Electrochimica Acta 203 (2016) 171–177

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Stationary Full Li-Ion Batteries with Interlayer-Expanded $V_6O_{13}$ Cathodes and Lithiated Graphite Anodes

Na Xu, Xiaoxuan Ma, Mengfan Wang, Tao Qian*, Jiaqi Liang, Wanli Yang, Ying Wang, Jun Hu*, Chenglin Yan*

*College of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, China*

ARTICLE INFO

*Article history:*
Received 7 March 2016
Received in revised form 7 April 2016
Accepted 9 April 2016
Available online 11 April 2016

*Keywords:*
Full batteries
Ultra-stable cathodes
$V_6O_{13}$
Interlayer expanded
Ultrathin nanosheets

ABSTRACT

Here we report a Li-metal-free full battery, using interlayer-expanded $V_6O_{13}$ ultra-thin nanosheets and prelithiated graphite for cathodes and anodes, respectively. This full Li-ion battery exhibits a superior specific capacity of 233 mAh $g^{-1}$ at a current density of 100 mA $g^{-1}$ and 91% capacity retention after 500 cycles. Our first-principle calculations reveal that the interlayer-expansion is induced by the interaction between $V_6O_{13}$ and water which breaks interlayer V-O bonds and forms hydroxyls. The unique structure provides short lithium-ion diffusion path, excellent charge transport, abundant binding sites and volume flexibility for $Li^+$ intercalation/deintercalation, thus leading to high capability (280 mAh $g^{-1}$) and cycling performance (capacity retain 96.1% at 2.4 A $g^{-1}$ for 1000 cycles). Using novel prelithiation process, the Li-metal-free full cells with high controllability and performance is expected to contribute significantly to the development of safe, green, and powerful energy storage devices.



## 1. Introduction

The sustainable and clean energy sources, derived from solar energy, hydropower, tidal energy, and geothermal heat, have been increasingly demanded due to the pollution of traditional non-renewable fossil resources. With the development of the renewable energy, it is now essential that energy storage devices are required to design to satisfy the power needs of storing a fair amount of energy. Lithium-ion batteries (LIBs) which coupled with high capacity, working voltage, and low toxicity are considered as one of the most promising energy storage devices [1–6]. However, commercialization of full LIBs has so far been limited due to both the energy density and power density problems associated with the tradition cathode materials such as $LiMn_2O_4$ and $LiCoO_2$.

Vanadium oxides have been widely investigated due to their low cost, easy to synthesize, being relatively environmentally friendly and high theoretical capacity (294 mAh $g^{-1}$ with 2 $Li^+$ ions inserted/extracted per unit formula) [7,8]. Amongst various vanadium oxides (e.g., $V_2O_5$ [9], $VO_2$ [10], $V_2O_3$ [11], $V_3O_7$ [12], $V_6O_{13}$ [13], etc.), $V_6O_{13}$ exists an impressive capacity, and energy density, due to the large number of lithium ions that can be reversibly intercalated into the V lattice [14]. Theoretically, $V_6O_{13}$ can electrochemically incorporate up to 8 $Li^+$ per formula unit with all the V ions being reduced to 3+ oxidation state, which gives a high theoretical specific capacity and energy of 417 mAh $g^{-1}$ and 900 Wh $kg^{-1}$ [15], respectively, much higher than those of conventional $LiMn_2O_4$ (148 mAh $g^{-1}$, 500 Wh $kg^{-1}$) [16], $LiCoO_2$ (140 mAh $g^{-1}$, 540 Wh $kg^{-1}$) [17]. However, it is difficult to achieve high capacities with good cyclability for $V_6O_{13}$ cells because of the phase transitions, which decrease in electronic conductivity upon lithium insertion, and the loss of electrode integrity [18]. Moreover, $Li^+$ ions exist as interstitial impurities in perfectly crystallized $V_6O_{13}$ and interact strong with the lattice O anions, which results in considerably slow mobility of $Li^+$ ions. In order to overcome these prejudicious issues, two approaches may be used: (1) introducing dipole molecules (e.g., $H_2O$) in the host lattice to transform $Li^+$ into much less polarizing solvated ions, thereby alleviating the host-guest interaction and increasing the ion diffusivity [19]; (2) drastically down-sizing the particles to nanoscale so that the Li diffusion length is short enough to ensure a decent apparent Li diffusivity [20,21].

Another major concern regarding LIBs system is the use of lithium-metal anode, which is well known to have some critical defects including chemical reactivity in commonly used organic electrolytes and dendritic growth of lithium during cycling, thus

* Corresponding authors.
*E-mail addresses:* tqian@suda.edu.cn (T. Qian), jhu@suda.edu.cn (J. Hu), c.yan@suda.edu.cn, chenglinyan.nano@gmail.com (C. Yan).

http://dx.doi.org/10.1016/j.electacta.2016.04.044
0013-4686/

leading to poor cycle and safety performance. Recently, carbon-type anode materials have been suggested as alternatives to replace the lithium-metal anode. Nevertheless, carbon-type anodes can only couple with lithium metal oxide cathodes such as $LiCoO_2$ [22], $LiNiO_2$ [23], $LiMn_2O_4$ [24], $LiFePO_4$ [25] to construct full batteries and deliver high power, thus making it a major challenge to effectively combine carbon-type anodes with Li-metal-free cathodes to form a full cell.

Herein, we demonstrate a stationary full cell configuration with a novel interlayer-expanded $V_6O_{13}{\cdot}nH_2O$ ultra-thin nanosheets (IEVOS) cathode and lithiated graphite anode. Our IEVOS introduce interlayer expansion as a general and effective approach to increase the intrinsic Li diffusivity of layer-structured intercalation hosts by modifying the lattice structure meanwhile weakening the interaction between $Li^+$ and the host without introducing adverse side effects. Inclusion of dipole molecules such as hydroxy radical in the lattice converts $Li^+$ to less polarizing solvated cations, thus foster electron transfer and intercalation of highly charged $Li^+$ ions. A peculiar technique was used to handle the commercial graphite which can provide the anode material ample source of $Li^+$. As a result of the above benefits, the assembled full battery delivers an improved capacity (233 mAh $g^{-1}$ with an average working voltage of about 2.4 V), high energy density (116.5 Wh $kg^{-1}$ based on the weight of active materials on the cathode and anode) and excellent cycling stability (nearly 91% capacity retention after 500 cycles at current density of 900 mA $g^{-1}$), which are much better than those of previous reported full cells. These results could advance the development of practical LIBs to a large extent, particularly for use in zero-emission vehicles. Safer, greener, and more powerful LIBs can be achieved by the new Li-metal-free process.

## 2. Results and discussion

The structures of the IEVOS samples were first examined by field emission scanning electron microscopy (FESEM) and High resolution transmission electron microscopy (HRTEM) measurements. As revealed by Fig. S1A and Fig. S1B, hollow microspheres with uniform size were obtained after hydrothermal reaction for 3 h. The FESEM image of the product (Fig. 1A) exhibits uniform two-dimensional (2D) ultra-thin nanosheets morphology with lateral dimensions of *ca.* 8 nm. More fine details are presented by the HRTEM image (Fig. 1B), which shows well-defined lattice fringes of the nanosheets crystals, where the lattice spacing of 1.31 nm is consistent with the (001) crystalline plane of IEVOS. Furthermore, a uniform thin carbon layer of *ca.*1.5 nm covers the surface of the nanosheets, which is also proved by the HRTEM image.

The crystal structures of IEVOS and stacked $V_6O_{13}$ (SVO) were determined by X-ray diffraction (XRD) (Fig. 1C). The XRD patterns of the samples are both well indexed to monoclinic $V_6O_{13}$ (lattice parameters a = 11.96 Å, b = 3.713 Å, c = 10.07 Å, β = 100.9°, JCPDS no.: 71–0297) and the interlayer distance is studied with the patterns. The lattice parameters were calculated from the XRD patterns as an average of six maximum intensity peaks of the IEVOS (001, 110, 003, 412, 020, and 62-1 planes) using MDI Jade 5.0 software. The lattice parameters were calculated for a = 13.455 Å, b = 3.728 Å, c = 14.188 Å, β = 100.48° with the space-group C2/m, which illustrate the swell in both a-direction and c-direction of the crystal structure. The diffraction peak appear at lower angles which indicates a bigger lattice distance according to Bragg's formula ($d = 0.5\,\lambda/\sin(\theta)$). The crystal structure is separated by large interlayer spacing corresponds to a diffraction peak at $2\theta = 6.9°$ and the interlayer distance is calculated to be 1.31 nm, which is according with the result of HRTEM image. For the pattern of IEVOS, the intensity of the diffraction peak much bigger than that of SVO, illustrating more interlayers are expanded with the ultra-thin nanosheets structures. Moreover, the XRD pattern of IEVOS are studied after a dehydration process (annealed at 800 °C under $N_2$ gas flow), which noted as DHVOS (Fig. S2). It is obviously that the peak attributed to the lattice distance of 1.31 nm is devided

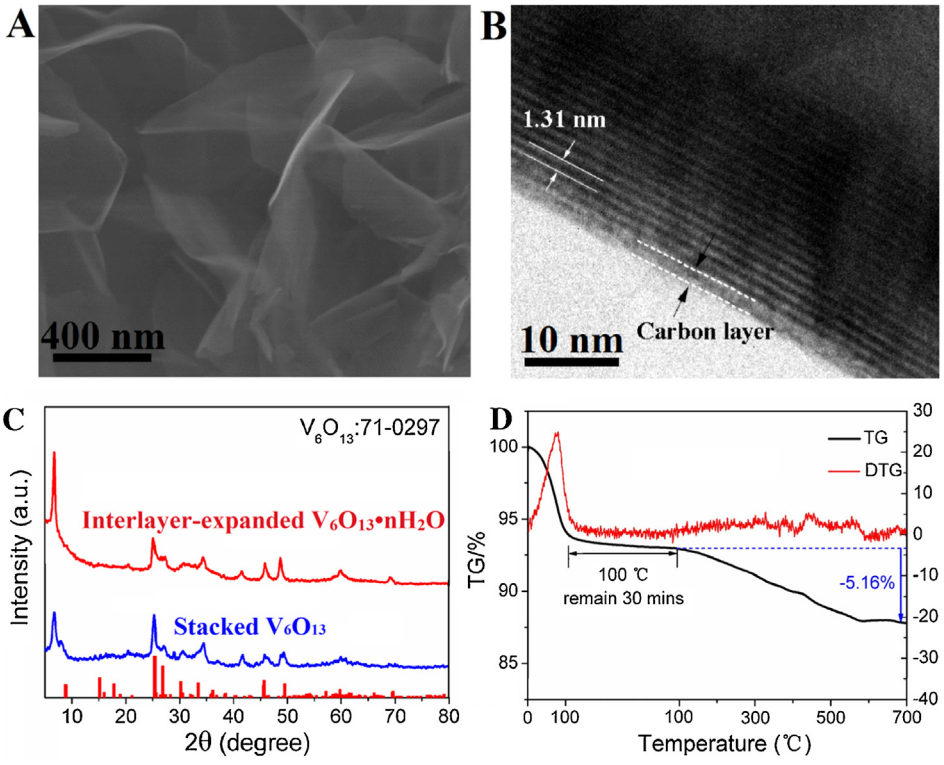


**Fig. 1.** (A) FESEM and (B) HRTEM images of IEVOS. (C) XRD patterns of as-prepared IEVOS and SVO. (D) TG and DTG curves of IEVOS in $N_2$.