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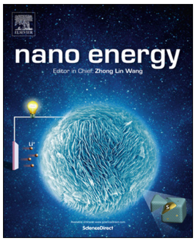

COMMUNICATION

Q2 Self-anchoring dendritic ternary vanadate compound on graphene nanoflake as high-performance conversion-type anode for lithium ion batteries

Q1 **Xinran Wang[a,b], Shili Zheng[a], Shaona Wang[a], Yi Zhang[a], Hao Du[a,*]**

[a]*Key Laboratory of Green Process and Engineering,*
National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology,
Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China
[b]*University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing, China*

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Abstract
Development of three-dimensional ternary vanadate compounds with excellent structural stability on exfoliated graphene nanoflacks allows the first success of conversion-type sodium vanadate anode candidate for high-rate and long-life lithium-ion batteries(LIBs). Corresponding additive-free self-anchoring behavior of active sodium vanadates material on graphene surface is representatively investigated, architecturing unique dendritic structure, a first-of-this-kind configuration, with robust flexibility and sufficient capability of structure-preservation. The prepared nanocomposite provides a high reversible capacity over 800 mA h g^{-1} and ultrafast charging/discharging capability with Li-ions via conversion-type reaction. More remarkably, the well-designed structure retains more than 96% of initial capacity with respect to their ultralong cycling stability, demonstrating the combined advantages of the facile hydrothermal protocol, high active material loading and architecture configuration for high-performance Li-ions storage. As a consequence, this research reveals the importance and effectiveness of self-assembling sodium vanadates on graphene nanoflakes with 3D hierarchial structure and indicates the significant potential of developing ternary vanadate compounds as promising anode candidate for LIBs.

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*Corresponding author. Tel./fax: +86 10 82544856.
E-mail address: duhao121@hotmail.com (H. Du).

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Introduction

Alloy/conversion-type electrode materials is under active exploration due to their theoretically high capacity and charateristic alloying or displacement mechanism for Li-ion storage. Nanostructuring design of these high capacitive yet insulating materials has provided unique promises on maximum utilizing their high gravimetric capacities and specific energy density in the wide range of application, including device portability, power-grid intellectualization, vehicle electrification and large-scale energy-harvesting, to name a few [1-5]. By means of size manipulation, prior strategy has offered acceptable capacity and energy density as the benefit of reduced transfer paths for both ion and electron to the electrochemical active site. However, the overall level of improvements that is achievable in most systems is not as effective as desired [6-9]. Multiple other limitations, such as particle self-aggregation and pulverization caused by the obvious volume change, still exist against the development of high-performance LIBs. Moreover, for most of this kind of materials, the inhomogeneous and repeated volume variation often causes severe fractures within electrodes, which creats defects on solid electrolyte interphase (SEI) layer and in turn, results in electrical contact loss, fast capacity degradation and poor cycling stability. In order to address these limits, progress has been made on the design of 3D nanocomposite with the significant structural advantage [10], reported as (1) robust self-accommodation with volume variation [11], (2) structure-preservation against physical loss of conductive contact [12], (3) synergistical promotion on both ion and electron transport, and (4) increase of overall conductivity. As a consequence, a variety of appealing structures, for instance zigzag-shape sodium vanadate nanowire [13] and pomegranate-shape Li-S battery [14], were continuously proposed with the state-of-the-art performance through bottom-up or top-down synthesizing protocols, including template-assisted modulation [15-17], surface modification (solution or vapor-based deposition) [18-21] or additive-free self-assembly [22-27]. More recent, there is rapid growth of interest on addtive-free 3D structure design due to their potential of controlling structure without any orientative molecules. The specific absorption of ions on certain lattice phase of substrates gives rise to their slef-assmbly behavior, resulting in demonstrated operational facility and cost-effectiveness [28]. In this case, however, it remains a great challenge to self-design effective structure in order to keep large reversible capacity for LIBs, much less than the sufficient high Coulombic efficiency and cycling stability for long lifespan.

Ternary vanadate compounds, in particular of NaV_3O_8 [29-31], NaV_6O_{15} [32-34], and NaV_2O_5 [35], have attracted considerable attention as intercalation-type cathode electrode material for organic, aqueous LIBs and sodium-ion batteries (SIBs) because of their high theoretical capacity, stable lattice structure, low cost and wide availability. The structure of sodium vanadates (SVs) are built up with polyhedral VO_x layers, including VO_6 octahedral or distorted trigonal VO_5 pyramids, sharing the edge and corner to form $[V_6O_{15}]_n$ or $[V_2O_5]_n$ layer. Na-ions predominantly reside in the octahedral or pyramides sites as pillar cations, providing larger interlayer distance and forming interstitials for Li-ion storage without major change in the lattice structure during the insertion/extraction process [36,37]. Different from interlation-type Li-ion storage, SVs can be potentially applied as high-performance anode candidate for LIBs with repect of their conversion-type charge storage. Theoretically, SVs could offer remarkable capacity as high as 801 mA h g^{-1} by reducing the oxidation state from V^{+5}/V^{+4} to V^{+2}. Unfortunately, the corresponding breaking and formation of chemical bonds created significant volume change during repeated lithiation/delithiation process and in turn, SVs anode are expected to suffer from risk of pulverization, loss of conductive contact and other problems aforementioned and the evaluation of their performance is unprecedented. Thereafter, means of 3D structure design is highlighted, getting access to the success of their first application as anode for LIBs. Moreover, corresponding formation protocol for additive-free synthesis of SVs with high performance must be carefully studied and examplified.

Herein, in this work, we proposed a facile, low-cost and additive-free protocol for in-situ self-assembling dendritic SVs (mixture of α-NaV_2O_5 and β-NaV_6O_{15}) on graphene nanoflakes (reduced graphene oxide, *r*-GO), where high-power rate and ultralong cycle stability for LIBs was significantly achieved and first addressed for this kind of material (Figure 1). The demonstrated structure, sodium vanadate/reduced graphene oxide (SVs/*r*-GO) nanocomposite was composed of branched, dendritic SVs 2D structure, which interconnected and tightly attached on *r*-GO surface, thus forming a unique 3D architecture. Furthermore, the structure allowed sufficient flexibility against volume variation, provided more reactive site for fast ionic transfer and facilitated the electron tranfer because of reduced crystal boundary. Accordingly, it can satisfy high specific capacity (over 800 mA h g^{-1}), remarkable rate capability and ultralong cycling stability with excellent capacity retention (96%) after 1000 cycles. Significant improvement has been made on the success of SVs anode material compared with conventional carbon-based intercalation anode candidates, and the effectiveness of anchoring SVs on graphene nanoflakes are proved and expected to offer insight into maximum utilization of other ternary vanadate compounds for high energy-density LIBs. The corresponding reaction of conversion-type Li-Ion storage was presented as following:

$$NaV_xO_y + \alpha Li^+ + \alpha e^- \longleftrightarrow Na_2O + Li_2O + VO \quad (1)$$

Experimental section

Materials

Natural graphite powder (C% ≥ 99.85%), sodium orthovanadate (C% ≥ 99.98%), 1-Methyl-2-pyrrolidinone (C% ≥ 99.85%) and poly(vinylidene fluoride) were purchased from sigma-aldrich without further purification. Ultra pure water (18 MΩ cm) was used for all experiments.

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