V₂O₃ nanoparticles anchored onto the reduced graphene oxide for superior lithium storage

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Abstract: The V₂O₃/reduced graphene oxide (V₂O₃-rGO) 3D gels are synthesized by a hydrothermal reaction and annealing process, using graphene oxide and NH₄VO₃ as raw materials. The V₂O₃ nanoparticles with the size of 4-10 nm are homogeneously and closely anchored onto the graphene foam. When used as anode material for lithium-ion batteries, the V₂O₃-rGO 3D gel exhibits high capacity (786 mAh g⁻¹ at 0.07 A g⁻¹), good cycle stability (350 mAh g⁻¹ at 1.86 A g⁻¹ after 1000 cycles) and excellent rate capability (192 mAh g⁻¹ at 37.2 A g⁻¹) as well as distinguished electrochemical properties at a wide temperature range of 0-75 °C. The desirable electrochemical performance should be attributed to the high content of V₂O₃, the nanoscale size of V₂O₃ and the 3D porous graphene network.

Keywords: Anode material; V_2O_3 ; Graphene; Lithium-ion batteries

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been reached a consensus as the most dominant power source nowadays, which is the most promising energy storage technology for electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their long cycle life and high energy density [1-4]. Because the low theoretical capacity (372 mAh g^{-1}) of traditionally graphite can't satisfy the requirements of high-performance LIBs for EVs or HEVs, many endeavors have been concentrated on exploring novel anode materials, such as transition metal oxides [5], molybdenum disulfide (MoS_2) [6], stannum (Sn) [7] and silicon (Si) [8]. Among the various anode materials candidates, vanadium trioxide (V_2O_3) has been recognized as one of the most promising and attractive one for LIBs, owing to its high theoretical capacity (1070 mAh g^{-1}), relatively low discharge potential, low-cost, safety and environment-friendly [9-12]. However, V_2O_3 suffers from volume change during cycle process, leading to the construct instability, further leading to poor performance stability and application. In addition, the low conductivity of V_2O_3 has become an obstacle factor to limit its application for energy storage. More importantly, the aggregation and uneven dispersion of V_2O_3 would also impact on its electrochemical properties [13]. To overcome these shortcomings, different V_2O_3 composites have been designed with various carbon materials (carbon nanotube [14], carbon fiber [15], ect.) to increase their conductivity and prohibit the electrode directly connect with electrolyte to modify the cycle performance. For instance, the synthesized V_2O_3 /ordered mesoporous carbon nanocomposite has a reversible capacity of 536 mAh g^{-1} at 0.1 A g^{-1} after 180 cycles [16]. The in-situ carbon-coated yolk-shell V_2O_3 microspheres shows a capacity of 437.5 mAh g^{-1} at a current density of 0.1 A g^{-1} after

100 cycles [17]. Obviously, it is still urgent to further improve the electrochemical performance of V_2O_3 -based anodes to meet the requirements of LIBs for EVs and HEVs.

Herein, we develop an efficient approach to fabricate the 3D porous V_2O_3 /reduced graphene (V_2O_3 -rGO) gels via hydrothermal treatment using graphene oxide, NH_4VO_3 and ammonia as raw materials. V_2O_3 nanoparticles are tightly and homogeneously anchored on the ultrathin rGO sheets with the size of 4-10 nm. Importantly, the porous and continuous graphene network not only provides a short pathway for rapid Li^+ diffusion and electron transportation, but also can act as a buffering effect to inhibit the huge volume expansion of pure V_2O_3 during the repeated lithiation/delithiation process [18]. Thus, the resultant V_2O_3 -rGO 3D gels exhibit excellent electrochemical performance for lithium storage with high reversible capacity, great high-rate capability and remarkable long cycle stability.

2. Experimental

2.1 Synthesis of V_2O_3 -rGO 3D gels

All reagents were analytical grade and used without further purification, purchased from Aldrich. The graphene oxide was prepared by using the modified Hummers method [19], and then the V_2O_3 -rGO 3D gels were synthesized as the following procedures. 0.16 g NH_4VO_3 powders were dispersed in 80 ml graphene oxide solution (2 mg ml^{-1}) by bath sonication for 30 min, and then 2 ml NH_3H_2O was added into the solution [20]. Subsequently, the resulting mixture was transferred to the Teflon-lined autoclave and hydrothermally treated at $180\text{ }^{\circ}\text{C}$ for 12 h, and then the VO_x -GO 3D gels were freeze-dried for 24 h. Finally, the VO_x -GO 3D gels were annealed at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ to $500\text{ }^{\circ}\text{C}$ for 3-12h under the 5% H_2 /Ar atmosphere, resulting in V_2O_3 -rGO-x 3D gels, where x stands for the annealing time.

For comparison, the rGO 3D gels were also synthesized, and the fabrication procedures were same as the preparation of the V₂O₃-rGO 3D gels just without NH₄VO₃ powders.

2.2 Materials characterization

The morphology and microstructure of the V₂O₃-rGO gels were investigated via field emission scanning electron microscopy (FESEM, JSM 7500, JEOL, Japan), transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN), X-ray diffraction (XRD, Rigaku D/max2500PC, Cu K α), and Vario EL cube (Elementar, Germany).

The specific surface area was executed via a Quantachrome QDS-MP-30 analyzer (USA) at 77 K. Thermogravimetric analysis (TG) was performed on a TA Instrument Q600 Analyser under air flow. X-ray photoelectron spectra were recorded by a Thermo Electron Corporation ESCALAB 250 XPS spectrometer using a monochromatized Al K α radiation with 200 eV pass energy with 30 eV step over the sample (500 μ m $\times$ 500 μ m).

2.3 Electrochemical measurements

The working electrode was constituted by the active materials, acetylene black and the polyvinylidene fluoride adhesive bonding on the stainless steel with the mass percent of 80:10:10, then dried at 120 °C for 12 h in the vacuum oven. To fabricate the lithium ion battery, the counter-electrode is metallic lithium foil, the electrolyte is LiPF₆ in ethylene carbonate, dimethyl carbonate and diethyl with the volume ratio of 1:1:1, and the separator is polypropylene film, then the lithium ion batteries were assembled into coin-type. The performance of charge and discharge was measured by the CT2001A system at a voltage range from 0 to 3V with different current density, and the nature of electrochemical impedance spectroscopy was tested by Autolab equipment (PGSTAT302N).

3. Results and discussion

The fabrication of V_2O_3 -rGO 3D gels are schematically illustrated in Figure 1. The VO_x -GO 3D gels were fabricated by hydrothermal using graphene oxide, NH_4VO_3 and $\text{NH}_3\text{H}_2\text{O}$ as raw materials at 180°C for 12 h. Then the resultant VO_x -GO 3D gels were further treated by freeze-drying, giving VO_x -GO 3D foam. The hybrid foam was subsequently annealed at 500°C for 3-12 h under H_2/Ar atmosphere, resulting in V_2O_3 -rGO 3D gels.

To explore the crystal structure and phase of the V_2O_3 -rGO 3D gels, X-ray diffraction measurement (XRD) was employed. As shown in Figure 2a, all of the diffraction peaks are precisely indexed to the rhombohedral crystalline phase V_2O_3 (JCPDS card no. 34-0187) [21]. The two weak peaks at about 26° and 43° correspondingly related to the graphite carbon and the restacked graphene nanosheets. In addition, with the annealing time extending from 3 to 12 h, the diffraction peaks of V_2O_3 get stronger and sharper, indicating that it is effective to accommodate the annealing time to adjust the size of V_2O_3 nanoparticles. The porous nature of the V_2O_3 -rGO 3D gels was further demonstrated by nitrogen physisorption measurement, as shown in Figure 2b. The nitrogen adsorption/desorption isotherms belong to the typical IV hysteresis loops, illustrating that the micropores and mesopores are coexistence. Barrett-Joyner-Halenda (BJH) calculations show that the pore size distributes in the range of 1 to 20 nm (Figure 2c). The specific surface area of V_2O_3 -rGO-3h sample is up to $107.6 \text{ m}^2 \text{ g}^{-1}$ calculated by Brunauer-Emmett-Teller (BET) equation. The rich porous structure was derived from the etching effect of ammonia during the hydrothermal process and the deprivation of water during the freeze-drying process as well as the reduction reaction between H_2 and oxygen-containing functional groups of graphene oxide during the annealing process.

If the annealing time was extended from 3 to 6 h, the specific surface area of V_2O_3 -rGO-6h sample increased from 107.6 to 344.8 $m^2 g^{-1}$, owing to the etching effect of H_2 . Interestingly, if the annealing time was further extended, the specific surface area of V_2O_3 -rGO-9h and V_2O_3 -rGO-12h samples decreased to 150.4 and 48 $m^2 g^{-1}$, respectively, because part of pore structure would be collapsed. The weight contents of rGO and V_2O_3 in the V_2O_3 -rGO-6h gel are calculated with 44 and 56 wt%, respectively (Figure 2d).

The elemental components and contents of V_2O_3 -rGO 3D gels were elucidated by elemental analysis and X-ray photoelectron spectroscopy (XPS) measurement. Based on the XPS surveys (V_2O_3 -rGO-12h illustrated in Figure S1), it is distinct that carbon, nitrogen, oxygen and vanadium species are assumed in all V_2O_3 -rGO 3D gels (Figure 3a), and the detail contents are illustrated in Table S1. The fitted C 1s peaks show three evident peaks at 284.7, 285.9 and 286.2 eV (Figure 3b), attributed to the pure graphitic carbon, C-N bond and C-O bond, respectively [19]. It is confirmed that the nitrogen was also doped into rGO during the synthesis process. As illustrated in Figure 3c, the complex N 1s peaks can be fitted to three types of nitrogen at 398.3, 399.9 and 401.3 eV, corresponding to pyridinic, pyrrolic and graphitic nitrogen, respectively [22]. The O 1s peaks at 530.1 eV derived from O-V bond to demonstrate oxidized vanadium (Figure 3d) [23]. The high-resolution V 2p³ spectrum can be fitted to three peaks at the binding energies of 516.0, 516.8 and 517.6 eV (Figure 3e), separately corresponding to the V^{3+} , V^{4+} and V^{5+} in oxidized vanadium [24]. Owing to the coexistence of oxygen free radical produced by the graphene oxide during the annealing process, part of V^{3+} on the surface of V_2O_3 nanoparticle will be oxidized into V^{4+} or V^{5+} , resulting in V^{3+} , V^{4+} and V^{5+} coexisting on the surface of V_2O_3 nanoparticle, while the main valence of V in the matrix of V_2O_3 nanoparticle is V^{3+} .

because of the main reduction reaction between V_2O_5 and H_2 .

To further identify the microstructure of V_2O_3 -rGO-6h sample, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out (Figure 4). Three-dimensional structure (insert in Figure 4a) and porous network structure with ultrathin nanowalls are observed (Figure 4a), which is resemblant of the reported graphene oxide hydrogels [25]. A typical TEM image (Figure 4b and 4c) reveals that V_2O_3 nanoparticles with the size of 4-10 nm are homogeneously and tightly anchored onto the rGO sheets, the interlayer distance is 0.248 and 0.272 nm (Figure 4d), agreeing well with the spacing both (110) and (104) plans of V_2O_3 crystals, respectively [26].

The electrochemical performance of V_2O_3 -rGO-6h 3D gel for lithium storage was primary tested by galvanostatic charge-discharge measurement at different current densities. Remarkably, the V_2O_3 -rGO-6h sample shows excellent stability at 0.07 A g^{-1} after 50 cycles (Figure 5a). A high reversible capacity of 786 mAh g^{-1} is achieved at a current density of 0.07 A g^{-1} after 50 cycles (Figure 5a and 5b). This value is much higher than the rGO gel (440 mAh g^{-1}) and other V_2O_3 -rGO samples (400-550 mAh g^{-1} , Figure S2) as well as reported V_2O_3 composites (131-665 mAh g^{-1}) [23]. Importantly, the V_2O_3 -rGO-6h sample exhibits distinguished high-rate capabilities at different current densities from 0.07 to 37.2 A g^{-1} (Figure 5c). The reversible capabilities of V_2O_3 -rGO-6h sample is up to 201 and 192 mAh g^{-1} at 18.6 and 37.2 A g^{-1} , respectively (Figure 5b and 5c), which are significantly higher than the contrast rGO gel and other V_2O_3 -rGO samples (Figure S2). When the current rate again reduced back to 0.07 A g^{-1} , the reversible capacity could be recovered and maintained at 710 mAh g^{-1} . Above results demonstrate that the V_2O_3 -rGO-6h sample shows the best high-rate performance among rGO gel and V_2O_3 -rGO gels, which should

attribute to its appropriate size of V_2O_3 nanoparticles, high specific surface area and high content of V_2O_3 . In addition, the series of V_2O_3 -rGO samples keep no attenuation at 1.86 A g^{-1} after 1000 cycles (Figure 5d and Figure S2), indicating the excellent long cycle performance, which should be attributed to the 3D porous network microstructures. Compared with the rGO gel, the reversible capability of V_2O_3 -rGO-6h gel is 350 mAh g^{-1} at a current density of 1.86 A g^{-1} , which is about three times than that of the rGO sample and higher than of other V_2O_3 -rGO samples (Figure S2). To further investigate the high and low temperature electrochemical performance of the V_2O_3 -rGO anode materials, the samples were tested from 0 to $75\text{ }^\circ\text{C}$, and the rGO electrode was also tested under the same conditions (Figure 5e). The V_2O_3 -rGO-6h sample shows perfect stability and good high and low temperature performance at a current density of 1.86 A g^{-1} . To explore the reason of the excellent electrochemical performance of the V_2O_3 -rGO-6h sample, the electrochemical impedance spectroscopy (EIS) measurement was employed after rate cycles and the equivalent circuit diagram of AC impedance was shown in Figure S3. It is noteworthy that the charge transfer resistance (R_{ct}) of V_2O_3 -rGO-6h electrode is only $11.0\text{ }\Omega$, which is much lower than that of rGO gel ($40.7\text{ }\Omega$) and other V_2O_3 -rGO gels (Table S2). Although V_2O_3 has a higher electrical and ionic resistances than reduced graphene oxide, the R_{ct} value also relates to the pore structure and the combining strength among rGO, because NH_4VO_3 has significant effects on the pore structure and volume of rGO gel (Figure S4) or V_2O_3 -rGO gels during the hydrothermal process, just like the effects of annealing time on the specific surface area of V_2O_3 -rGO gels. The excellent electrochemical performance of V_2O_3 -rGO-6h electrode should attributed to the high content of V_2O_3 active, the graphene network and the porous structure. Detailly, the high content of V_2O_3 can achieve a high

reversible capacity. The continuous graphene network provides a short pathway for rapid Li^+ diffusion and electron transportation. Importantly, the porous network structure not only can effectively promote the entrance of electrolyte and maintain stability of the structure during the charge-discharge process [27,28], but also can act as a buffering effect to inhibit the huge volume expansion of pure V_2O_3 during the repeated lithiation/delithiation process.

4. Conclusions

We have developed an efficient approach to fabricate V_2O_3 -rGO 3D gel via hydrothermal treatment with the graphene oxide and NH_4VO_3 as raw materials, then subsequently annealing at 500 °C for 6 h under H_2/Ar atmosphere. The V_2O_3 -rGO-6h 3D gel exhibits excellent electrochemical performance, including the high reversible capacity, the excellent high-rate capacity, the distinguished electrochemical performances at the temperature ranging of 0-75 °C and the good long cycling stability for lithium storage. The excellent electrochemical performance should be attributed to the following reasons. Detailly, the high content of V_2O_3 nanoparticles combined with the homogeneous dispersion and nano-size microstructure can improve the reversible capacity. The graphene with multi-porous structure and continuous 3D network as backbone could effectively inhibit the volume expansion of V_2O_3 and prevent aggregation during the electrodes working processes. Moreover, the porous and continuous graphene network provides a short pathway for rapid Li^+ diffusion and electron transportation. The remarkable electrochemical performance of V_2O_3 -rGO-6h 3D gel make a great foundation for the practical application of lithium storage. We believe that the synthesis protocol would provide new suggestions to realize the fabrication of other metal anchoring onto graphene with wide applications in fuel cells, lithium ion batteries and other electrochemical and catalytic applications.

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Figure 1. Schematic illustration of synthesis of V_2O_3 -rGO 3D gels

Figure 2. XRD patterns (a), nitrogen adsorption/desorption isotherms (b), pore size distribution (c) and TG curves (d) of the V_2O_3 -rGO 3D gels

Figure 3. (a) XPS survey of the V_2O_3 -rGO-3h, V_2O_3 -rGO-6h and V_2O_3 -rGO-9h samples.

High-resolution XPS spectra of C 1s (b), N 1s(c), O 1s (d) and V 2p³ (e)

Figure 4. Typical SEM (a), TEM (b,c) and HRTEM (d) of the V_2O_3 -rGO-6h 3D gel

Figure 5. Charge-discharge curves of V_2O_3 -rGO-6h sample at a current density of 0.07 A g^{-1} (a) and 0.07 - 37.2 A g^{-1} (b). (c) The rate capacities of V_2O_3 -rGO-6h and rGO samples at the current density from 0.07 to 37.2 A g^{-1} . (d) Cycling performance of V_2O_3 -rGO-6h and rGO samples at 1.86 A g^{-1} for 1000 cycles. (e) The cycling performance of V_2O_3 -rGO-6h and rGO samples at 1.86 A g^{-1} at the different temperature from 0 to 75°C . (f) Nyquist plots of V_2O_3 -rGO-6h and rGO samples after rate-cycling with an amplitude of 5 mV