Electrochimica Acta 170 (2015) 269–275

Contents lists available at ScienceDirect

Electrochimica Acta

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

A new carbon additive compounded $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C cathode for plug-in hybrid electric vehicles

Wenhui Wang [a], Jiaolong Zhang [a], Yue Lin [a], Fei Ding [b], Zhenyu Chen [b], Changsong Dai [a,*]

[a] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China
[b] National Key Laboratory of Power Sources, Tianjin Institute of Power Sources, Tianjin 300381, PR China

ARTICLE INFO

Article history:
Received 16 March 2015
Received in revised form 26 April 2015
Accepted 28 April 2015
Available online 30 April 2015

Keywords:
Lithium vanadium phosphate
performance carbon additives
composite cathode
capacitor
lithium ion battery
Plug-in hybrid electric vehicles

ABSTRACT

The application of lithium ion batteries in plug-in hybrid electric vehicles (PHEVs) requires safety, high energy density, high power density, excellent cyclability and good low temperature performance. On the basis of thermally stable $Li_3V_2(PO_4)_3$/C and cost-effective performance carbon additives, we designed a $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB) (PB stands for performance carbon additives PBX101) cathode that meets the above requirements for PHEVs battery. Firstly, its Ragone plot presents an excellent energy density retention at high power rates; secondly, the excellent capacity retention and high Coulombic efficiency of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB)-Li half-cell clearly indicates a potential good cyclability of full cells based on $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB) cathode. Finally, we believe the good low temperature performance of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB) (*i.e.* retains 91.6% and 76.3% of its capacity at ~25 °C, when cycled at 0 and -15 °C) is also beneficial to its application in PHEVs.

1. Introduction

For a green and much more sustainable modern society, the revolution of the transportation technology[1], by reducing the dependence on fossil oil and decreasing the carbon footprint, is one inevitable way to go. To realize such a dream, extensive studies are focusing on the exploration of devices that are able to store cleanly huge quantities of electrical energy[2], derived from, but not limit to, wind and solar energy. In the extensive devices, lithium-ion battery (LIB) has emerged as one of the most promising storage systems, and has been developing dramatically since its first communization by Sony Corporation in 1991[3], due to its relatively high energy density (discharge capacity × operating voltage)[4] and fairly long service life (500 cycles). LIB with ayered transition metal oxides as cathode materials, such as graphite/$LiCoO_2$, is now widely used in cell phones, digital cameras, personal computers and other portable electronics, however, its extensive application in plug-in hybrid electric vehicles (PHEVs) and/or electric vehicles (EVs) is still very challenging and limited, because of its limited power density (rate performance) and cycle life (> 1000 cycles are needed). In addition, the introduction of layered transition metal oxides as cathode material in power LIB may result in thermal safety concerns, especially at high charge states[5]. Therefore, the design and discovery for alternative cathode materials with thermal safety features has attracted global academic and industrial research equally[6].

Among the extensive cathode materials for power LIB, monoclinic $Li_3V_2(PO_4)_3$ (LVP) has been considered as one of the most promising candidates due to its high reversible capacity[7] and high operating voltage[8,9]. In addition, it displays a more attractive thermal stabilities and low temperature performance, comparing to layered lithium metal oxides[10]. However, its practical implementation is still challenging from both limited electronic conductivity and structural stability upon cycling, regarding to the application for power LIB. To improve its electronic conductivity, several approaches have been proposed: (1) nanocrystallization[11]; (2) surface coating (*i.e.* carbon[12], and/or metals[13]); (3) morphology control[14–16] and/or (4) metal ion doping (*i.e.* Nb, Fe, Al, K, Mg, Ca, Sc, Na, Ni, *etc.*)[17–23]. To enhance its structural stability upon cycling, SiO_2 coating[24] and Zn^{2+} doping[25] were successful reported. Unfortunately, to date, there is no report targets to obtain LVP electrode with both enhanced electronic conductivity and structural stability.

Therefore, in this contribution, we devoted to design a composite cathode with both good rate performance and long cycle life based on Zn^{2+} stabilized LVP/C[25] and a cheap performance carbon additive (PBX101, Cabot Corp.; hereafter denoted as PB) with both good electronic conductivity and capacitor nature. On one hand, the $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+*x*PB)

---

* Corresponding author. Tel.: +86 451 86413721; fax: +86 451 86418616.
E-mail address: changsd@hit.edu.cn (C. Dai).

http://dx.doi.org/10.1016/j.electacta.2015.04.163
0013-4686/

composite cathode should own enhanced rate performance due to the good electronic conductivity and capacitor nature of PB. At this junction, it should be noted that the capacitor nature of PB can improve the rate performance of the composite electrode becasuse it could store energy via fast ion adsorption/desorption, which in return shorten the response time of the composite electrode upon charging/discharging process[26]. On the other hand, PB may lower the overall energy density of the composite electrode due to its much lower specific capacity comparing to LVP. Therefore, there is trade-off between the power and the energy density of the composite electrode. Base on these properties, we successfully design $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB) as a promising cathode for PHEVs battery, which requires high power density, but moderate energy density. Firstly, Ragone plot of estimated $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB)-Graphite full cell indicates its ability to meet the demands of both power density and energy density for PHEVs. Secondly, $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB)-Li half-cell shows 100% of its initial discharge capacities (109 mAh g^{-1}) among the 1000 cycles with an average Coulombic efficiency (CE) about 100%, when charged at 20 C rates and discharged at 1 C rates, which is among the best for $Li_3V_2(PO_4)_3$/C and its derivates. And the 100% of both capacity retention and CE may granrantuee the excelllent cyclabilty of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB) in full-cell configuration. Thirdly, even at low temperature as -15 °C, $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+10PB)-Li half-cell could deliver 76.3% of its capacity at ~25 °C (112.5 mAh g^{-1}), indicating an excellent low temperature performance.

2. Experimental

2.1. Synthesis of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C

$Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C was prepared by ball-mill assisted carbothermic reduction method. And the detailed process could be described as follows. (1) $LiOH·H_2O$ (A.R.), V_2O_5 (A.R.), $(CH_3COO)_2Zn·2H_2O$ (A.R.), $NH_4H_2PO_4$ (A.R.) and sucrose were mixed at a molar ratio of 3:0.985:0.05:3:2/3; (2) the mixture was ball-milled together for 7 h with absolute ethanol, and then dried at 80 °C for 12 h before ground in an agate mortar (denoted as precursor); (3) the obtained precursor was heated to 300 °C for 4 h in a furnace under argon flow, and then ground; (4) the sample obtained after step (3) was sintered again at 800 °C for 8 h in a flowing reducing atmosphere (10% H_2 in Ar, by volume); (5) finally, the sample was ground for later use.

2.2. Characterization of PB and $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C

The morphology and particle size of PB was observed with a scanning electron microscope (SEM, HITACHI S-4700, Japan) coupled with an energy dispersive spectrum X-ray detector (EDS). Nitrogen adsorption and desorption isotherm (ADI) was examined on ASAP2020 analysis meter (Micromeritics Corp., America) after the samples were vacuum dried at 120 °C overnight. The surface-enhanced Raman scatting (SERC) spectra were recorded from 800 to 2000 cm^{-1} on a Renishaw inVia micro-Raman spectroscopy system, using TE air-cooled 1040 × 256CCD array in a confocal Raman system (wavelength: 633 nm). The incident laser power was kept at 1.5 mW, and a total accumulation time of 10 s was employed.

Please refer to *ref.* [25] for detailed characterizations (crystal structure, morphology, and particle size) of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C.

2.3. Electrode preparation and electrochemical analysis

$Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+*x*PB) cathodes were coated on Al foils with a slurry of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C, PB, acetylene black (AB) and polyvinylidene fluoride (PVdF) at a mass ratio of (80-*x*): *x*: 10: 10 in *n*-methyl-2-pyrrolidone (NMP). The cathode sheet was vacuum dried at 110 °C overnight before it was cut into wafers with a diameter of 15 mm and a typical mass loading of 2.0-2.5 mg cm^{-2}. Electrode with a composition of PB:AB:PVdF = 8:1:1 (by weight) and a typical mass loading of 1.2-2.0 mg cm^{-2} was also tested.

CR2025-type coin cells were assembled in a glove box filled with high-purity argon. The Li discs with thickness of ~0.30 mm were used as reference and counter electrode. Celgard 2400 was used as separator. 1 M $LiPF_6$ in a mixture of EC, DMC and DEC (a volume ratio of 1:1:1) was used as electrolyte.

The coin cells were galvanostatically charged/discharged at different rates over the potential range of 3.0~4.3 V using a multichannel battery test system (Neware, Shenzhen). Note that, (1) the galvanostatically charge process was followed by a 10 minutes constant-voltage charge process; (2) 10 minutes of rest was employed between each charge and discharge process; (3) both the specific capacities and the current density were normalized to the weight of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+*x*PB); (4) for rate performance test, the charge rate was set to be 1 C (1 C = 133 mA g^{-1}). All experiments were carried out at a temperature of 25±2 °C unless specified.

3. Results and discussion

3.1. Characterization of PB and $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C

To determine the morphological structure of PB, SEM, EDS spectrum and nitrogen ADI were collected (Fig. 1a-c). Fig. 1a demonstrates the secondary PB particles are aggregated from nano-sized carbon particles, which more or less indicates its porous structure. Moreover, the ADI of PB (Fig. 1b) displays a typical IV curve with H1 hysteresis loop, further indicating an ordered mesoporous structure. For more details, its BJH (Barret-Joyner-Halenda) pore-size distribution (calculated from the adsorption branch; Fig. 1c) and BET (Brunauer-Emmett-Teller) surface area were determined by the nitrogen ADI. The result show the average pore size and BET surface are 8.58 nm and 1100 $m^2 g^{-1}$, respectively. Combined with the above analysis, it is not difficult for us to speculate that PB carbon additive can serve as electrochemical capacitors[26]. And the capacitance characteristic of PB was well manifested by the charge/discharge test. As shown in Fig. 1d and its insert, PB shows a typical capacitive behavior with a linear slope charge/discharge profile and good rate performance. Therefore, PB is expected to effectively enhance the rate performance of $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C due to its fast adsorption/desorption energy storage mechanism.

Another important phenomenon should be noted from the charge/discharge test was the increasing CE of PB in the first few cycles (Fig. 1d), which was tentatively ascribed to the irreversible side reaction causing by the absorbed oxygen-containing groups and/or oxygen element in the nano-sized carbon. And the existence of the absopted oxygen-containing groups and/or oxygen elements is clearly comfirmed by EDS spectrum in the right bottom of Fig. 1a. Thus, the annealing process of PB or $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+*x*PB) composites under reducing atmosphere (*i.e.* H_2/Ar mixing gas flow) may futher enhance its electronic conductivity and capacitance characteristics due to the removal of the absorbed oxygen-containing groups and/or oxygen element (*i.e.* the enhancement of the carbon to oxygen atomic ratios).

Raman analysis was conducted to further estimate the role of PB on $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/(C+*x*PB) composites, and the results are presented in Fig. 2a-b. The Raman spectra of both PB and $Li_3V_{1.97}Zn_{0.05}(PO_4)_3$/C show two broad bands center at about 1335 and 1590 cm^{-1}, and both of which, the D band (disorder