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Hierarchically porous Li_3VO_4/C nanocomposite as an advanced anode material for high-performance lithium-ion capacitors

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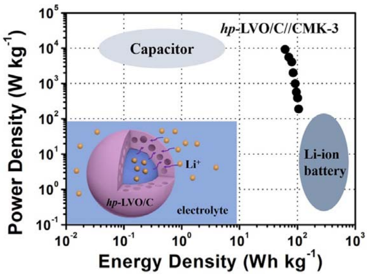
HIGHLIGHTS

- Hierarchically porous Li_3VO_4/C nanocomposite was synthesized.
- This composite has macropores at the center and mesopores in the wall.
- Macropores promote electrolyte penetration into the interior.
- Mesopores benefit the accommodation to volume change upon cycling.
- Lithium-ion capacitors of Li_3VO_4/C//CMK-3, show superior performances.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-ion capacitors, as a hybrid electrochemical energy storage device, realize high specific energy and power density within one device, thus attracting extensive attention. Here, hierarchically porous Li_3VO_4/C nanocomposite is prepared by a solvo-thermal reaction, followed with a post-annealing process. This composite has macropores at the center and mesopores in the wall, thus effectively promoting electrolyte penetration and structure stability upon cycling simultaneously. Compared to mesoporous Li_3VO_4, the enhanced rate capability and specific capacity of hierarchically porous Li_3VO_4/C indicate the synergistic effect of mesopores and macropores. Inspired by these results, this composite is coupled with mesoporous carbon (CMK-3) for lithium-ion capacitors, generating a specific energy density of 105 Wh kg^{-1} at a power density of 188 W kg^{-1}. Even if the power density increases to 9.3 kW kg^{-1}, the energy density still remains 62 Wh kg^{-1}. All these results demonstrate the promising potential of hierarchically porous Li_3VO_4 in lithium ion capacitors.

1. Introduction

Electrochemical energy storage devices, including but not limited to lithium ion batteries (LIBs) and capacitors (supercapacitors and electric double-layer capacitors), have achieved great successes in the past decades, due to extensive applications in portable electronics, electric vehicles, and so on [1–3]. The ever-growing development of these applications strongly needs an energy storage device with both high power and energy density. LIBs hold the advantage of high energy density (150–200 W h kg^{-1}), but are subject to a relatively low power

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density (1–5 kW kg^{-1}) and a limited cycle life (500–2000 cycles) [4,5]. In contrast, capacitors show an excellent specific power ($10–10^3$ kW kg^{-1}) and a long cycle life (10^4-10^6 cycles), but the specific energy density is quite low, usually less than 10 Wh kg^{-1} [5,6]. So, it is highly desirable to combine these features within one device.

In this context, lithium-ion capacitors (LICs), a hybrid electrochemical energy storage system derived from capacitors and batteries, attract intense attention. In a typical LIC, one electrode works on the basis of redox reactions, and the other functions by double layer charging/discharging on the surface. So, the electrodes show the features of capacitors and batteries in the same device, likely realizing the high power and energy simultaneously [7]. In most reports, carbon materials like activated carbon (AC), mesoporous carbon (CMK-3), etc [8–14] are employed as the cathode. Therefore, the selection of anode materials in LICs becomes critical. Up to date, many intercalation anodes have been explored for this purpose, including titanium-based compounds ($Li_4Ti_5O_{12}$, [14–20] TiO_2, [21–23] $H_2Ti_6O_{13}$ [11,24], TiP_2O_7 [25], $LiTi_2(PO_4)_3$ [26]), V_2O_5 [8,27–29] and Nb_2O_5 [30–32]. In these materials, titanium-based compounds show a long cycle life, but suffer from small capacity (170–250 mA h g^{-1}) and high voltage plateau (~1.7 V). These shortcomings affect the power/energy density of LICs. Conventional transition metal oxides like Fe_3O_4 [33] offer a high capacity, but suffer from inferior capacity retention and rate performance. Thus, the exploration of new anode materials is urgent. Until recently, Yu et al. reported that Li_3VO_4 might be appropriate as an anode material for LICs, because of fast electrochemical kinetics, appropriate voltage plateau (0.5–1.0 V *vs.* Li/Li^+) and moderate theoretical capacity (~394 mAh g^{-1}) [34]. Peapod-like Li_3VO_4 nanowires coated by N-doped carbon delivered an energy density of 24.4 Wh kg^{-1} at a specific power of ~11 kW kg^{-1}. To the best of our knowledge, there are rare reports involving Li_3VO_4 as the electrode for LICs, although the application of Li_3VO_4 in LIBs has been well documented [35–41].

Herein, hierarchically porous Li_3VO_4/C, denoted as *hp*-LVO/C, was synthesized by a solvothermal reaction, followed with a post-annealing process. This composite presents a unique structure, where the wall of hollow Li_3VO_4/C nanostructures is also highly porous. Such a specific structure is not synthesized for Li_3VO_4 before, although hollow Li_3VO_4 structure, in which a pore locates at the center [39,41], or mesoporous Li_3VO_4, where the pores randomly distribute throughout the particle [40], have been fabricated in previous works. Moreover, the resultant performances are better than those of mesoporous Li_3VO_4/C, indicating the synergistic effect of mesopores and macropores. Encouraged by these results, *hp*-LVO/C is paired with mesoporous carbon (CMK-3) for LICs, where the energy density could be maintained as 62 Wh kg^{-1} at 9.3 kW kg^{-1}. This result well indicates the promising potential of Li_3VO_4 in LICs.

2. Material and methods

2.1. Chemical synthesis

Hierarchically porous LVO/carbon nanocomposite (*hp*-LVO/C) was prepared through a facile solvothermal method, followed by a post-annealing process. In detail, 0.234 g of NH_4VO_3 was dissolved in 30 mL of ethylene glycol (EG). Then, the solution was stirred for 40 min. After 1.47 g of $LiOH{\cdot}H_2O$ was added, it was stirred for another 20 min. The suspension was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 60 mL. After treated at 180 °C for 2 h, the autoclave was cooled to room temperature. The product was collected by filtration, washed with absolute ethanol, and dried at 60 °C overnight in vacuum. The resultant powders were annealed at 550 °C for 2 h in Ar, producing *hp*-LVO/C. The solvent effect on the product was investigated by mixing distilled water with EG. The volume ratio of water/EG was controlled at 1:5, 1:2 or 2:1, but the total volume was kept as 30 mL. The other conditions were the same as that stated above.

2.2. Structure characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker D8 Adv, Germany) with monochromatized Cu Kα line as the radiation (λ = 1.5418 Å). Field-emission scanning electron microscope (SEM) and transmission electron microscope (TEM) images were collected on a field emission scan-ning electron microscope (SUPRA 55, Germany) and a transmission electron microscope (JEOL JEM, 1011, Japan). High resolution transmission electron microscope (HRTEM) images were acquired on a field-emission transmission electron microscope (JEOL JEM 2100F, Japan). Raman spectra were measured using a MicroRaman spectrometer using a laser of 632 nm as an excitation (Nicolet NEXUS 670, USA). Thermogravimetric analysis (TGA) was conducted on a thermal analyzer (Mettler Toledo TGA/SDTA 851, Switzerland) in air at a heating rate of 10 °C min^{-1}. N_2 sorption isotherms were obtained from a Micromeritics analyzer (ASAP 2020, USA) at 77 K. Specific surface areas were calculated by Brunauer-Emmett-Teller (BET) theory.

2.3. Electrochemical measurements

The working electrode was made of 70 wt% active materials (*hp*-LVO/C), 20 wt% acetylene black and 10 wt% of carboxyl methyl cellulose (CMC). These materials were blended with a trace of distilled water, hand-milled for 0.5 h and casted on a Cu foil. Then, the film was dried at 60 °C for 24 h in vacuum. After that, the electrodes were roll-pressed and cut into discs with a diameter of 12 mm. The mass loading of active materials was controlled at ~1.5 mg cm^{-2}. A piece of discs assembled with a lithium disc in an argon-filled glove box (Mikrouna, Super 1220/750/900) for CR2032 coin cells. Celgard 2400 membrane was served as a separator and 1 M $LiPF_6$ in the mixture of ethylene carbonate-dimethyl carbonate-ethyl methyl carbonate (EC-DMC- EMC, 1: 1: 1 in volume ratio) was used as electrolyte. Discharge/charge tests were performed on a battery test system (Land CT2001A, China). Cyclic voltammograms (CV) were carried out on an electrochemical workstation (Lanlike LK2005A, China). Electro-chemical impedance spectra (EIS) were evaluated on an electrochemical workstation (Autolab PGSTAT302N, Switzerland) in the frequency range of 1 MHz-0.01 Hz with AC modulus at an amplitude of 5 mV.

In asymmetric lithium ion capacitors, the counter electrode was fabricated by the same protocol as that used for *hp*-LVO/C, except an Al foil as a current collector and CMK-3 (pore diameter: 3.8–4 nm, SSA: > 900 m^2/g, XFNano Inc. China) as the active material. Before the assembly, *hp*-LVO/C was electrochemically activated in a half battery and stabilized at 0.8 V. The mass ratio of CMK-3 to *hp*-LVO/C was controlled as 6:1 (CMK-3: ~9 mg cm^{-2}, *hp*-LVO/C: ~1.5 mg cm^{-2}) to balance the charge stored in cathode and anode [13,22]. The separator and electrolyte was kept as the same as those in half cells. On the other hand, *hp*-LVO/C//CMK-3, where *hp*-LVO/C was not electrochemically activated, was also tested to clarify the effect of this treatment. In CMK-3//CMK-3, the mass ratio of anode to cathode was controlled as 1: 1 (CMK-3: ~1.5 mg cm^{-2}).

2.4. Energy density and power density on lithium ion capacitors

The specific energy density and specific power density of LICs were calculated based on the total mass of active materials in anode and cathode using the following formula [33,34].

$$E = \int_{t1}^{t2} IVdt \tag{1}$$

Where E is the specific energy density (Wh kg^{-1}), I is the applied current density (A g^{-1}), V is the voltage, *t1* and *t2* are the beginning and ending time in the discharge process.

$$P = E/t \tag{2}$$