



High power high safety battery with electrospun $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode with 95% energy efficiency



Chaofeng Liu^{a,1}, Shuhua Wang^{a,1}, Changkun Zhang^a, Haoyu Fu^a, Xihui Nan^a, Ya Yang^{a,*}, Guozhong Cao^{a,b,*}

^a Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, 100083, China

^b Department of Materials Science and Engineering, University of Washington, Seattle, Washington, 98195, USA

ARTICLE INFO

Article history:

Received 16 May 2016

Received in revised form

3 June 2016

Accepted 11 June 2016

Available online 15 June 2016

Keywords:

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$

$\text{Li}_4\text{Ti}_5\text{O}_{12}$

Energy efficiency

High power

Li ion battery

ABSTRACT

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) were chosen as the cathode and the anode to build a full battery owing to their robust structures. Electrospinning method was adopted to control the electrode materials with the expected microstructures - nanowires that shorten solid state diffusion pathway and enhance the surface area for improving their electrochemical performances. LVP cathode and LTO anode can deliver reversible specific capacities of 108 and 149 mAh/g at a rate of 5 C, respectively. No appreciable degradation can be perceived in both electrodes over 500 cycles. In addition, the relatively high voltage of LTO anode ensures the safe rapid charge and discharge (no dendrite growth) and the minimal or no initial loss of lithium ions as there is no formation of SEI layer. A full battery with LVP cathode and LTO anode delivers a maximum power density of 12,046 W/kg, reaching the strength of supercapacitors, while offers a high energy density of 90 Wh/kg at a power density of 1,350 W/kg with a charging or discharge time of 7 min. This battery demonstrates an energy storage efficiency close to 95% at a rate of 2 C and maintains > 90% efficiency at 20 C.

© 2016 Published by Elsevier B.V.

1. Introduction

The great advancements have been taking place in the smart portable electronics that make us contact with each other or share information anywhere at any time. At the same time the popularity of electric vehicles has been stimulating to change the approaches on energy harvest and utilization, especially the combustion of fossil fuels induces the globe warming. Both aspects not only reflect the roaring progress of industrial technologies, but also suggest the increasingly public concerns on environment and health. It goes without saying that power sources play a pivotal role in the operations of these electricity-powered devices, and the higher energy density in power sources are required for increasing the lasting mileage or working time. Currently, rechargeable batteries are the main power sources to drive smart electronics or electric vehicles owing to the high energy density of > 100 Wh/kg in comparison with another energy storage package, supercapacitors, however, the latter delivers a lower energy density of ~10 Wh/kg due to ions sorption/desorption mechanism on the

surface of materials [1,2]. Batteries rely on the redox reaction in electrode materials accompanying with the working ions insertion/ extraction in crystal lattices and charges poured into / dragged out the 3d orbital of cation. Besides, the energy density of batteries is a product of specific capacity and operating voltage, and the specific capacity depends on the number of the reversible working ions and the voltage derives from the difference of electrochemical potentials between cathode and anode [3–5]. Logically, the properties of electrode materials determine the performances of batteries, especially, the cathode materials. Over the past years, great efforts have been devoted to explore reliable materials or modify the properties of the known materials for coping with the increasingly more challenges in energy storage [6–9]. Unfortunately, there is no cathode with both high specific capacity and electrochemical potential in the current material systems [10,11], albeit the exploration and design of new materials are never ceased. Therefore, choosing and improving the known electrode materials with high-rate capability and stable cyclability is an alternative yet effective approach to save time in the charging process, which satisfies the requirements in practical applications before new high energy density and high power density materials are firmly established.

Lithium cobalt oxide (LiCoO_2 , LCO) is widely used as commercial cathode in Li-ion battery because of its high average potential of ~3.7 V and a good specific capacity of ~140 mAh/g [12].

* Corresponding authors at: Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, China.

E-mail addresses: yayang@binn.cas.cn (Y. Yang),

gzciao@u.washington.edu (G. Cao).

¹ Chaofeng Liu and Shuhua Wang equally contribute to this work.

However, the toxic and expensive cobalt sources and unstable structure at high-rate process hinder the sustainable development and utilization for high power devices in the future. Lithium iron phosphate (LiFePO_4 , LFP), also a commercial cathode, renders chemical and thermal stability, while the low ion diffusion coefficient (10^{-14} – 10^{-16} cm^2/s) and electrochemical potential of 3.45 V limit the energy density of batteries [13]. Lithium manganese oxide (LiMn_2O_4 , LMO) presents a high operating potential of 3.8 V, but suffers from the relatively low reversible capacity of 100 mAh/g and the detrimental phase transformation from spinel to cubic [14]. Vanadium pentoxide (V_2O_5) possesses a high theoretical capacity of 443 mAh/g when three Li ions inserted into the crystal lattices, whereas the low working potential and no removable Li ions in pristine lattice restrict the practical applications at current levels [15,16]. Therefore, amongst the known cathodes, monoclinic lithium vanadium phosphate ($\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LVP) is considered as a promising cathode for Li-ion batteries owing to the high average potential of > 4 V, robust crystal structure, excellent thermal and chemical stability and a three dimensional pathways for ion diffusion [17–19]. In particular, the stable crystal structure and multi-dimensionally ionic channels impart it the excellent cycling stability and high-rate capability. However, the poor electrical conductivity of 2.0×10^{-8} S/cm [20] limits the performance on high-rate operation of LVP electrode.

With respect to anode materials, the categories are abundant on the possibility and can be sorted with three varieties through reactive mechanisms: intercalation, alloying and conversion [21,22]. Graphite, an intercalated anode, plays an irreplaceable role in the currently commercial batteries owing to the high reversible capacity of ~ 300 mAh/g, excellent electrical conductivity of > 50 S/cm and low electrochemical potential that expands the operating voltage of full batteries [23–25]. In practice, the low tap density of ~ 1.0 g/cm³ and limited rate capability inhibit the gravimetric energy density in high-rate full batteries [26,27]. Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO), the other intercalation compound, works at a high-rate with stable cyclability owing to zero strain in the charge/discharge process, though the electrochemical potential at 1.5 V reduces the working voltage of a full battery [28]. In the alloying category, silicon and tin attract more interests due to the ultrahigh theoretical capacity, such as 4200 mAh/g in $\text{Li}_{22}\text{Si}_5$. Unfortunately, the huge volume expansion induced the cracks of particles results in a rapid cycling degradation [7]. Among the conversion anodes, oxides, fluorides and nitrides have been studied extensively with a relatively high theoretical capacity (> 600 mAh/g), but the low coulombic efficiency at the initial cycle, inferior electrical conductivity, and the sloping potential profiles make them with an impossible application in Li-ion batteries [29].

By contrasting the strengths and weaknesses between the known cathodes and anodes mentioned above, LVP and LTO are the reliable electrodes for designing and fabricating high-rate Li-ion full battery. However, LVP and LTO also confront with some challenges, such as poor conductivity in LVP and intrinsically high potential for LTO. Thus, modifications or designs are needed to improve or avoid the drawbacks for extending their practical applications. Modifications of a given material can be divided into three aspects: doping, composites and designing microstructures [17]. Doping can tune the atomic environment and electronic structure of the host in virtue of the unique characters of the foreign atoms [3,30]. Composites integrate the strengths of each component to counteract their weakness, and designing microstructures help expose the preferential facets or shorten the pathways for ions and charges transport to improve the kinetics and energetics in electrochemical reactions [17,31]. Electrospinning approach as one of efficient and reliable method is extensively used in the fabrication of nanostructured electrode materials for the application in energy storage owing to its high

feasibility, tunable shape, homogeneous product and mass production with low cost [32–34]. In the present investigation, LVP and LTO with controlled microstructures were fabricated by means of electrospinning followed with pyrolysis and annealing, and the resulting microstructures shorten the pathways for ions transport, at the same time the porous carbon coating on LVP enhance the electrical conductivity of host materials, which renders the electrode a better rate capability. In addition, a full battery was built on these high-rate LVP cathode and LTO anode and displayed an excellent cycling stability at high rate of 5 C over 500 cycles.

2. Experimental section

2.1. Electrospinning $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nanowires

The precursor solution was prepared by dissolving 7 wt% oxalic acid in a mixture solvent contained N,N-Dimethylformamide (DMF) and deionized water with a volume ratio of 25/75, and then NH_4VO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$ and H_3PO_4 were added with a molar ratio of 2:3:3 to form a transparent blue solution after continuously stirred for 2 h at room temperature. Poly(4-vinyl) pyridine (PVP) (Alfa Aesar, $M_w = 1,300,000$) was dissolved into the solution to adjust the viscosity of the precursor solution for guaranteeing the expected nanowires to be obtained. The optimal concentration of PVP in precursor solution was 11 wt%, and the total concentration of NH_4VO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$ and H_3PO_4 was 6.8 wt%. The electrospinning device mainly consists of a high voltage supplier, a plastic syringe with needle of small diameter and a collector. The precursor solution was poured into a 5 mL plastic syringe with a 24-gauge stainless-steel needle, and subsequently electrospun at a constant flow rate of 0.2 mL/h. The applied high voltage and the distance between the injector nozzle and the collector were 14 kV and 18 cm, respectively. The nanowires composite were presintered at 350 °C (5 °C/min) in air for 4 h, and then annealed in argon atmosphere at 700 °C (5 °C/min) with 6 h.

2.2. Electrospinning $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowires

All chemicals from commercial sources were analytical pure grade and used without further purification. First, ethanol (5.0 g), acetylacetone (0.5 g), and acetic acid (1.6 g) were mixed in a glass bottle and stirred for 10 min to form a homogeneous solution. Then, 1.4218 g of tetrabutyl titanate (98% purity) and 0.2298 g of lithium acetate (99.9% purity) were added into the above solution. After stirring for 2 h, 0.55 g of PVP ($M_w = 1,300,000$) was dissolved into the solution. A transparent yellow precursor was formed after followed stirring for 24 h at room temperature. The precursor solution was added into a 10 mL plastic needle tube tipped with a 24-gauge stainless-steel needle at a rate of 0.8 mL/h. The applied high voltage between the injector nozzle and the collector was 15 kV, and the distance was about 7 cm. The nanowires composite were annealed in air atmosphere at 700 °C for 6 h with a heating rate of 5 °C/min.

2.3. Morphology and structure characterizations

The phase composition of samples were investigated on a X'Pert3 diffractometer (PANalytical, Netherlands) with a Cu-K α radiation source ($\lambda = 1.54056$ Å) at a step size of 0.013° and time per step of 50 s. The microstructures were observed via a cold field emission scanning electron microscope (FESEM, HITACHI SU8200, Japan) with an accelerating voltage of 5 kV and a beam current of 10 μA . The lattice image of LVP crystals was observed by means of high resolution transmission microscopy (HRTEM, FEI/Tecnai G2 F20 S-TWIN TMP) with an accelerating voltage of 200 kV. Nitrogen

Download English Version:

<https://daneshyari.com/en/article/1564560>

Download Persian Version:

<https://daneshyari.com/article/1564560>

[Daneshyari.com](https://daneshyari.com)