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Sulphur-reduced self-assembly of flower-like vanadium pentoxide as superior cathode material for Li- ion battery

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ABSTRACT

Flower-like self-assembly of vanadium pentoxide (V_2O_5) has been synthesized via a facile, eco-friendly and bottom-up approach using hydrothermal process at low temperature with high-yield for the first time. This hierarchical flower-like structure is found to be accumulated with numerous plate-like sub-units, and each unit seems to be a complete structure of randomly grown hexagonal nano/micro plates. A possible reaction mechanism for the formation of hierarchical flower-like structures of V_2O_5 has also been proposed. The reduction process (from $V^{5+}$to V^{4+} or some mix oxidation states)is carried out through sulphur-reduction by using an advanced homemade CVD system with argon as the carrier gas at different temperatures. The sulphur reduced V_2O_5 structure formed shows excellent lithium storage and rate capability. After sulphur-reduction, the specific capacity of the flower-like V_2O_5 as the cathode material can achieve 400 mAh g^{-1}, 300 mAh g^{-1}, 250 mAh g^{-1} and 100 mAh g^{-1} at different rates of 0.07C, 1C, 2.3C and 29 C, respectively between 1.75 V and 4 V.

1. Introduction

Sustainable energy is a crucial issue with the cumulative problems of global warming in the near future. New efficient means for gaining & storing energy needs to be developed for future use in devices as well as vehicles. Li-ion batteries are the most promising candidates for the energy storage systems due to their outstanding electrochemical performance with high specific capacity and energy density. The improvement of Li-ion battery is strongly urged to fulfil with the demand of high capacity storage, rate capability and energy density. Commercial cathode materials such as Lithium iron phosphate ($LiFePO_4$), lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel oxide ($LiNiO_2$), and lithium cobalt manganese nickel oxide (LCMNO)have the specific capacity within a range of 120–160 mAh g^{-1}. The specific capacity of some material such as LCMNO can reach around 200 mAh g^{-1}depending on its C-rates [1–5]. However, the futuristic use for energy storage and vehicles requires much higher values.

Vanadium oxide, especially vanadium pentoxide (V_2O_5) with a layer structure has been proven as one of the most potential cathode materials. Recently, V_2O_5 has been extensively investigated due to its low cost, abundance as well as its high theoretical capacity that is highly depending on the modifications of its structural phase clearly manifested as plateaus during the charge and discharge cycling. The typical reaction of electrochemical performance during Li intercalation into V_2O_5 proceeds is as:

$$V_2O_5 + xe - +xLi + \rightarrow Li_xV_2O_5; \quad 0 < x \leq 3$$

The α-phase of $Li_xV_2O_5$ exists for $x < 0.01$, ε-phase for $0.35 < x < 0.7$, δ-phase for $0.7 < x < 1$ and γ-phase for $1 < x < 2$. The third lithium ion inserting into V_2O_5 leads to the irreversible formation of ω-phase ($2 < x < 3$), $Li_xV_2O_5$ with a rock salt type structure (294 mAh g^{-1} with 2 Li ions intercalation/de-intercalation per unit formula; 440 mAh g^{-1} with 3 Li ions intercalation/de-intercalation per unit formula) [6–11]. V_2O_5 can deliver relatively high capacity than most of other commercial cathode materials such as $LiCoO_2$ (140 mAh g^{-1}) and $LiMn_2O_4$ (146 mAh g^{-1}) [12–14], even only one Li ion intercalates or de-intercalates.

A controlled mechanism with desired composition and morphology for fabricating nanostructures inheriting superior or even unusual physic–electrochemical properties is the issue that needs tremendous efforts to solve. Metal oxides with the hierarchical structures or various morphologies would inherit the superior characteristics of the micro/nano building block and obtain

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additional benefits simultaneously from its secondary structure [15–19].Self-assembly of nano/microstructural units have attracted tremendous research activities for diverse applications along fundamental and industrial perspectives to considerate the mechanism of driving forces and to mimic them into continuous structures without any obstacles. Several studies focus on the organization of different nanostructural units, and these formed hierarchical self-assembled structures resulting unique geometries including nanowires, nanorods, nanorings, nanosheets, nanoplates, nanochains, X-marks, and even twisted ribbons have been well-studied and documented [20–29]; however, the mechanisms of self-assembling large nanostructures and their driving forces for complex structures are still in the early stage. Self-assembly of different nanostructures can tie low dimensional materials and well-recognized micro-scale technologies with new building blocks for unique application. The interaction (attraction/repulsion) among different nanostructure subunits forming self-assembly, ion exchange and their physicochemical properties of the surrounding media plays a crucial role to engineer the self-assembling structures.

Herein, we report a facile, environmental friendly and high yield hydrothermal process to synthesize the flower-like V_2O_5 structure. It is revealed that the micro/nanostructures of as-synthesized V_2O_5 structure is controlled under critical hydrothermal treatment at 180 °C and the schematic process of flower-like vanadium oxide is shown in Fig. 1a. A mixture states were obtained after sulphur-reduction at different temperatures via a novel CVD system as shown in Fig. 1b. The primary building block of flower-like structure is nanoplates, and the secondary structure is composed of those nanoplates to form the flower-like V_2O_5 self-assembly.

2. Experimental section

2.1. Materials and methods

For the synthesis of V_2O_5 self-assembled flower-like morphology, ammonium metavanadate (0.8 gms) was dissolve in deionized water (100 ml) while stirring at 60 °C to form a clear light yellow solution. Concentrated (60–70%) Nitric acid was added drop-wise to this solution while stirring until the final pH of the solution reached between 3 and 4. As prepared clear orange solution was transferred into a Teflon bottle with a stainless steel shell. The assembly then was sealed and maintained at 180 °C for 24 h. After the reaction was finished, the sol was cooled to room temperature. The resulting bright-orange powder was collected, washed with distilled water and ethanol several times to remove by-products or any ions remaining in the final product, and then dried at 60 °C in vacuum oven for 12 h. To get pure V_2O_5 the obtained product was calcined at 300 °C for 2 h in air. After the annealing, the sulphur-reduction was carried out at different temperatures e.g. 200 °C, 400 °C, 500 °C, 600 °C in argon atmosphere. For sulphur-reduction, the sample was kept in ceramic boat and placed downstream in the CVD chamber, heated up to different temperatures for 2 h as shown in Fig. 1b. Sulphur powder (99.99% purity), was placed outside the CVD system and heated with the help of an external heating coil. S powder was evaporated at 150 °C and carried to CVD chamber with the help of Argon gas (flow rate 100 sccm) to react with V_2O_5 powder. The pressure in CVD chamber was maintained at 1 Torr.

2.2. Cell preparation

For the preparation of the lithium ion battery cathodes, as-synthesized V_2O_5 powder was mixed with conducting carbon (Super P) and PVDF binder (binder solution was prepared by dissolving 2 wt. % PVDF in N-methyl-2-pyrrolidone (NMP) solution) in the ratio of 8:1:1 (V_2O_5: super P: binder = 80%:10:10) were mixed well with stainless steel balls at 400 rpm for 15 min. The resultant slurry pasted on an Al foil and dried at 90 °C for 4 h. Then the coin cells (2032) were assembled in an argon-filled glove box using a lithium foil as the anode, Celgard 2600 was used as separator, and 1M $LiPF_6$ dissolved in ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and ethylene carbonate (EC) with a weight ratio of 1:1:1 and with addition of 1% vinylene carbonate (VC) as the electrolyte. Cells were tested at ambient environment. The testing voltage in the constant current mode was in a range of 1.75 V~ 4 V.

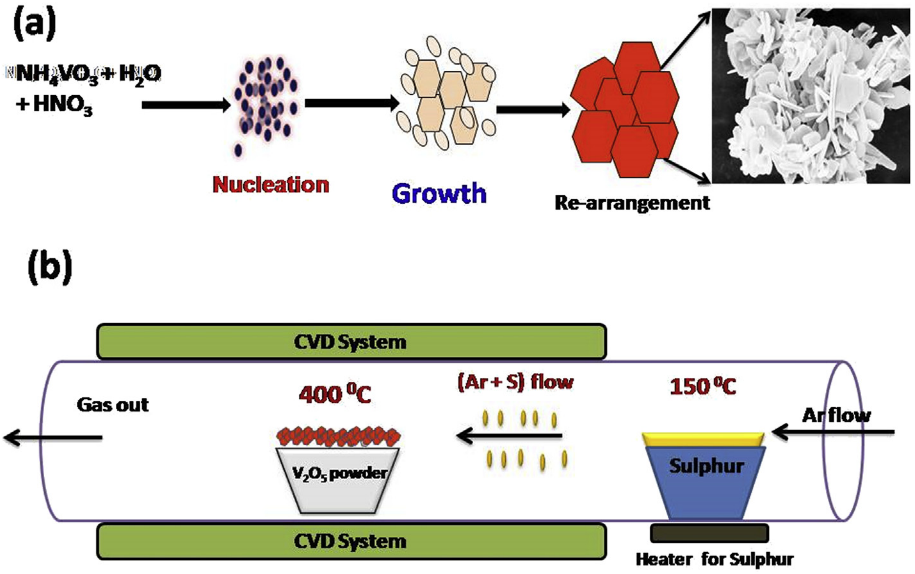

Fig. 1. (a) Nucleation & growth mechanism and (b) Schematic for sulfurization of flower like V_2O_5self-assembled system, synthesized by hydrothermal method. Sulphurization of V_2O_5 powder was carried out in a CVD system at centre of the horizontal of tube furnace at different temperature time in (Ar + S) environment.