS.

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