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Short communication

Scalable and template-free synthesis of nanostructured $Na_{1.08}V_6O_{15}$ as high-performance cathode material for lithium-ion batteries

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ABSTRACT

Developing high-capacity cathode material with feasibility and scalability is still challenging for lithium-ion batteries (LIBs). In this study, a high-capacity ternary sodium vanadate compound, nanostructured NaV_6O_{15}, was template-free synthesized through sol-gel process with high producing efficiency. The as-prepared sample was systematically post-treated at different temperature and the post-annealing temperature was found to determine the cycling stability and capacity of NaV_6O_{15}. The well-crystallized one exhibited good electrochemical performance with a high specific capacity of 302 mAh g^{-1} when cycled at current density of 0.03 mA g^{-1}. Its relatively long-term cycling stability was characterized by the cell performance under the current density of 1 A g^{-1}, delivering a reversible capacity of 118 mAh g^{-1} after 300 cycles with 79% capacity retention and nearly 100% coulombic efficiency: all demonstrating its significant promise of proposed strategy for large-scale synthesis of NaV_6O_{15} as cathode with high-capacity and high energy density for LIBs.

1. Introduction

Due to their high energy density, lithium-ion batteries (LIBs) has dominated the current choice of energy-storage devices with a wide range of applications, such as portable devices, vehicle electrification and self-powering aerospace equipment [1–4]. Accordingly, considerable effort has been made on developing competitive electrode materials for next-generation LIBs, such as the well-known silicon anode with the state-of-the-art capacity over 3000 mAh g^{-1} [5,6]. However, the development on LIBs is still suffering from drawback of low capacity and energy-density. The major challenge arises from the unsatisfactory development on cathode candidates, which exhibited insufficient characterization on capacity and cycling stability. The current, well-defined and commercially available transition metal oxide candidates, including $LiFePO_4$ (LFP), $LiCoO_2$ (LCO), $LiNiCoMnO_2$ (NCM) and $LiNiCoAlO_2$ (NCA), have achieved acceptable success on the commercialization. However, their relatively low capacity (less than 200 mAh g^{-1}) cannot completely satisfy the rapid demand of high energy-density in some practical fields, for instance electric vehicles (EVs) or hybrid EVs (HEVs). Furthermore, these transition metal oxide candidates will probably generate considerable strain on resources as well as problem on cost-effectiveness considering their intensive application on the fields aforementioned. Therefore, exploring competitive cathode materials with sufficient capacities, energy density and long-lifespan stability is critically important on addressing current issues for LIBs [7–9].

Prior work has illustrated the promise of vanadium oxide compounds, VO_x (*e.g.* V_2O_5, VO_2, V_2O_3, V_6O_{13}), as cathode candidates for LIBs and sodium-ion batteries due to high theoretical specific capacities through multiple Li-ions accommodation accompanied with their wide range of oxidation state from V^{+2} to V^{+5}. Moreover, recent study has revealed the improvement of electrode performance by the addition of alkaline metal ions into the VO_x host in the form of LiV_3O_8 and NaV_3O_8. In this regard, unlike the 2D layered crystal structure of most VO_x, the alkaline ions in these compounds were arranged to form 3D pillars with tunneled structure, which could stabilize the overall structure and facilitate better cycling performance. In addition, owing to higher ionic transfer efficiency, the well-organized 3D pillars can promote the ion diffusion rate in the bulk material as well. All these features demonstrated its significant promise of superiority on ion-transfer and kinetics as high-capacity cathode candidate.

More recent, a sub-class of the vanadium oxide-based compounds, sodium hexa-vanadate compound (NaV_6O_{15}), has gained considerable attention due to its unique magnetic,

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superconductive and potential properties on Li-ion storage. The structure of NaV_6O_{15} is composed of quadruple VO_6 octahedra and VO_5 distorted trigonal bipyramids, sharing the edges and corners to form a continuous $[V_6O_{15}]$-$_n$ layers. Two VO_6 octahedra connect by the corner-shared oxygen and act as pillars for Li-ion storage. Such unique rigid 3D tunneled structure allows a comparatively rigid lattice organization that could buffer the lattice expansion and prevent the partial amorphism during lithiation/delithiation process [10–16]. In order to further improve the electrode performance, in this case, nanostructured NaV_6O_{15} was designed and underscored with advantages on cell performance in virtue of the reduced lithium ion transfer pathway, more active site for lithium ion insertion and alleviated lattice expansion. Accordingly, corresponding protocols, including hydrothermal process, solvothermal method and sol-gel method, have been investigated and reported as effective procedures on synthesizing nano-sized NaV_6O_{15} with orientative molecules [17–21]. Among these strategies, additive-free sol-gel process is promising owing to their high efficiency, controllability, reproducibility, and the absence of additives that allowed high throughput and cost-effectiveness to meet the requirement of scalable production. Unfortunately, little systematic work has been conducted on it, much less on its success to produce nanostructured NaV_6O_{15} cathode with sufficient capacity and cycling stability for LIBs.

Herein, an additive-free sol-gel route for scalable synthesis of nanostructured $Na_{1.08}V_6O_{15}$ was proposed with relatively high producing efficiency and sufficient cell performance when used as the cathode material for LIBs. The as-prepared sample was systematically post-treated at different temperatures and the crystallinity was well identified. Prepared $Na_{1.08}V_6O_{15}$ nanorods with good crystallinity had a single phase with preferred orientation growth along *c* axis. It exhibited reversible lithiation/delithiation process, delivering capacity as high as 302 mAh g^{-1} when cycled at current density of 0.03 A g^{-1}. Meanwhile, its long-term cycling stability was characterized by the galvanostatic cycling test under 1 A g^{-1}, which demonstrated a sufficient capacity retention approaching 80% after 300 cycles. By comparison, the well-crystallized $Na_{1.08}V_6O_{15}$ nanorods performed much improved power rate than that of pure V_2O_5, which further suggested the significant promise of this proposed strategy on large-scale synthesizing cathode material with high capacity and sufficient cycling stability for LIBs.

2. Experimental

All chemicals used in this study were of analytical grade and were used without further purification. In a typical synthesis, the precursor of sodium orthovanadate (0.1 M) was catalyzed by concentrated hydrochloride (12 M) to form vanadium sol solution [22]. By consequently providing more acid into the reaction system, transfer from vanadate sol to gel was triggered as maintaining the pH at 2.0 followed by incubation for 4 h. The gel precipitates were separated through vacuum filtering, washed with water several times to ensure the complete removal of absorbed residuals and dried at 80 °C overnight. Different temperature for sol-gel process was applied to evaluate the yielding. Subsequent annealing process was conducted at different temperatures (80 °C–450 °C) for 2 h with the heating rate of

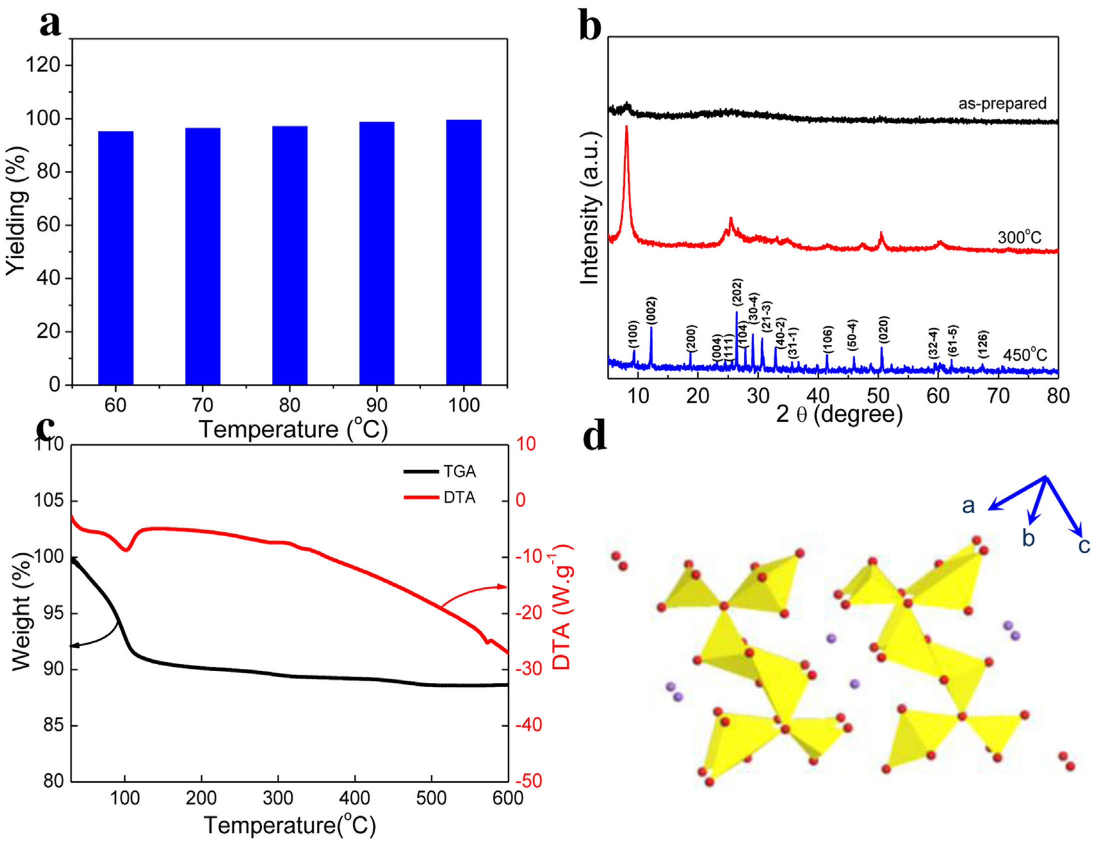

Fig. 1. Crystallographic properties of prepared $Na_{1.08}V_6O_{15}$: (a) yielding of sol-gel process with different reaction temperature; (b) XRD patterns of samples with different post-annealing temperature in argon; (c) TG/DSC results; and (d) the scheme of crystal structure of NaV_6O_{15} (red dots represent oxygen atom, purple dots represent sodium atom and yellow polygens are vanadium quadruple VO_6 octahedra and VO_5). Samples for the XRD and TG/DSC experiment were initially synthesized from sol-gel process at 90 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)