Stable anode performance of vanadium oxide hydrate semi-microspheres and their graphene based composite microspheres in sodium-ion batteries

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A simple and versatile method for preparation of new crystalline vanadium oxide hydrate semi-microspheres is developed via a simple hydrothermal route, which are tested as a novel high-energy anode materials for sodium-ion batteries. The enhancement of electrochemical performance for the vanadium oxide hydrate electrode is offered by addition of graphene. The graphene-based vanadium oxide hydrate microsphere composite shows a high discharge capacity of 336.1 mA h g$^{-1}$ for the second cycle between a 0.05–3.0 V voltage limit at a discharge current density of 10 mA g$^{-1}$. A reversible capacity of 303.1 mA h g$^{-1}$ is retained after 20 cycles.

1. Introduction

Nowadays, there is a remarkable demand for rechargeable batteries with reversible and efficient electrochemical energy storage and conversion in the field of portable electronic consumer devices, electric vehicles, and large-scale electricity storage in smart and intelligent grids.  Sodium-ion batteries are promising rechargeable batteries owing the hugely abundant and low-cost sodium resources. However, it is difficult to find anode materials that can insert and remove sodium ions reversibly, just as commercial graphite does in the lithium-ion battery, which restricts the future application of sodium-ion batteries. The discovery of commercial and applicable anode materials for sodium-ion batteries is a matter of great urgency.

Current concerns have led to an increasing interest in low cost, high safety anode materials for sodium-ion batteries with a long cycle life and high energy-density. Now, researchers in growing numbers are starting to pay attention to the electrochemical properties of various anode materials, for example, carbon-graphene composites, carbon nanosheets, Sn, Sn–P composites, titanate, amorphous phosphorus–carbon composites, sulfides, organic sodium-ion batteries and so on.

Vanadium oxides and bronzes offer the advantages of being cheap, easy to synthesize, plentiful in the earth and with high-energy density. Therefore, they have attracted much interest in energy conversion and storage. A few researchers were attracted to study vanadium oxide, sodium vanadate nanostructures, hollow VOOH microspheres and ammonium vanadium bronzes as cathode materials for sodium-ion batteries. Little attention was attracted by vanadium oxide anode materials for sodium-ion batteries.

Herein, we report the synthesis of new crystalline vanadium oxide hydrate semi-microspheres via a simple hydrothermal method requiring low cost manufacturing and ultra-low power consumption. When they were used as anode materials for sodium-ion batteries, graphene based vanadium oxide hydrate microspheres showed better cycling stability and higher discharge capacity.

2. Experimental

Vanadium oxide hydrate semi-microspheres were prepared according to the following procedure. 1.44 g oxalic acid and 0.4 g ammonium metavanadate ($\text{NH}_4\text{VO}_3$) were dissolved in 30 ml deionized water under stirring at room temperature for 2 hours. After that, the mixture was transferred to a 50 ml Teflon-lined stainless autoclave, sealed, kept at 200 °C for 24 hours, cooled to room temperature, washed with deionized water and dried at 70 °C for 12 hours. Under the same procedure, graphene based composites were prepared with 1.44 g oxalic acid, 0.4 g ammonium metavanadate ($\text{NH}_4\text{VO}_3$) and 3 mg graphene.
The morphological characteristics of the as-synthesized materials were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM). Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G20 electron microscopy instrument. X-Ray diffraction (XRD) patterns were recorded on a diffractometer (Co Kα, PANalytical, and X’Pert). XPS measurements were performed with a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source (hν = 1486.6 eV). A pass energy of 160 eV was used to record the survey spectrum, while an 40 eV pass energy was used for high-resolution measurements. The element analyses were performed with a Vario-EL analyzer Solaar S2 and a Vario EL elemental analyzer from German Elementar Analysen Systeme GmbH. Thermal analysis measurements were performed using a Rigaku TG-DT Analyzer. Raman spectra were recorded at room temperature using a Micro-Raman spectrometer from English Renishaw. An Nd:YAG laser (532 nm) was used as the excitation source. A Land CT2001A battery tester was used to measure the electrode activities at room temperature.

The vanadium oxide hydrate semi-microspheres and their composites based on graphene were tested as anode materials for sodium-ion batteries. The negative electrode material composite consisted of the active material, a conductive material (super-pure carbon) and the binder, polyvinylidene difluoride (PVDF), in a weight ratio of 7/2/1. Na metal was used as the counter electrode. The electrolyte was 1 M NaClO4 dissolved in propylene carbonate (PC) solvent with the addition of 5 wt% fluoroethylene carbonate (FEC). The cells were charged and discharged between a 0.05–3.0 V voltage limit at a current density of 10 mA g⁻¹.

3. Results and discussion

Vanadium oxide hydrate and its composite based on graphene were prepared by a facile hydrothermal method, as described in the Experimental section. X-Ray diffraction was performed to identify the crystalline structure of the as-synthesized sample and the graphene based composite in Fig. 1a and b, respectively. For the graphene based composite, extra small peaks appear at 19.25°, 21.24°, 22.52°, 32.57°, 38.74°, 53.54° and 56.72°, which implies the presence of impure crystalline phase. The two samples cannot be ascribed to known compounds in the XRD database.

SEM observations show that the as-synthesized sample consists of semi-microspheres, as shown in Fig. 2a. The magnified SEM image confirms that semi-microsphere-like particles are consisted of superimposed platelets in Fig. 2b. Under our experimental conditions in the presence of superfluous oxalic acid, it is very difficult to get the vanadium precursor precipitate except from a blue solution after a short period of reaction time. A small amount of precipitate with a microsphere morphology was obtained at 200 °C for 24 h. Therefore, we did not perform time-dependent experiments to research the formation process of microspheres. According to our understanding and experiences, at the initial stage of the reaction, NH₄VO₃ was reduced to VO²⁺ by oxalic acid and the excess oxalic acid would react with VO²⁺ to form V(IV)O(C₂O₄)₂⁻. During hydrothermal treatment at 200 °C, primary crystallites were slowly formed and organized quickly into microspheres to minimize the surface free energy. In the further process of crystal growth or phase conversion, nanoflakes may form on the surface and assemble spontaneously to form regular arrays. As graphene was added, adjacent microspheres were obtained, as shown in Fig. 2c. The magnified SEM image shows that the microspheres consist of superimposed rods, as shown in Fig. 2d.

X-Ray photoelectron spectroscopy (XPS) was performed to identify the elemental covalence of V. The V2p high-resolution XPS spectrum of the as-synthesized sample shows a wide peak at 516.6 eV, corresponding to V(IV) in Fig. 3. Elemental analysis (EA) shows that there is no N element in the as-synthesized sample. TG curve (Fig. 4) shows that there is a weight loss of 19.4% from 250 to 400 °C, due to the release of H₂O. Based on the above analysis, the formula of the as-synthesized sample can be expressed as VO₂·1.65H₂O.
The Raman spectrum of graphene-based vanadium oxide hydrate composite exhibits a series of bands at 142, 194, 281, 405, 520, 689, 990, 1351 and 1589 cm\(^{-1}\), the same as those of V\(_2\)O\(_5\) in Fig. 5. The peak at 990 cm\(^{-1}\) is characteristic of the V=O bond. Therefore, the Raman spectrum shows that there are at least two kinds of carbon (disordered carbon and graphene) in the graphene-based composite. Elemental analysis (EA) was used to analyze the content of graphene, which was 5.6 wt% graphene. Transmission electron microscopy (TEM) was further performed to study graphene based composite. Black sphere-like particles surrounded by thick layers of thin graphene sheets were observed and are displayed in Fig. 6a. Fig. 6b shows that an image of a graphene block can be linked to the surface of the microspheres. Fig. 6c and d show that some graphene is dispersed to the fringe of microspheres. Thus, we can conclude that graphene appears on the surface of vanadium oxide hydrate in a different amounts.

The electrochemical performances of VO\(_2\cdot1.65\)H\(_2\)O and its graphene composite were evaluated. Fig. 7a and b show the 1st, 2nd and 20th charge–discharge profiles of the graphene based composite and VO\(_2\cdot1.65\)H\(_2\)O semi-microspheres at a current density of 10 mA g\(^{-1}\), respectively. It can be observed that both have similar shaped charge–discharge profiles, but the graphene based composite shows better charge properties for the superposition of the charge curves. Fig. 7c shows their cycling performance. The graphene based composite electrode delivers a second discharge capacity of 336.1 mA h g\(^{-1}\). A reversible capacity of 303.1 mA h g\(^{-1}\) remains after 20 cycles. As for VO\(_2\cdot1.65\)H\(_2\)O semi-microspheres, the second discharge capacity is 338.8 mA h g\(^{-1}\). A reversible capacity of 181.9 mA h g\(^{-1}\) remains after 20 cycles. The second discharge capacities are 338.8 and 336.5 mA h g\(^{-1}\) for VO\(_2\cdot1.65\)H\(_2\)O semi-microspheres and graphene based microspheres, which correspond to 1.42 and 1.41 Na\(^+\) inserting into one VO\(_2\cdot1.65\)H\(_2\)O.
The possible electrochemical process is as follows: VO$_2$·1.65H$_2$O$^+$ $\leftrightarrow$ Na$_x$VO$_2$·1.65H$_2$O (0 $< x \leq$ 1.42). The capacity decay during cycling is ascribed to the bad conductivity of the electrode materials, irreversible sodium ion insertion and the deintercalation and slow transfer rate of sodium ion for large ion radii. Further work will concentrate on overcoming those problems by the modification of electrode materials’ crystalline structure via intercalation of Na$^+$ and improving the electrolyte, glass fiber film, binder and conductive materials. For example, Super P, and sodium carboxymethyl cellulose–poly (acrylic acid) (1 : 1) could be used to take the place of super-pure carbon and PVDF, respectively. Decreasing the particle size is also a consideration for the improvement of electrochemical performance. It would be apt to prepare larger particles at the sub-micrometer/micrometer scale via hydrothermal route. Sol–gel, solvo-thermal and solid phase syntheses may be facile methods to prepare nano-sized particles. Small particles, such as nanoparticles, have a high surface area and would reduce the ionic and electronic diffusion distance to promote the easier penetration of sodium ions and electrons into the electrode materials. Therefore, a notable improvement of electrode performance would be obtained.

Electrochemical impedance measurements were performed to elucidate the difference in electrochemical properties of graphene based composite and VO$_2$·1.65H$_2$O in Fig. 8. It can be found that both have the same fitting impedance circuit model and similar total impedance. The equivalent electrical circuit consists of an active electrolyte resistance $R_e$ in series with the parallel combination of the double-layer capacitance $C_1$, $C_2$ and the impedance of a faradaic reaction. In this model, the impedance of a faradaic reaction consists of an active charge transfer resistance $R_{ct}$ and a specific electrochemical element of diffusion $W$, called a Warburg element.

### 4. Conclusions

VO$_2$·1.65H$_2$O semi-microspheres and their composites based on graphene microspheres were prepared with cheap reagents on a large scale via a facile template-free method. The enhancement of electrochemical performance for VO$_2$·1.65H$_2$O semi-microspheres is offered by addition of graphene. This facile method is significant for the fabrication of other novel crystalline sodium-ion battery anode materials with high discharge capacity.

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### Notes and references