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COMMUNICATION

Solvothermal synthesis of GO/V₂O₅ composites as cathode material for rechargeable magnesium batteries

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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Herein GO/V₂O₅ composites as cathode material for rechargeable magnesium batteries are presented. Synthesized by solvothermal reaction of vanadium oxytriisopropoxide (VOT) and graphene oxide (GO), the GO/V₂O₅ composites exhibit greatly enhanced electrochemical performances, attained a high discharge capacity up to 178 mAh/g at rate of 0.2 C.

Rechargeable magnesium (Mg) batteries have been long considered as a future prospective alternative energy storage device¹⁻³. Mg possesses several characteristics that rank it as one of the most auspicious metal anode for high energy-density batteries. Due to its bivalency and density, its specific volumetric capacity reaches 3833 mAh/cm³, much higher than that for Li metal (2046 mAh/cm³). Meanwhile, Mg is a benign and abundant metal being in the earth's crust. Furthermore, Mg is not plagued by dendrite formation, which is a significant safety issue that has dissuaded the commercialization of rechargeable batteries utilizing a lithium metal anode.³⁻⁵

Although rechargeable Mg batteries possess attractive advantages in competition, researches of the batteries are still in infancy. The major obstacles that prevent Mg batteries from practices are (1) the kinetically sluggish diffusion of Mg in cathode materials; (2) the high polarizing ability of the divalent Mg²⁺ cation.⁶ Thus, the search for appropriate cathode material is intrinsically urging. Aurbach *et al.* combined Chevrel phase Mg_xMo₃S₄ cathode with 0.25M Mg(AlCl₂EtBu)₂/THF electrolyte in 2000,² which achieved excellent performance. To date, various cathode materials such as Chevrel phase M_xMo₃T₈ (M=metal, T=S, Se),⁷ Mg_xM_ySiO₄ (M=Mn, Fe, Co, x+y=1),⁸⁻¹⁰ transition metal oxide (MnO₂),¹¹ and conductive sulfur-containing material,¹² have been successfully used as

cathode materials to improve the electrochemical properties of rechargeable Mg batteries.¹³ Unfortunately, the actual performances of rechargeable Mg batteries achieved are not as desired due to the bad cycling.

In order to overcome the problems which are perplexed the development of rechargeable Mg batteries, V₂O₅ has long been recognized as a promising alternative.¹⁴⁻¹⁷ Significantly results are presented for dry V₂O₅ gels,^{16,17} but the measurement is under severe condition with aqueous electrolyte solution (e.g., 1M Mg(ClO₄)₂ + 1M H₂O/acetonitrile) and lower current (C/40, i.e., duration of one cycle is about 40 h), as well as in rapid capacity fading. To improve the capacity and cycle stability for rechargeable Mg batteries, GO/V₂O₅ composites as an effective material were prepared by solvothermal reaction, which exhibited remarkably enhanced cycling performance as cathode material in LIBs.¹⁸⁻²¹

In a typical procedure (Fig. 1), 10 mg of graphene oxides (GO) was dispersed in 35 mL of isopropanol (IPA) by ultrasonication for 2h,²² followed by addition of 200 μL of vanadium

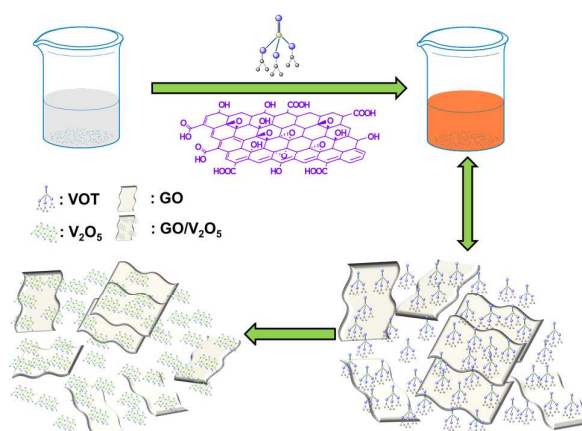


Fig. 1 Schematic illustration of the fabrication process of GO/V₂O₅ composites for rechargeable Mg batteries.

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† Electronic Supplementary Information (ESI) available: Experimental section, XRD pattern, SEM images and some more details of rechargeable Mg batteries. See DOI: 10.1039/x0xx00000x

oxytriisopropoxide (VOT). Then, the mixture was sealed in a Teflon-lined autoclave and solvothermally treated at 200 °C for 12h. The precipitate was collected by centrifugation, washed thoroughly with isopropanol (IPA) and deionized water several times (see ESI). Ultimately, GO/V₂O₅ composites were obtained from a calcinating process at 800 °C in Ar.

The electrochemical performances of the as-obtained composites are tested as cathode for rechargeable Mg battery. The electrode was prepared by pressing a powder mixture of GO/V₂O₅ composites, acetylene black, and poly(vinylidene fluoride) (PVDF) in a weight ratio of 80:10:10 onto an Al foil. After drying, the foil was cut into pellets with 2.0 mg of electrode materials for every pellet. Then the pellets were dried at 80 °C overnight under vacuum. Coin-type cells were assembled in a glove box, with magnesium foil as the counter and reference electrode, Celgard 2400 as the separator, and 0.25M Mg(AlCl₂EtBu)₂/THF as the electrolyte. The charge-discharge performance was tested between 1.0 and 2.8 V using the LAND CT2001A multichannel battery testing system at room temperature.

As-prepared GO/V₂O₅ composites were characterized by X-ray diffraction (XRD) employing a Bruker D8 Focus X-ray Diffraction with Cu K α radiation. The morphology and structure were obtained on SEM (Hitachi S-4800) and TEM (Tecnai G2). X-ray photoelectron spectroscopy (XPS) was collected on Thermo ESCALAB 250 electron spectrometer.

Fig. 2 shows the powder X-ray diffraction (XRD) pattern of GO/V₂O₅ composites. All the diffraction peaks can be indexed to orthorhombic V₂O₅ ($a=11.512$ Å, $b=3.564$ Å, $c=4.368$ Å, JCPDS card no. 65-0131). To give insight into the crystalline structure evolution of GO/V₂O₅ composites, XRD patterns of the precursors is exhibited in Fig. S2. Clearly, there is obvious change in the diffraction peak when GO/V₂O₅ composites were heated at 800 °C.

The SEM and TEM micrographs of the as-prepared GO/V₂O₅

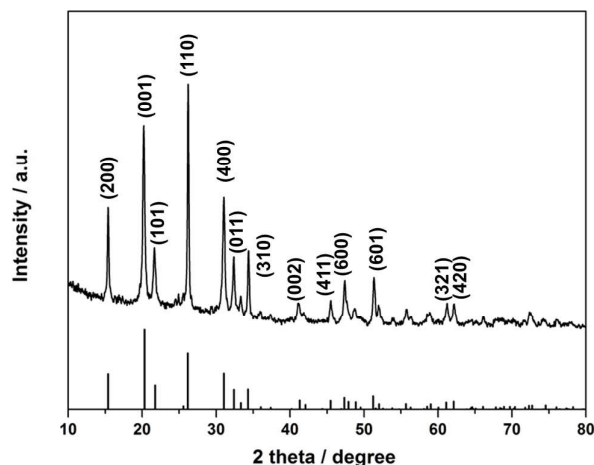


Fig. 2 The X-ray diffraction (XRD) pattern of as-synthesized GO/V₂O₅ composites.

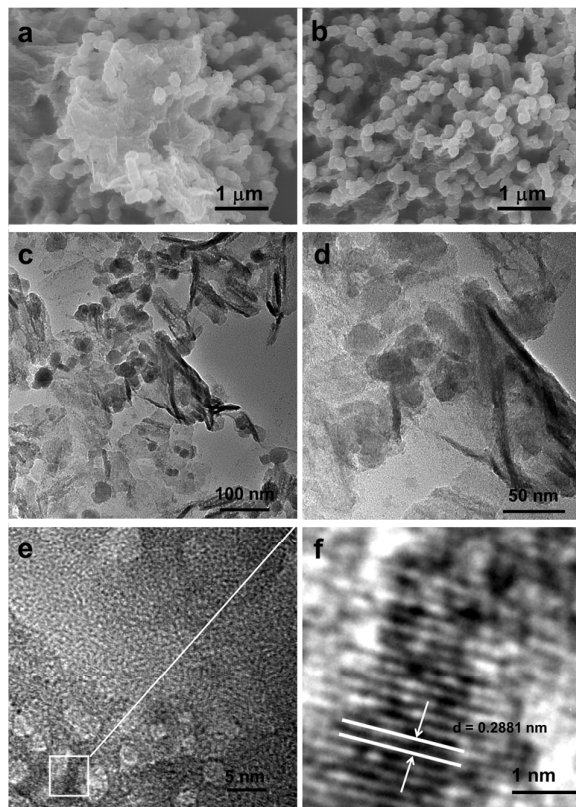


Fig. 3 The SEM and TEM micrographs of as-synthesized GO/V₂O₅ composites. (a)(b) SEM images. (c)(d) TEM images. (e)(f) HRTEM images.

composites are shown in Fig. 3. From SEM images in Fig. 3a and Fig. 3b, it can be seen that the GO and V₂O₅ microparticles are well cohered. The V₂O₅ microparticles are wrapped up around GO sheets, particularly exhibited in Fig. 3b. The TEM micrographs (Fig. 3c and Fig. 3d) clearly demonstrate the firm contact between GO and V₂O₅ microparticles. The SEM and TEM images disclose the *in-situ* growth relationship between GO and V₂O₅ microparticles. In comparison with Fig. 3e, Fig. 3f and Fig. S7, the weakness of crystallinity degree of V₂O₅ microparticles presented in Fig. 3f reveals that the existence of GO has an effect on structure of V₂O₅. In HRTEM image (Fig. 3f), the fringe spacing of 0.2881 nm is corresponding to the (400) plane of orthorhombic V₂O₅. The conclusion drawn from the discussion of SEM and TEM images is that the *in-situ* grown GO/V₂O₅ composites could gain well-deserved electronic conductivity and obtain large reaction areas, where Mg ions would be absorbed, then exchanged and diffused.

XPS is recognized as a useful method to accurately determine the chemical compositions and electronic structures of nanomaterials. Fig. 4a shows the survey spectrum of as-obtained GO/V₂O₅ composites, from which it

could be obviously noted that the characteristic peaks of O, C and V exist in the GO/V₂O₅ composites. The high-resolution

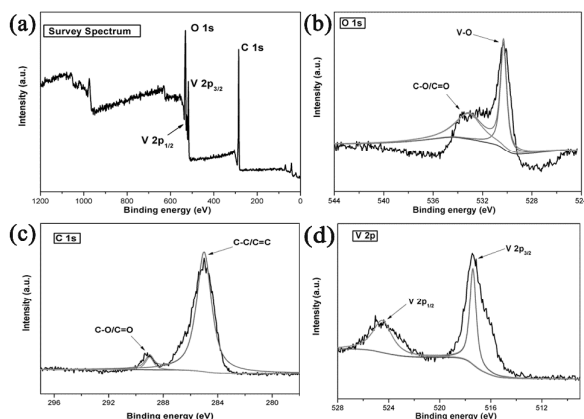


Fig. 4 (a) Survey XPS spectrum of as-synthesized GO/V₂O₅ composites. XPS spectrum for (b) O 1s, (c) C 1s, and (d) V 2p regions of as-synthesized GO/V₂O₅ composites.

spectrum of as-obtained GO/V₂O₅ composites, from which it could be obviously noted that the characteristic peaks of O, C and V exist in the GO/V₂O₅ composites. The high-resolution XPS spectrum of the O 1s, C 1s and V 2p for the GO/V₂O₅ composites are displayed in Fig. 4b-d. As shown in Fig. 4c, we can clearly find a peak at 284.6 eV, which is consistent with the binding energy of C 1s. One more broad peak at around 289 eV was observed, which is attributed to C-O/C=O bonding, confirming the existence of GO. The about 8 eV gap between V 2p_{3/2} and V 2p_{1/2} is a typical value for V⁵⁺ in the standard line of XPS spectrum. However, the high-resolution XPS spectra of V 2p_{3/2} and V 2p_{1/2} in Fig. 4d is obviously observed at 517.2 eV and 524.9 eV, respectively, which increases nearly 5 eV. According to rationale of XPS and the synthesis of GO/V₂O₅ composites, the increasing of binding energy would be caused by the multi-electron excitation and multiplet splitting. Valence shell electrons of vanadium element transit to the higher energy level. Relaxation effect is generated by the decline in kinetic energy of photoelectron. XPS spectrum

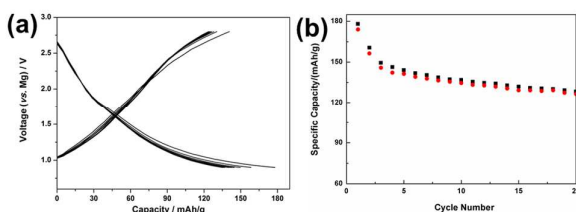


Fig. 5 Electrochemical properties of as-synthesized GO/V₂O₅ composites: (a)(b) Electrochemical cycling performance curves of GO/V₂O₅ composites at a rate of 0.2 C.

reveals that the superior recombination of GO and V₂O₅ microparticles, which is mentioned *in-situ* growth of V₂O₅ microparticles on GO, transforms coordinating ability of vanadium element.

Intrigued by the structural features of GO/V₂O₅ composites for rechargeable Mg batteries, we employed electrochemical measurements to test the behaviours of the as-obtained GO/V₂O₅ composites. Fig. 5a and Fig. 5b show cycling performances and discharge-charge profiles of GO/V₂O₅ composites, in which the current density was fixed at rate of 0.2 C, and the potential is in the range 1.0 to 2.8 V. The first discharge capacity of GO/V₂O₅ composites is 178 mAh g⁻¹. According to the equation mentioned by Gregory *et al.*,^{1,6,21} the GO/V₂O₅ composites as cathode material for rechargeable Mg batteries could host about 0.6 Mg ions per formula unit (see ESI). Both discharge and recharge curves do not show clear plateaus. The reversible discharge capacity of the second and third cycles fades to 160 and 150 mAh g⁻¹ and diminishes tardily for the subsequent cycles, still remains 140 mAh g⁻¹ at 20th cycle, and the SEM micrographs of GO/V₂O₅ composites after cycling can be seen in Fig. S11b. The significant capacity drop at the beginning cycles can be ascribed to the formation of MgO passivated film.

On the basis of the above results, the enhanced cycle life of the GO/V₂O₅ composites cathode can be attributed to the architecture features of the *in-situ* grown composites structure as well as the synergistic effects of GO and V₂O₅: (1) The disordered structure and superior recombination can improve the electronic conductivity, shorten the Mg²⁺ and electrolyte molecules' transportation length and increase the electrolyte/active material contact area as well as facilitate the penetration ability of the electrolyte molecules. (2) The disordered structure and superior recombination can also retard the volume change during repeated charge-discharge cycles.

In summary, a new kind of GO/V₂O₅ composites has been prepared as a cathode material for rechargeable magnesium batteries. The integration of GO and V₂O₅ microparticles results in significantly enhanced performances. As-prepared GO/V₂O₅ composites can deliver a high capacity of 178 mAh g⁻¹ and maintain 140 mAh g⁻¹ even after 20 cycles, which provide a new direction to explore cathode materials for rechargeable Mg batteries. This described synthetic strategy could motivate further exploration for next-generation, high-performance rechargeable Mg batteries or other fields of energy storage and conversion.

This work is financially supported by the National Natural Science Foundation of China (Grant no. 20111061).

Notes and references

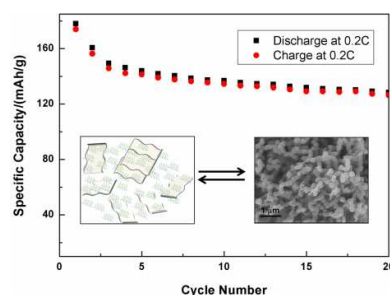
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Graphic abstract and table of contents

Solvothermal synthesis of GO/V₂O₅ composites as cathode material for rechargeable magnesium batteries

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GO/V₂O₅ composites prepared from solvothermal reaction exhibited greatly enhanced electrochemical performances as cathode material for rechargeable magnesium batteries.