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Carbon-coated $Li_3V_2(PO_4)_3$ derived from metal-organic framework as cathode for lithium-ion batteries with high stability

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ABSTRACT

Recently, Metal-Organic Frameworks (MOFs) derived carbon-based materials have attract wide interest in electrochemical devices due to their large surface area and favorable conductivity. In this work, instead of using MOFs for direct carbon sources, we employed vanadium metal-organic framework (MIL-101(V)) precursor as both carbon sources and vanadium sources for synthesizing carbon-coated $Li_3V_2(PO_4)_3$ nanocomposites (LVP@M-101). The electrochemical property of LVP@M-101 has been investigated as cathode electrode at a voltage of 3.0–4.8 vs Li^+/Li, to compare with $Li_3V_2(PO_4)_3$ prepared using V_2O_5. It is shown that the composite material displays a remarkably improved electrochemical stability with a high reversible capacity of 113.1 and 105.8 mA h g^{-1} at the rate of 0.5C and 1C after 1000 cycles, together with a superior rate performance at various current densities from 0.1C to 10C. Moreover, we have applied ex-situ PXRD and EPR spectroscopy to investigate the lithiation/delithiation process of LVP@M-101 electrode. Through detailed characterizations and electrochemical tests, we believe that the novel nanocomposites LVP@M-101 retain the two-phase transition nature of $Li_3V_2(PO_4)_3$ and the enhanced cathodic performance in lithium-ion battery is largely due to its unique structural stability.

1. Introduction

Lithium ion batteries are essential available alternative energy storage devices due to their superior electrochemical potentials and relatively low cost to make commercially viable energy packages. Lithium transition metal phosphates such as $LiMPO_4$ (M = Fe, Co, Ni, Mn) [1–6], $Li_3M_2(PO_4)_3$ (M = Fe, V, Ti) [7–13], and $LiVPO_4F$ [14,15] have been regarded as highly promising cathode materials for rechargeable lithium batteries. Among these mentioned phosphates, the monocline $Li_3V_2(PO_4)_3$ cathode has attracted great attention over the years due to its high average potential (4.0 V) and specific capacity (197 mA h g^{-1}) with benign ion mobility and excellent thermal stability. [16] Unfortunately, $Li_3V_2(PO_4)_3$ has an essentially low electronic conductivity (2.4×10^{-7} S cm^{-1}) as $LiFePO_4$ (10^{-10} to 10^{-9} S cm^{-1}), [17] which greatly restricts its practical applications.

Hence, various methods were applied to solve this problem, including designing and controlling microstructures [18–20], doping with foreign atoms [21–24], and coating electronically conductive material such as carbon [25–29]. Carbon from different kind of sources has been widely applied to coat the electrode materials in order to improve their electrical conductivities. Besides, the electrochemical performance of $Li_3V_2(PO_4)_3$ was strongly influenced by the nature of carbon sources. For instance, Zhong et al. synthesized the $Li_3V_2(PO_4)_3$ samples by carbon-thermal reduction. It was shown that the leaving residual carbon was beneficial to the stabilization of V^{3+}, resulting in greatly improved electrochemical performance. [30] Rui et al. prepared the carbon coated $Li_3V_2(PO_4)_3$ composites using four different carbon precursors: starch, polyvinylidene difluoride (PVDF), glucose, and citric acid as both carbon source and reducing agent. The best performance was achieved by those obtained by the pyrolysis of PVDF with a carbon content of 12.68%, leading to lower impedance and a discharge specific capacity of 95 mA h g^{-1} at 5C in 3.0–4.3 V [31].

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Recently, the metal-organic frameworks (MOFs) have attracted an increasing attention due to their high specific surface areas and ultrahigh porosities, which are resulted from the enriched organic ligands and metal ions in the MOFs structure [32–35]. MOFs have been also widely applied as precursors for synthesizing metal oxides and the carbon materials used for anodes in batteries [36–38]. However, there are few reports on employing MOFs to produce cathode materials.

In this work, we firstly attempted to employ the vanadium MOF $[V_3O(BDC)_3(H_2O)_2Cl_{0.7}(HBDC)_{0.3}]\cdot 2H_2O\cdot 0.5EtOH$ (MIL-101(V) [39]) as both carbon source and vanadium source, instead of V_2O_5, to synthesis the carbon-coated $Li_3V_2(PO_4)_3$ composite material. MIL-101(V) owns a rigid and mesoporous cages structure, exhibiting the largest specific surface area among vanadium MOFs [39–41]. By using the pyrolysised MIL-101(V) as the reaction processor, the as-synthesized carbon-coated $Li_3V_2(PO_4)_3$, referred to as LVP@M-101 in the following, exhibits laminated structures with some hollow bubbles inside and the residual carbon outside. The electrochemical performances of LVP@M-101 as cathode has also been investigated, especially with long charge-discharge cycles, to compare with the $Li_3V_2(PO_4)_3$ (LVP in the following) prepared using V_2O_5 as vanadium sources. Furthermore, we have employed the ex-situ XRD and EPR spectroscopy to investigate the mechanism of Li^+ intercalation and deintercalation process.

2. Experimental section

2.1. Synthesis of MIL-101(V)

The MIL-101(V) was synthesized following a typically reported method [39]. H_2BDC (10 mmol, 1.66 g) and VCl_3 (10 mmol, 1.57 mg) were dissolved in 50 mL pure ethanol. After that, the mixture was transferred into 100 mL Teflon-lined autoclave and stirred for 30 min. After sonicating for 15 min, the autoclave was placed in an oven at 120 °C for 48 h. Then the autoclave was cooled down to room temperature in a fume hood. After washing with ethanol, the green powders were collected by centrifugation. The final product was dissolved in DMF and was activated by heating at 70 °C for 3 h under N_2. The same procedure was repeated with ethanol as the solution. Finally, the precursor was dried under vacuum for 16 h at 120 °C.

2.2. Preparation of LVP@M-101 composite materials

LVP@M-101 carbon composite were prepared by a reported method [39,42], but using the prepared MIL-101(V) as precursor instead of V_2O_5. Stoichiometric MIL-101(V), $LiOH\cdot H_2O$, $NH_4H_2PO_4$, and appropriate acetone were grounded and pressed into pellets. Subsequently, the mixture was decomposed at 300 °C for 4 h in an argon atmosphere, and was then sintered at 750 °C for 6 h in flowing argon to obtain MIL-101(V) derived $Li_3V_2(PO_4)_3$ composite material (referred to as LVP@M-101). For comparison, $Li_3V_2(PO_4)_3$ (referred to as LVP) was also prepared by using V_2O_5 as the vanadium source instead of MIL-101(V) in a same process.

2.3. Materials characterization

The powder X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60) measurement using high-density Cu-Kα radiation ($V = 30$ kV, $I = 25$ mA, $\lambda = 1.5418$ Å) was applied to study the crystalline phase of the as-prepared materials. Solid-State NMR measurements were performed on a Bruker AVANCE-III 9.4T spectrometer. Samples were packed into 4 mm Zirconia rotors and were spinning at 10 kHz in a triple-resonance probe. ^6Li spectra was recorded at room temperature using a Hahn-Echo pulse sequence with $\pi/2$ pulse of 3 μs. Chemicals shifts were referenced to LiCl solid sample at 0 ppm. The residual carbon content of LVP@M-101 composite and LVP was verified by thermogravimetric analysis (TGA) using simultaneous thermo-analyzer (STA 449 F3 Jupiter®) at a heating rate of 10 °C /min from 25 °C to 800 °C. Specific surface areas and pore size distributions were calculated from the results of N_2 adsorption/desorption at 77 K (Micromeritics ASAP, 2020) using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The morphologies and internal structures of the samples were observed though Transmission electron microscope (TEM, JEOL JEM-2100F) and scanning electron microscope (SEM, HITACHI, JAPAN S-4800 operating at 10 kV, 100 μA). Continuous-wave (CW) X-band EPR measurements were performed at 2 K with a Bruker EMX plus 10/12 spectrometer at National Magnetic Field Laboratory of the Chinese Academy of Sciences (CHMFL). Microwave power and modulation amplitude were respectively set to 2 mW and 2 G.

2.4. Electrochemical measurements

Electrochemical performances of the samples were evaluated in coin cells. Firstly, active materials, Super-P carbon black (conducting additive), and Polyvinylidene Fluoride (PVDF, binder) were prepared in a weight ratio of 7:2:1, and then were mixed uniformly in distilled water to produce a slurry. The obtained slurry was coated onto a piece of aluminium foil by a doctor blading method, dried at 110 °C in vacuum oven for 12 h, and then punched into round plates (diameter of 14.0 mm) as the cathode electrodes. The loading density of the active materials was calculated as 1.5–2.5 mg/cm^2. Finally, the as-prepared anode, a Celgard 2325 separator (diameter of 19.0 mm), a pure lithium counter electrode, electrolyte of 1M $LiPF_6$ in EC/DEC/EMC (1:1:1 vol %) were assembled into a coin cell (CR2032) in an argon filled glove box (O_2 and $H_2O \le 0.1$ ppm). The assembled coin-type cells were aged for at least 12 h before electrochemical tests. Galvanostatic charge-discharge cycles were performed using a LAND 2001A battery test system in the voltage range of 3.0–4.8 V (vs. Li/Li$^+$). Cyclic voltammetry (CV) was performed using a CHI 660a electrochemical workstation between the voltage ranges of 3.0–4.8 V at a scan rate of 0.1 mV s^{-1} and different scan rates of 0.05–0.25 mV s^{-1}. Electrochemical impedance spectroscopy (ESI) measurements were carried out on the same workstation (CHI 660a) with the frequency range of 10^4 Hz to 10^{-2} Hz.

3. Results and discussion

We firstly show the XRD and TG analysis of the MIL-101(V) MOF prepared in this work in Figs. S1 and S2. It is shown that the diffraction peaks of activated MIL-101(V) match well with those of cubic structured Cr-MIL-101 [43] Therefore, the as-prepared MIL-101(V) compound is isostructural with Cr-MIL-101. TG analysis prove that the thermal decomposition of MIL-101(V) occurred around 200 °C. Further decomposition above 400 °C gave V_2O_5 as the only final product with a relative mass ratio of 31.3%. By using this value, we could readily estimate vanadium contents in MIL-101(V), which thus enables the stoichiometric synthesis of LVP compound in our work. Form the SEM pattern shown in Fig. S3, we can observe that MIL-101(V) crystallized as octahedral nanoparticles with sizes of 200–250 nm. This precursor was applied as a vanadium source to synthesis LVP@M-101 compounds according to stoichiometric ratio.

We believe that the use of MIL-101(V) as a precursor for preparing LVP-analogous also give rise to certain carbon coating on the final nanoparticles, as deduced from various previous reports of MOF-derived porous carbon materials [44–46]. Appropriately