Vanadium Oxide/Graphene Nanoplatelet as a Cathode Material for Mg-Ion Battery

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Abstract
The aim of the present work is to introduce a high performance cathode for magnesium-ion batteries. A simple ball mill process is employed to synthesize (V$_2$O$_5$)$_{1-x}$(Graphene Nanoplatelets (GNP))$_x$ nanocomposite, (where $x = 0, 5, 10, 15, 20$ and 25 wt.% GNP). The synthesized samples are characterized using scanning electron microscope (SEM), X-ray diffraction (XRD) technique, impedance spectroscopy, cyclic voltammetry and charge-discharge test. The maximum conductivity of the investigated samples was found to be $6 \times 10^{-1}$ S/cm for optimum composite film (25 wt.% GNP) at room temperature. Room temperature rechargeable magnesium batteries are constructed from Mg as anode material, (V$_2$O$_5$)$_{1-x}$(Graphene Nanoplatelets (GNP))$_x$ as a cathode material and the simple non-aqueous electrolyte based MgNO$_3$·6H$_2$O. Mg/V$_2$O$_5$ cells employing as-prepared electrolyte exhibit initial discharge capacity $\sim 100$ mAhg$^{-1}$ while Mg/(V$_2$O$_5$/GNP (x = 25t.%) cathode produces a lower initial capacity of $\sim 90$ mAhg$^{-1}$. The high initial discharge capacity of V$_2$O$_5$ can be attributed to the presence of a large (001) interlayer spacing ($\sim 11.53$ Å) for facile Mg$^+$ insertion/extraction.

Keywords
Magnesium Batteries, Vanadium Oxide, Graphene, Conductivity

1. Introduction
Costly Cheveral phase Mo$_6$S$_8$ cathode, and complicated electrolyte based Mg [ALCL$_2$BuET]$_2$/tetrahydofuran (volatile) are traditional materials in early rechargeable magnesium batteries, although, these batteries suffer from low voltage, low energy density, kinetic sluggish of Mg$^{2+}$ insertion/extraction [1] [2] [3] [4]. Various cathode materials for magnesium battery have been suggested in recent years, such as TiS$_2$ nanotubes [5], MoS$_2$ [6], GeO$_2$ [7], TiS$_3$ [1], V$_2$O$_5$ [8] and MnO$_2$ [9]. Vanadium pentaoxide (V$_2$O$_5$)

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is a semiconductor material (E\textsubscript{g} = 2.4 eV), where tuning of fermi level due to ion insertion is expected. The intercalation reaction of Mg in V\textsubscript{2}O\textsubscript{5} can be written as follows: 
\[ \text{Mg} + \text{V}_2\text{O}_5 \leftrightarrow \text{Mg}_x + \text{V}_2\text{O}_5. \]
During this reaction the vanadium atoms are partially reduced from a V\textsuperscript{5+} to a V\textsuperscript{4+} formal oxidation state [10]. V\textsubscript{2}O\textsubscript{5} is belonging to the layered transition metal oxides which possess the ability to structural deformations during the insertion of Mg\textsuperscript{2+} or other bivalent ions. The superior electrochemical performances of V\textsubscript{2}O\textsubscript{5} could be ascribed to the unique structure revealing the presence of a large (001) crystal planes interlayer spacing (\textsim 11.53 Å), which provide large interlayer spacing for facile ion insertion/extraction [11] [12] [13]. V\textsubscript{2}O\textsubscript{5} has been studied very intensively as a cathode material for Li-ion batteries [14]. Because the ionic radii of Li\textsuperscript{+} and Mg\textsuperscript{2+} are comparable in magnitude, 68 and 65 pm, respectively, the replacement of Li\textsuperscript{+} ions by Mg\textsuperscript{2+} ions in insertion compounds is possible. On the other hand, although the electrochemical performance of V\textsubscript{2}O\textsubscript{5} has shown great improvement, it suffers from its poor electronic conductivity, which may lead to both of poor capacity and the cyclic ability of V\textsubscript{2}O\textsubscript{5} electrodes. Graphene nanoplatelets represent a new class of carbon nanoparticles with multifunctional properties. Graphene nanoplatelet addition can provide barrier properties, while their pure graphitic composition makes them excellent electrical [15] and thermal conductors and can prevent the vanadium dissolution, and alleviate the aggregation of the particles. Since graphene, the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, exhibits superior electrical conductivities, high surface areas and chemical tolerance intrigue, many researchers have studied the V\textsubscript{2}O\textsubscript{5}/graphene cathode [16] using different preparation methods to control particle size and particle shape, aiming to improve the efficiency of rechargeable batteries. In the present work we will introduce a new rechargeable magnesium battery from electrolyte system based on reaction products of Mg\textsubscript{2}O\textsubscript{3} \textbullet 6H\textsubscript{2}O, succinonitril, tetraethylene glycol dimethyl ether solvent, and ((V\textsubscript{2}O\textsubscript{5})\textsubscript{0.75}/GNP\textsubscript{0.25}) nanocomposite cathode. One of our important goals is to reduce the cost of the battery. So the starting materials will be from market and the ball mill process is the desirable one.

2. Experimental

Graphene Nanoplatelets Grade M GNP was characterized by average (7 nm thickness, 10 nm particle diameter, 10\textsuperscript{7} S/m Electrical conductivity and surface area \textsim 120 - 150 m\textsuperscript{2}/g) have been imported from XG Science company. Composites of V\textsubscript{2}O\textsubscript{5} and GNP were prepared by ball milling process under 4 hours’ time duration. The resulted product is designated here as (V\textsubscript{2}O\textsubscript{5})\textsubscript{1-x}(GNP)\textsubscript{x} composites. The morphology of the nanocomposite was examined using SEM (JOEL-JSM Model 5600). The XRD patterns of the films were taken using Rigaku diffractometer type RINT-Ultima IV/S. The diffraction system based with Cu tube anode with voltage 40 KV and current 40 mA. The current–voltage characteristics of the cathodes were carried out by means of a computer controlled 2400 Keithley electrometer. For electrochemical performance testing, working electrodes (V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{5}-graphene composite powder) were prepared by mixing
85 wt.% sample as the active material, 6 wt.% conductive agent (carbon black, Super-P-Li), and 9 wt.% poly-vinylidene difluoride (PVDF) binder, N-methylpyrrolidone (Alfa) was then added to produce a viscous slurry and the resultant slurry was pasted onto copper foil. The as-prepared working electrodes were then dried in a vacuum oven at 373 K for 2 h. Electrochemical cells (CR2032 coin type) were assembled in room temperature and ambient pressure by using the working electrode, a separator (filter paper), Mg ribbon as the reference and counter electrode, and 4 gm MgNO₃·6H₂O in a 2:10 (w:v) mixture of succinonitril, tetraethylene glycol dimethyl ether, respectively, as the electrolyte. Figure 1 shows the structure scheme of MgNO₃·6H₂O, succinonitril and tetraethylene glycol dimethyl ether. Where MgNO₃·6H₂O is the Mg²⁺ pump, tetraethylene glycol dimethyl ether is a solvent and succinonitril is a plasticizer agent to dissociate ions and improve ionic conductivity. Cyclic voltammograms (CVs) were conducted in three-electrode cell using an electrochemical instrument of CHI604E Electrochemical Workstation. The cells were charged and discharged on a multi-channel battery test system (NEWARE BTS-TC35) over the voltage range of 0 - 1.6 V versus Mg/Mg⁺² at constant constant current density ~40 μAcm⁻¹.

3. Results and Discussion

Figures 2(a)-(c) shows SEM images for V₂O₅ and V₂O₅/GNP nanocomposites. The graphene nanoplatlets are crumpled to a curly and wavy shape. By adding GNP nanoplatlets to V₂O₅, the later was found to be uniformly distributed in GNP and well distributed on the 2D graphene nanoplatelets, as shown in Figures 2(a)-(c). Moreover, the graphene sheets can prevent the aggregation of V₂O₅ particles to a certain extent, which can be of great benefit to electrochemical reactions. The XRD patterns of the synthesized (V₂O₅)₁₋ₓ(GNP)ₓ composites (where x = 0, 5, 10, 15, 20 and 25 %wt GNP) are shown in Figure 3. The XRD spectrum for x = 0% indicates that the V₂O₅ composites

![Figure 1. Schematic illustrates the electrolyte structure.](image-url)
Figure 2. SEM micrographs of (V$_2$O$_5$)$_{1-x}$(GNP)$_x$ composites: (a) 0 wt% GNP; (b) 15 wt% GNP; (c) 25 wt% GNP.

Figure 3. XRD pattern of (V$_2$O$_5$)$_{1-x}$(GNP)$_x$ composites.

are highly crystallized in structure and the entire diffraction peaks match well with Bragg reflections of the pure orthorhombic phase of V$_2$O$_5$ nanoparticles, which is consistent with the standard JCPDS No.41-1426 (space group Pmmn) [17] [18]. However, for $x > 0\%$ an additional diffraction shoulder peak around 26.77°, partially overlapping with the V$_2$O$_5$ (110) peak ($2\theta = 26.39°$), originates from the (002) diffraction of the graphite. The intensity of the later peak increases linearly when $x$ increases from 5 to 25% and its position corresponds to $\sim 31$ nm (according to the relation: $\lambda/(2 \cdot \sin \theta, \theta = 26.39°)$ spacing between atomic planes [19]. Also, the XRD spectra show a weak peak at 54.8° which corresponds to the (004) reflection of the graphite. It can be noticed that the graphite (002) peak position shifts to the lower angles for $x = 5\%$ and to higher angles for $x = 10\%$. This can be related to the amount of oxygen functional groups formed between the platelets of the graphite. From the XRD measurements, no additional
phases related to structural defects can be detected, while orthorhombic V$_2$O$_5$ can be detected after ball milling of V$_2$O$_5$ and GNP. Small shift in peak positions of V$_2$O$_5$ after doping by GNP was observed which confirm change in (001) interlayer spacing. The crystallite size ($\tau$) of the investigated samples (V$_2$O$_5$)$_{1-x}$(GNP)$_x$ nano-composites (where $x = 0, 5, 10, 15, 20$ and $25$ %wt GNP) can be calculated using the first sphere approximation of Debye-Scherrer formula [20] $\tau = \frac{K \lambda}{\beta \cos \theta}$, where $K$ is the shape factor, $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity in radians, and $\theta$ is the Bragg angle. Using this formula, crystallite dimensions of about 30 nm could be calculated from the high intense peaks. Figure 4(a), shows the current voltage (I&V) characteristics of (V$_2$O$_5$)$_{1-x}$(GNP)$_x$ nano-composite. Generally, the current increases linearly with increasing voltage obeying Ohm law. The dc conductivity was calculated using the equation: $\sigma_{dc} = \frac{1}{R} \times \frac{L}{A}$ [21], where $t$ is the thickness of the sample and $A$ is the surface area of the sample. The value of the resistivity $R$ was measured from the slopes of the straight lines in ohmic region $I \alpha V$ Figure 4(a). The effect of graphene content on the dc conductivity $\sigma_{dc}$ of (V$_2$O$_5$)$_{1-x}$(GNP)$_x$ is shown in Figure 4(b). The dc conductivity of the composites exhibits insulator behavior for pure V$_2$O$_5$ recording $\sim 10 \times 10^{-6}$ S/m, whereas semiconductor behavior for low graphene content up to $x = 10$ wt% was recorded. The electrical conductivity increased as the content of graphene was close to percolation threshold up to $x = 5$ wt%. Above the percolation threshold $\sigma_{dc}$ was found to increases exponentially before it reach to the saturated point ($x = 10$ wt%) which may be attributed to the formation of filler network and the composites may reach to the metallic behavior. This behavior can be described according to the percolation theory as the following power relation [22],

$$\sigma_{dc} = \sigma_c (V_{GNP} - V_c)^t$$ for $V_{GNP} > V_c$

where $\sigma_c$ is the conductivity of conducting component, $V_{GNP}$ is the volume fraction of Graphene, $V_c$ is the critical volume fraction or percolation threshold, and the exponent $t$ reflects the dimensionality of the system and has been calculated to be either 1.3 or 2.0 corresponding to two or three dimensions, respectively [23]. Figure 4(b) (inset) shows a fitting of percolation equation for (V$_2$O$_5$)$_{1-x}$(GNP)$_x$ composites. The exponent $t$ was found to be about 1.4. This result confirms that the GNP nanoparticles are not located on the surface of the host material matrix particles, but it coordinated in the V$_2$O$_5$ crystal structure and the formation of graphene three dimensional network will enhancement.

**Cyclic voltammetry and discharge curve**

Figure 5(a) shows the schematic of the cell configuration of the Mg$^+$ V$_2$O$_5$ cells in this study. The activity of V$_2$O$_5$ and V$_2$O$_5$-graphene nanocomposite for hosting Mg$^{2+}$ ions was evaluated using cyclic voltammetry (CV) and galvanostatic discharge-charge techniques. Figure 5(b), shows the CV results obtained from 2.5 to 0 V using V$_2$O$_5$ and V$_2$O$_5$-graphene nanocomposite as a working electrode in a three-electrode cell employing magnesium metal as the counter and reference electrode at a scan rate of 0.05 mV s$^{-1}$. Although GNP succeeded to increase conductivity of V$_2$O$_5$, it failed to increase
Figure 4. (a) I-V curves of (V₂O₅)ₓ/(GNP)₁₋ₓ composites; (b) Variation of dc conductivity of (V₂O₅)ₓ/(GNP)₁₋ₓ composites at different graphene concentrations.
Figure 5. (a) Schematic illustrates Mg$^{2+}$ insertion/extraction within V$_2$O$_5$; (b) Comparison of the CV curves (at 5 mV s$^{-1}$) for V$_2$O$_5$ and V$_2$O$_5$/graphene nano-composite.
Figure 6. Discharge-charge profiles of (a) V$_2$O$_5$ (b) V$_2$O$_5$/graphene nano-composite cathodic materials.
the cathodic and anodic current density. This can be attributed to that the introduction of GNP in V_2O_5 using ball mill technique can perturb the (001) interlayer spacing of V_2O_5 and may be reduce intercalation rate. The perturbation in the interlayer spacing probably decreases the probability of Mg^{2+} insertion/extraction between interlayer spacing and hence decrease the specific capacity as we will see.

Figure 6(a) & Figure 6(b) show discharge/charge profiles of Mg/V_2O_5 and Mg/(V_2O_5/GNP) coin cells, in which current density was fixed at \( =40 \mu \text{Acm}^{-1} \) and the cells were discharged to 0 V and charged to 1.6 V. The initial discharge capacity of Mg/V_2O_5 and Mg/(V_2O_5/GNP) coin cells are approximately 100 and 90 mAh g\(^{-1}\), respectively. The combination of V_2O_5 with GNP decrease the discharge capacity compared to pure V_2O_5. We could not obtain more than 2 and 4 cycles for pure and graphitized V_2O_5, respectively. We think the structure property of V_2O_5 which give the advantage (001 large interlayer spacing (\( \sim 11.53 \) Å)) of facile Mg\(^{2+}\) insertion/extraction was deformed after initial cycling. The intercalation of Mg\(^{2+}\) may perturb the bonding scheme of V_2O_5 and losses it this property.

4. Conclusion

In summary, V_2O_5/GNP cathode was synthesized by a ball mill method. The integration of V_2O_5 and graphene nanoparticles enhanced the electrical performances. This improved performance could be attributed to the formation of framework nanoscale electrode of 2D graphene decorated with well-dispersed V_2O_5 nanoparticle. Although GNP perturbed the (001) interlayer spacing hence, it failed to enhance the electrochemical performance. As-prepared V_2O_5 and V_2O_5/GNP cathodes can deliver a high capacity of 100 and 90 mAh\(\cdot\)g\(^{-1}\) respectively, which provides a new direction to explore cathode materials for rechargeable Mg batteries. Further extensive investigations are required, however, to raise the performance of the magnesium-based rechargeable cells to practical levels.

References


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