Interchain-Expanded Vanadium Tetrasulfide with Fast Kinetics for Rechargeable Magnesium Batteries

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ABSTRACT: Magnesium batteries are promising energy storage systems because of the advantages of low raw material cost, high theoretical capacity, and high operational safety properties. However, the divalent Mg2+ has a sluggish kinetic in the cathode materials which resulted in poor electrochemical performance. Many strategies were adopted to improve the mobility of Mg2+ in the host structures. In this paper, we report on the optimization of chain-like structure VS4,0@reduced graphene oxide (VS4,0@rGO) through expanding interchain distance to increase the ion diffusivity. By combining theoretical calculations and experimental inves-
tigations, the expansion of interchain distance and reversible intercalation of MgCl+ are revealed. With the fast kinetics of MgCl+ (instead of Mg2+) intercalation into expanded VS4,0@rGO, higher capacity of 268.3 mA h g

INTRODUCTION

Currently, Li-ion batteries (LIBs) have achieved great progress in the last few decades; however, the unsolved Li-dendritic problem and unsustainability and high cost of lithium source impede their rapid development in recent years.1-4 The rechargeable multivalent batteries (such as Mg2+, Zn2+, and Al3+ based batteries) have attracted increasing interest as promising energy storage sources because of the advantages of low cost, high energy density, and high safety properties. Therefore, they can be better options for large-scale energy storage systems.5,6 Among them, the Mg battery (MB) technology has gained tremendous research attention for the unique properties of Mg anodes, such as high volumetric capacity and large reserves in the earth.7-9 More remarkably, the Mg metal is resistant to the formation of dendritic structures owing to its unique electrodeposition behavior as well as high coulombic efficiency in suitable electrolytes.10-12 Other anode materials such as Li4Ti5O12, Bi, and bismuth oxyfluoride as well as some specific optimization strategies were also reported, and excellent electrochemical performance was obtained.13-15

However, in an effort to search for high-performance Mg cathodes, the sluggish kinetics originated from the stronger polarizing nature between divalent Mg2+ and host materials is a big obstacle.16-18 In most cases, the conventional cathodes, which are mature in LIBs, exhibit low or even no capacities in MBs.19 Up to now, the Chevrel phase (CP) Mo6S8 reported by Aurbach et al. had demonstrated excellent cycling stability (over 2000 cycles with little capacity loss) and reasonable kinetics of Mg2+, which has been the benchmark for MBs, despite its uncompetitive low working voltage (ca. 1 V vs Mg/ Mg2+) and discharge capacity (ca. 100 mA h g

Supporting Information

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interchain distances of VS₄ are expanded, thus higher capacity static intermittent titration technique (GITT) tests demonstrate pre-intercalation of [BMP]⁺ (1-butyl-1-methylpyrrolidinium chloride, [BMP]Cl) on other crystal structure materials is rarely reported. It is well known that VS₄ is consisted of chainlike fragments connected by weak dispersive force, and the interchain distance is as high as 5.83 Å which is comparable to the interlayer distance (such as layered VS₂, 5.8 Å). The neighboring chains can be pushed apart to a certain degree. It is effective but challenging to obtain interchain-expanded VS₄ accompanied with enhanced performance when used as the cathode material for MBs.

Herein, we present the optimization strategy for VS₄ through pre-intercalation of [BMP]⁺ (1-butyl-1-methylpyrrolidinium chloride, [BMP]Cl). With the intercalation of [BMP]⁺, the interchain distances of VS₄ are expanded, thus higher capacity and enhanced rate performance have been obtained. Energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) analysis show the pre-intercalation of [BMP]⁺ and reversible intercalation of MgCl²⁻. The galvanostatic intermittent titration technique (GITT) tests demonstrate faster kinetics of MgCl²⁻ in VS₄@rGO compared to that of Mg²⁺, resulting in a great improvement of the reversible capacity and rate capability. Furthermore, in situ X-ray diffraction (XRD), ex situ Fourier transform infrared (FTIR), and Raman investigations were performed to characterize the structural evolution during the electrochemical MgCl²⁻ (de)intercalation in following cycles.

**EXPERIMENTAL SECTION**

**Synthesis of VS₄@rGO.** The VS₄@rGO was synthesized through a similar hydrothermal reaction reported in previous publications. First, 0.366 g sodium metavanadate and 0.240 g sodium hydroxide were dissolved in the mixture of 22.5 mL GO (2.0 mg mL⁻¹, purchased from XFNANO company) and 7.5 mL deionization (DI) water. At the same time, 1.127 g thioacetamide was dissolved in the mixture of 7.5 mL GO and 2.5 mL DI water. After continuous stirring, the two as-obtained solutions were mixed together and stirred for 1 h. Then, the final suspension was transferred to a 50 mL Teflon-lined autoclave and kept at 160 °C for 24 h. After cooling naturally, the products were collected and washed with DI water several times and finally dried in vacuum at 60 °C for 6 h.

**Preparation of Electrolytes.** The all-phenyl-complex (APC) electrolyte, a solution of 0.25 M [Mg₂Cl₃⁻][AlP₆H₆Cl₄⁻]/tetrahydrofuran (THF), was prepared according to Mizrahi et al. A suitable amount of [BMP]Cl (purchased from Macklin) was added in the APC electrolyte to obtain the concentration of 0.25 M.

**Material Characterization.** XRD and in situ XRD measurements for the samples were performed using a D8 Advance X-ray diffractometer with a Cu Kα X-ray source. Field-emission scanning electron microscopy (SEM) images were collected with a JEOL-7100F microscope. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning TEM-high-angle annular dark-field (HAADF) images, and EDS were recorded using a Titan G2-300 instrument. Thermogravimetric analysis (TGA) was performed using a NETZSCH-STA449F5 thermoanalyzer. Raman spectra were obtained using Renishaw inVia micro-Raman spectroscopy. FTIR spectra were recorded by using a Nicolet 60-SXB IR spectrometer. XPS measurements were obtained using a VG Multilab 2000 instrument. Inductively coupled plasma (ICP) measurements were conducted using a PerkinElmer Optima 4300DV spectrometer.

**RESULTS AND DISCUSSION**

First, XRD was performed to identify the crystallinity of VS₄@rGO composites. As shown in Figure 1a, all the peaks are consistent with the monoclinic VS₄ phase (JCPDS no. 87-0603). The mass change of VS₄@rGO with the gradually increasing of temperature is exhibited in Figure 1b. The TGA curve exhibits three processes of mass loss. The first process (4 wt %) observed below 190 °C is caused by the removal of absorbed water; the second process (33 wt %) between 190 and 240 °C may result from the reaction of VS₄ and O₂; and the third process (10.1 wt %) from 380 to 450 °C is caused by the burning of rGO. Figure 1c–f shows the morphology of the VS₄@rGO composite. The synthesized VS₄ nanoparticles with the size of ~100 nm are distributed on rGO sheets. The EDS mapping displays the homogeneous distribution of V and S elements on the rGO. The HRTEM image (Figure 1f) shows the spacing of 5.58 and 5.95 Å (corresponding well with (110) and (002) crystal plane of monoclinic VS₄, respectively) and
graphene sheets, which confirms the good combination of VS₄ nanoparticles with amorphous graphene.

The electrochemical performance of the APC electrolyte with and without [BMP]Cl was investigated by cyclic voltammograms (CVs, Figure 2a) at a scan rate of 25 mV s⁻¹ in the three-electrode beaker cell. As shown in Figure 2a, the APC electrolyte with [BMP]Cl exhibited higher enclosed area and peak current than those of pure APC, which represent higher capacity and activity. Both the electrolytes display reversible Mg deposition‒dissolution processes with high efficiencies (100 and 95.6%, respectively) and high anodic stability (above 2.5 V), which guarantee the practical use in the full cell. Figure 2b displays the typical voltage‒time curves of both electrolytes in the two Mg electrode cells at the current of 20 μA. The batteries were first charged with the time of 4 h, and the APC electrolyte with [BMP]Cl shows a much higher initial discharge capacity which may be caused by the intercalation of [BMP]⁺ and its effect on the VS₄@rGO structure. To investigate the reason for the higher capacities, XPS and EDS were conducted to confirm the intercalation species at various stages. All the electrodes were washed thoroughly with THF in the glovebox to remove the electrolytes. The XPS spectra (Figure 2d) show the signals of Cl, Mg, and N at stage 2. The existence of the N element is attributed to the intercalation of [BMP]⁺, and the atomic ratio of Mg to Cl is close to 1:1, indicating the intercalation of MgCl⁺. In addition, the EDS results (Figure 2e,f) agree well with the ones of XPS and ICP tests (Table S2). Figure 2d shows that the peak intensities of Cl and Mg further increase.
when discharged to stage 4 and decrease again when charged to stage 5, while the N 1s peak has little change. The results indicate that only MgCl\(^+\) intercalation/deintercalation occurs from stage 2 to 5. The remaining [BMP]\(^+\) and partial MgCl\(^+\) in VS\(_4\)@rGO at stage 5 are responsible for the irreversible capacity loss at the initial discharge process. However, in the EDS elemental mappings of VS\(_4\)@rGO discharged to 0.2 V in the APC electrolyte without [BMP]Cl addition (Figure S2), only the Mg element is detected, and the Cl and N elements are absent, demonstrating that the inserted species is Mg\(^{2+}\). In comparison, the pristine VS\(_4\)@rGO was immersed in the APC electrolyte with [BMP]Cl for 24 h, and the same washing/drying process was conducted to test the existence of [BMP]Cl through EDS mapping (Figure S3). The absence of Mg, N, and Cl elements confirms that the intercalation of [BMP]\(^+\) into VS\(_4\) changed the intercalation species (from Mg\(^{2+}\) to MgCl\(^+\)) during the magnesium storage.

To further investigate the structural evolution of VS\(_4\)@rGO during the processes of [BMP]\(^+\) and MgCl\(^+\) insertion/extraction, time-resolved in situ XRD was conducted. Figure 2g displays the results and the corresponding discharge/charge curves of the first two cycles. There is little change in the XRD patterns before being discharged to 1.0 V (about 320 mA h g\(^{-1}\)) in the discharge process, which represents no obvious structural change with the evolution of [BMP]Cl/VS\(_4\)@rGO. The high structural stability with large discharge capacity is attributed to the large interchain distances and weak connection of van der Waals bonding between chains, which can promote the charge transfer kinetics and accommodate the inserted ions. The inserted ions push the neighboring chains apart, just like what happens with interlayers in layered materials.\(^{37}\) With the discharge going on, the two main peaks of VS\(_4\) located at 15.8° and 17.0° corresponding to the (110) and (020) lattice plane, respectively, become weaker and disappeared in the end. With the further intercalation of MgCl\(^+\) ions, the interchain spaces were expanded and further been pushed apart to a certain degree. In the charging process, there was little change in the XRD patterns, and the main peaks of VS\(_4\) did not appear, demonstrating the irreversible reaction in the first discharge process. The corresponding ex situ XRD (Figure 2h) analysis exhibited the same results.

In order to investigate the structural evolution of VS\(_4\)@rGO, ex situ Raman and FTIR spectroscopies were conducted. Figure 3a shows the Raman spectra of original and different states of VS\(_4\)@rGO. It should be noted that the Raman spectrum of original VS\(_4\)@rGO contains all the intensive vibration modes of VS\(_4\), same as those published in previous papers.\(^{29,38}\) The identified bonds located at 192 and 279 cm\(^{-1}\) are ascribed to V–S stretching (A1) and bending (B1) modes.\(^{38}\) The intensities of the two peaks were decreased with the ions intercalated, suggesting weakening of V–S stretching and bending. When charged to 2.0 V, the two peaks recovered to their original status to some extent, indicating the reversibility of the V–S stretching. In the subsequent cycle, the Raman spectra exhibited the same trends. FTIR spectra of the VS\(_4\)@rGO at the corresponding states were also measured (Figure 3b). The bonds located at about 545 and 997 cm\(^{-1}\) are the resemblance of the V–S–V bending mode and the terminal V═S stretches, respectively.\(^{38}\) The intensities of the two peaks were decreased with the ions intercalated, suggesting weakening of V═S stretching and bending. When charged to 2.0 V, the two peaks recovered to their original status to some extent, indicating the reversibility of the V═S stretching.

A schematic illustration about the structural evolution of VS\(_4\) at different stages is shown in Figure 3e. The obtained VS\(_4\) is a linear chain structure; Figure 3c,d exhibits the detailed chains
in different views. The neighboring chains are connected with weak van der Waals forces, which have a large distance of 5.83 Å. In this respect, a loosely stacked structure is formed, and a large number of potential sites are provided between chains. To give further evidence of the interchain expansion with the intercalation of [BMP]+, first-principles computations based on density functional theory were conducted using the CASTEP code in Materials Studio (version 2017 R2) of Accelrys Inc (more details are provided in the Supporting Information). When the [BMP]+ intercalated into the VS4 interchains, the distance is expanded to 12.52 Å with the volume expansion of 130.19%. In this way, MgCl+ ions begin to insert into the structure, and the distance is further expanded. In the following discharge, a large number of MgCl+ intercalation caused the phase change. It is worth mentioning that the chains are not destroyed for the unchanged peak locations of Raman and FTIR. After these steps, a small amount of [BMP]+ ions stayed between the chains of VS4 (denoted as expanded VS4@rGO), which contribute greatly to the reversible insertion/extraction of MgCl+.

The electrochemical performances of expanded VS4@rGO and unexpanded VS4@rGO were attained to identify the improvement. As shown in Figure S4, expanded VS4@rGO demonstrates a high reversible capacity of 268.3 mA h g⁻¹ (higher than that of branched VS4 nanodendrites, 195 mA h g⁻¹, ref 39) and maintains 147.2 mA h g⁻¹ after 100 cycles at 50 mA g⁻¹ based on the mass of VS4@rGO. It is 225.2 and 124.1 mA h g⁻¹ when calculated based on the mass of [BMP]0.26VS4@rGO (calculated from Table S2 and Figure S5). To confirm the repetitions of the electrochemical performance based on expanded VS4@rGO, the box plots about the electrochemical performance are provided in Figure 4a. However, pristine VS4@rGO only exhibited about 40 mA h g⁻¹ after the first cycle (Figure 4a). Figure 4b displays the discharge/charge curves of VS4@rGO. The expanded VS4@rGO exhibit remarkable rate capability (Figure 4c). When the current densities increased to 100, 200, 500, and 1000 mA g⁻¹, the discharge capacities are as high as 157.9, 132.8, 116.2, and 101.4 mA h g⁻¹, respectively. Even at a high current density of 2000 mA g⁻¹, a reversible discharge capacity of 85.9 mA h g⁻¹ (or 70.9 mA h g⁻¹ based on the mass of [BMP]0.26VS4@rGO) is still achieved. When the current density is recovered to 50 mA g⁻¹, the capacity recovers to 187.8 mA h g⁻¹. In comparison, pristine VS4@rGO shows much lower capacity at all current densities. The corresponding discharge/charge profiles of expanded VS4@rGO at various current densities are shown in Figure 4d. The long-cycle performance of expanded VS4@rGO at 500 mA g⁻¹ is exhibited in Figure 4e. The initial discharge capacity is as high as 123.8 mA h g⁻¹ and still remains 78.9 mA h g⁻¹ even after 200 cycles, the capacity...
retention is 63.7% compared with the first cycle. It is worth mentioning that the coulombic efficiency remains higher than 98% except for the first few cycles. The corresponding discharge/charge profiles are shown in Figure S6. To identify the improved Mg-storage performance of expanded VS₄@rGO and exclude the side effect of [BMP]⁺ ions in the electrolyte during cycling, the VS₄@rGO at stage 5 is used to fabricate a new cell in the pure APC electrolyte. As shown in Figure S7, the charge/discharge curves of the first cycle indicating the capacity can be retained and is much higher than the unexpanded VS₄@rGO.

The potential application of expanded VS₄@rGO as the cathode material of the Mg full cell at high and low temperatures was also studied (Figure 5a). A high capacity of 296.6 mA h g⁻¹ is obtained when the temperature increases to 55 °C, corresponding to the insertion of about 1.97 MgCl⁺ per unit of VS₄@rGO. Surprisingly, the cell demonstrated 35.4 mA h g⁻¹ even at relatively low temperature of −35 °C. More importantly, the expanded VS₄@rGO showed excellent temperature adaptability (Figure 5b). At 55 °C, a higher discharge capacity of 156.5 mA h g⁻¹ is retained after 100 cycles. Even at −20 °C, the capacity of about 40 mA h g⁻¹ is remained in 100 cycles. The coulombic efficiency is low at first and improved to about 95% after 30 cycles, which may be caused by the sluggish kinetics of the electrolyte at low temperatures. To investigate the origin of the excellent rate capability and high discharge capacity, the kinetics of MgCl⁺ solid-state diffusion in expanded VS₄@rGO were studied via GITT after the battery is stabilized.²⁵,⁴⁰ In the GITT measurement (Figure 5c), the VS₄@rGO displays a high discharge capacity of 282.4 mA h g⁻¹, corresponding to 1.87 MgCl⁺ insertion per formula. The MgCl⁺ diffusivity (Figure 5d) decreases from 1.12 × 10⁻¹² to 3.67 × 10⁻¹² cm² s⁻¹ with the increasing of MgCl⁺ concentration. The average MgCl⁺ diffusivity during the intercalation process is about 2.72 × 10⁻¹¹ cm² s⁻¹, which is as fast as TiS₂ (MgCl⁺ diffusivity, 10⁻¹¹ cm² s⁻¹) and one order of magnitude higher than that of Mo₆S₈ (Mg²⁺ diffusivity, 10⁻¹² cm² s⁻¹) and poly(ethylene oxide)-intercalated MoS₂ (Mg²⁺ diffusivity, 4.4 × 10⁻¹² cm² s⁻¹).²⁷,⁴¹,⁴² The calculated Mg²⁺ diffusivity in pristine VS₄@rGO is at the level of 3.21 × 10⁻¹⁵ cm² s⁻¹ (Figure S8), which is much lower than that of MgCl⁺ in expanded VS₄@rGO. The expanded interchain distances enabled fast kinetics of MgCl⁺ ions, resulting in the higher specific capacity and excellent rate performance.

CONCLUSIONS

In conclusion, we conducted the optimization of chainlike structure VS₄ through in situ preintercalation of [BMP]⁺ to expand the interchain distances and systematically investigated the expanding process. The expanded VS₄@rGO sample exhibits higher Mg storage capacity (268.3 mA h g⁻¹), remarkable rate performance (85.9 mA h g⁻¹ at 2000 mA g⁻¹), and outstanding temperature adaptability (−35 to 55 °C) among the reported cathodes of MBs. Our work demonstrates that the intercalation species have a direct relation with the interchain distance and a large impact on the electrochemical performance. Compared with the reported Mg²⁺ intercalation cathodes, the fast kinetics of MgCl⁺ enables the larger specific capacity and better rate capability. The successful utilization of MgCl⁺ ion intercalation into host materials indicates a promising direction to improve the performance of MBs.

ASSOCIATED CONTENT

* Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b09592.

Cycling performance and voltage profiles of VS₄@rGO between the voltage of 0.8−2 V, EDS color mapping images of VS₄@rGO discharged to 0.2 V in the APC electrolyte, EDS color mapping images of VS₄@rGO immersed in the APC electrolyte with [BMP]⁺Cl for 24 h and conducted the same washing/drying process, cycling
performance of expanded VS@rGO at 50 mA g⁻¹, TGA for the samples of state 1 and 4 in a nitrogen flow, voltage profiles of expanded VS@rGO in 0.25 M APC with 0.25 M [BMP][Cl], charge/discharge curves of the new fabricated cell using pristine VS@rGO and the expanded VS@rGO at stage 5 in the pure APC electrolyte, Mg ion diffusivity versus the state of discharge in the pure APC electrolyte, detail of first-principles calculations, and characterization of [BMP]₂[(MgCl)₃VS]@rGO based on EDS and ICP–optical emission spectroscopy analysis (PDF)

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The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

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