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High-rate and long-life VS₂ cathodes for hybrid magnesium-based battery Ruimin Sun^a, Cunyuan Pei^a, Jinzhi Sheng^a, Dandan Wang^b, Lu Wu^a, Sijie Liu^a, Qinyou An^{a,*},



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ABSTRACT

Rechargeable magnesium-ion batteries (MIBs) have received growing attention due to high safety, low cost and high volumetric capacity. However, the sluggish Mg^{2+} kinetics in host materials because of high polarization of Mg^{2+} impede electrochemical performance of MIBs. To circumvent this problem, designing hybrid system composed of fast Li⁺ insertion cathode and safe Mg anode is a promising solution. Herein, graphene wrapped VS₂ (VS₂-GO) as cathode for hybrid magnesium-based batteries is presented for the first time. It delivers remarkable electrochemical performance with a high discharge capacity of 235 mA h g⁻¹, ultra-high rate capability (129 mA h g⁻¹ at 80 C) and long life (capacity of 146 mA h g⁻¹ even after 10,000 cycles at 5 C). A reversible phase transition during the electrochemical performance demonstrates that the novel VS₂ athode has great potential for the development of the next generation safe and large-scale energy storage.

1. Introduction

With the growing demands of advanced energy storage applied in portable electronic devices and electric vehicles (EVs), developing safe, low-cost and high-capacity rechargeable batteries has become urgent [1-3]. Over the past decades, lithium-ion batteries (LIBs) are the most popular energy storage devices due to their high energy density and long cycle life [4]. However, the safety concern and high cost of lithium limit the further application of LIBs [5,6]. Among the various battery systems, magnesium-ion batteries (MIBs) are receiving growing attention due to the superiority of safety, low-cost and high-volumetriccapacity. Magnesium (Mg) with divalent Mg2+ as charge carrier possesses a volumetric capacity of $3833 \text{ mA h cm}^{-3}$, which is much higher than that of lithium (Li) (2046 mA h cm^{-3}) [7–9]. Moreover, Mg is one of the most abundant elements in the earth's crust, resulting in lower production cost [10]. And most of all, different from the Li and sodium (Na) electrode, Mg electrode is dendrite-free during deposition/dissolution, enabling Mg as a highly safe anode [11-13]. These advantages make MIBs more competitive in energy storage systems. Despite the above advantages of Mg over Li as anode material, the development of MIBs still faces many challenges. The lack of suitable cathode materials is one of the main bottlenecks due to slow solid-state diffusion of highly polarizing Mg²⁺ in most cathode materials. Furthermore, the most common electrolytes in MIBs deliver narrow

voltage windows and high corrosiveness to the battery shells and current collectors, which hinder the usability of the high-voltage battery system [14,15].

Recently, in order to expand the selection of cathodes and avoid the sluggish Mg²⁺ transport in host materials, hybrid magnesium-lithiumion batteries (MLIBs) have attracted much attention since the cells combine both the advantages of the Mg anode (safety and low cost) and Li intercalation cathode (fast kinetics and high reversibility) [16-18]. The working mechanism of MLIBs is shown in Fig. 1a: the reversible Li⁺ intercalation/deintercalation dominates the reaction of cathode side and Mg deposition/dissolution occurs on the anode side. It's worth mentioning that the cathode must match with the complex electrolyte. Despite the anodic stability of all-phenyl complex (APC) is limited to 3.0 V (vs. Mg/Mg²⁺), the stable electrochemical window should ≤ 2.1 V (vs. Mg/Mg²⁺) to avoid the corrosion of non-inert metal current collectors (stainless steel) by electrolyte [19]. Therefore, the chosen cathodes should have redox potential within the electrochemical stability window and keep inert to electrolyte. Previous cathode materials in MLIBs deliver good Li intercalation properties in hybrid battery systems, such as: Mo₆S₈ [20], TiS₂ [19,21], TiO₂ [22], Li₄Ti₅O₁₂ [23,24], MoS₂ [25], and relatively high voltage LiFePO₄ [18], Prussian Blue [26], LiMn₂O₄ [27], etc. However, the energy density and voltage are relatively low for the first category, while the higher voltage of the second category exceeds the stability window of the electrolyte when

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Fig. 1. (a) Schematic illustration of working mechanism of the hybird MLIBs. (b) GITT curves of the hybird MLIBs. (c) Li* diffusivity versus state of discharge.

the systems use low cost stainless steel as current collector. These disadvantages restrict the practical application. Given these, it is imperative to find desirable cathodes with high energy density and stability in the hybrid battery system.

During the past decades, the outstanding properties (similar to graphene) of two-dimensional (2D) layered transition-metal dichalcogenides (TMDs) have aroused the interest in a variety of fields such as energy storage [28,29], catalysis [30], electronics [31], etc. TMDs with unique physical and chemical properties become outstanding candidates for battery electrode materials. VS₂ is a typical member of TMDs with hexagonal structure. The structure is made up of a metal vanadium layer between two sulfide layers to form a sandwich S-V-S. Triple layers connect to each other by weak Van der Waals force to form a layered structure with an interlayer spacing of 5.76 Å [32]. The interlayer distance of VS₂ is large enough for rapid insertion and extraction of the lithium (ionic diameter: 1.36 Å) and sodium ions (ionic diameter: 1.96 Å) [33]. In addition, VS₂ has great superiority as a potential cathode for Mg-based energy storage system. Therefore, in this work, we propose to utilize VS2 cathode to improve the energy density and cycling stability of MLIBs.

Herein, we report a novel hybrid MLIB, consisting high conductivity graphene wrapped VS₂ (VS₂-GO) cathode, dendrite-free Mg anode, APC-LiCl electrolyte and Mo foil current collector for the first time. The battery exhibits a high reversible capacity of 235 mA h g⁻¹ at a current density of 0.5 C (1 C = 180 mA g⁻¹). It also delivers long cycling stability and excellent rate capability. A capacity of 129 mA h g⁻¹ can be achieved even at an ultrahigh rate of 80 C (discharge/charge in 32 s). The outstanding performance is attributed to the highly stable crystal structure of VS₂ for fast ion diffusion and conductive graphene

for rapid electron transport. Furthermore, the detailed electrochemical reaction mechanism has been investigated. The *ex-situ* X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectra (EDS) characterizations enable us to connect the excellent electrochemical behavior of VS₂ to the structure changes occurring during the electrochemical process.

2. Experimental section

All the reagents used in the experiment were analytical grade and used without further purification.

2.1. Sample preparation

In a typical synthesis, 2 mmol NH_4VO_3 was first dissolved in the mixture of 30 mL distilled water and 2 mL ammonium hydroxide. Then 20 mmol C_2H_5NS (TAA) was dissolved in sequence with continuous stirring. The solution was kept stirring 1 h at room temperature. After that, the solution was loaded into a Teflon-lined sealed autoclave and maintained at 180 °C for 20 h. The obtained suspension was centrifuged and the product was washed thoroughly with distilled water and ethanol several times and then dried at 60 °C in a vacuum oven for 12 h. Finally, the products were annealed at 300 °C for 2 h to obtain VS₂ nanosheets.

The graphene was synthesized by a modified Hummers method [38]. To obtain the graphene wrapped VS₂ nanosheets (noted as VS₂-GO), 0.1 g VS₂ was dispersed in water by ultrasonic process. Then 2.6 mL graphene (2 mg mL⁻¹) solution was added into the suspension



Fig. 2. (a) XRD patterns and (b) Raman spectra of VS₂-GO and VS₂. (c) TEM image and (d-e) HRTEM image of VS₂-GO. (f) EDS elemental mapping of V, S and C, showing uniform elemental distribution.

and the mixture was stirred for 12 h. The final obtained suspension was centrifuged and then dried at 60 $^{\rm o}{\rm C}$ in a vacuum oven for 12 h.

2.2. Materials characterization

XRD patterns of the samples were collected by using a D8 Advance X-ray diffractometer with Cu K α X-ray source at room temperature. SEM images and EDS mappings were collected with a JEOL-7100F microscope. XPS measurement was performed using a VG Multi Lab 2000 instrument. TEM and HRTEM images were recorded using a JEM-2100F STEM/EDS microscope. Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system.

2.3. Preparation of electrolytes

All-phenyl complex (APC) electrolytes for MIBs were prepared according to Oren Mizrahi et al. [40]. All chemical preparations and experiments were carried out under pure argon atmosphere in Vigor glove boxes (<1 ppm of oxygen and water) at room temperature. Firstly, 0.667 g aluminum chloride (Aldrich, 99.99%) slowly dissolved in 15 mL THF (Aldrich, 99.9% and dried by activated 4 Å molecular sieves) under vigorous stirring and kept for 12 h. Then the transparent solution was dropwise added to phenyl magnesium chloride (Macklin, 2 M solution in THF) under continuous stirring for another 12 h to form the APC solution. Finally, for hybrid cell, 1 M LiCl was added into the APC electrolyte.



Fig. 3. (a) Cyclic performance of VS₂-GO and VS₂ at current density of 0.5 C. (b) Discharge-charge curves of the VS₂-GO electrode in the voltage range of 0.5–2.0 V at 0.5 C. (c) Rate performance of VS₂-GO and VS₂. (d) Discharge-charge curves of the VS₂-GO at different rates. (e) CV curves of VS₂-GO at a scan rate of 0.1 mV s⁻¹. (f) Nyquist plots of VS₂-GO and VS₂ at initial state.

2.4. Measurements of electrochemical performances

3. Results and discussions

The electrochemical properties were performed with 2016 coin-type cells in an argon-filled glove box. Mg foils were employed as the counter and reference electrodes. The working electrodes were fabricated on Mo foil current collectors. The slurry was obtained by mixing the as-synthesized materials, acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 6:3:1. Glass fiber was employed as the separator. 1 M APC-LiCl was used as electrolyte. Galvanostatic measurements were performed over a potential range of 0.5–2.0 V *vs.* Mg/Mg²⁺ by using a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) was tested by an electrochemical workstation (CHI 760D). Electrochemical impedance spectroscopy (EIS) was conducted with Autolab Potentiostat Galvanostat (PGSTAT302N). All of the measurements were carried out at room temperature.

The composite synthesized via a facile hydrothermal method followed by a physical mixing process of VS₂ nanosheets and graphene. The kinetics of Li⁺ and Mg²⁺ solid-state diffusion in VS₂ cathode were investigated via galvanostatic intermittent titration technique (GITT) [34–36]. The GITT method is based on chronopotentiometry to determine the chemical diffusion coefficient in an electron/ion mixed conductor. The lithium/magnesium host electrode is subjected to intercalation/deintercalation by applying a constant current flux for a limited time period, after which the compound has known lithium/magnesium content. VS₂ cathode (Fig. 1b) delivers a specific capacity of 241 mA h g⁻¹ in the GITT measurement. Moreover, the Li⁺ diffusivity D^{GITT} can be calculated from the potential response to a low constant current pulse (20 mA g⁻¹) using the following equation [36,37]:

$$D^{GITT} = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\triangle E_s}{\triangle E_\tau} \right)^2$$

where τ is the constant current pulse time, m_B , V_M , S, and M_B represent the mass, molar volume, electrode-electrolyte interface area, and molar mass of VS₂, respectively. ΔE_s is the voltage difference during the open circuit period, and ΔE_{τ} is the total change of cell voltage during a constant current pulse (more details see Fig. S1). The average Li⁺ diffusivity of VS₂ cathode over the entire intercalation process is ~ 1.40 × 10⁻¹³ cm² s⁻¹ (Fig. 1c), which is around two orders of magnitude higher than the average Mg²⁺ diffusivity (2.38 × 10⁻¹⁵ cm² s⁻¹) in VS₂ (Fig. S2). The GITT results indicate that Li⁺ ions dominate intercalation on the cathode side.

The X-ray diffraction (XRD) patterns of the VS₂ and VS₂-GO are shown in Fig. 2a. All the characteristic peaks of both samples can be indexed into hexagonal VS2 phase (space group: P-3m1) (JCPDF No. 01-089-1640) without impurity. ICP and C-S analyzers were performed to investigate the mass ratio of V/S elements. As shown in Table S1, the contents of V and S were 43.05 wt% and 50.77 wt%, respectively, which corresponds to an atomic ratio of approximately 1:2. The Raman spectra are shown in Fig. 2b to confirm the existence of graphene in VS₂-GO. Typical peaks located at around 1330 and 1590 cm⁻¹ are attributed to the D (defects and disorders in the graphene layers) and G (vibration of sp² carbon atoms) bands of the graphene, respectively [39,41]. The morphology and detailed crystal structure of VS_2 nanosheets are further revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The VS₂ flowers are assembled by nanosheets and the thickness of the nanosheet is estimated to be around 50-100 nm (Fig. S3a). The size of the VS₂ nanosheets shows little change after graphene wrapping (Fig. S3b). The TEM images (Fig. 2c and d) show a direct look that the nanosheets are wrapped by graphene [42,43]. The lattice spacings of 2.51 and 2.00 Å in the high-resolution TEM (HRTEM) (Fig. 2e) are in agreement with the (011) and (012) planes of VS₂, respectively. Moreover, the energy dispersive X-ray spectrometric (EDS) mapping (Fig. 2f) of the VS₂-GO confirms the existence and uniform distribution of V, S and C. The VS2-GO in air atmosphere at 800 °C forms the V₂O₅, SO₂ and CO₂, and the carbon content is further estimated to be 6.21%, according to the thermogravimetric curve (Fig. S4).

2016-type coin cells of VS₂ cathode with metallic magnesium as the anode and APC-LiCl as electrolyte were assembled to investigate the electrochemical performance. The electrochemical performance of both VS2-GO and VS2 are shown in Fig. 3. The cycling performances of VS2-GO and VS₂ at 0.5 C are shown in Fig. 3a. VS₂-GO cathode delivers better cycling performance than the VS_2 cathode. The initial discharge capacity of VS₂-GO is 315 mA h g^{-1} and the second cycle is 250 mA h g^{-1} . The capacity still maintains 200 mA h g^{-1} after 100cycles (capacity retention of 80% compared with the second cycle). The coulombic efficiency (CE) gradually increases to 100% after a few cycles and then can be stabilized. The specific capacity of the composite cathode is calculated on the total mass of the electrode. The GO shows negligibly small contributions to the total capacity (Fig. S5). The main capacity is attributed to VS₂ in this composite. Fig. 3b displays the typical charge and discharge curves of the VS₂-GO electrode at 0.5 C. Rate performance of the two electrodes at progressively increased current density (ranging from 0.5 to 80 C) was measured (Fig. 3c and d). Obviously, the VS₂-GO exhibits remarkable rate performance. It can be seen that VS₂-GO delivers specific capacities as high as 235, 204 and 180 mA h g⁻¹ at 1, 10 and 20 C, respectively. Even at an extremely high-rate of 80 C, a capacity of 129 mA h g⁻¹ can be achieved (discharge/charge in 32 s). When the current density is reduced from 80 to 0.5 C, almost 100% of the initial capacity can be recovered for the VS2-GO. The superior electrochemical performance of VS₂-GO is greatly better than the current advanced cathodes in MLIBs (see Table S3 for comparison). Fig. 3e shows the cyclic voltammogram (CV) curves of VS₂-GO vs. Mg/Mg²⁺ at a scan rate of 0.1 mV s⁻¹ in the electrolytes of both APC/LiCl and pure APC. The intercalation and deintercalation of lithium contribute to the cathodic and anodic peaks, respectively. Four couples of redox peaks at around 1.75/1.65, 1.66/1.58, 1.58/1.53 and 1.45/1.41 V are observed, which match well with the discharge-charge curves (Fig. 3b). The CV curves of VS₂-GO in pure APC electrolyte exhibit no obvious cathodic and anodic peaks, indicating few Mg²⁺ insertion/extraction. To provide further insight for the enhanced electrochemical performance of VS2-GO, the electrochemical impedance spectra (EIS) were measured (Fig. 3f). The EIS spectra show a compressed semicircle in the high to medium frequency region of each spectrum, which is related to the charge transfer resistance (R_{ct}) of the electrodes, and an inclined line in the low frequency range which corresponds to the Warburg impendence (Z_w). The R_{ct} of the VS₂-GO and the VS₂ cathodes are 1645 and 4697 Ω at the initial state, respectively, which show large impedance. But the charge transfer resistance decreases significantly after cycling activation (Fig. S6). The $R_{\rm ct}$ of the VS₂-GO and the VS₂ cathodes decreases to 104 and 239 Ω after 50 cycles, respectively. Generally, this small impedance is beneficial for the application of hybrid magnesium-based battery. Moreover, the slope in the low frequency range of the VS₂-GO is a little larger than VS_2 . The lithium ion diffusion coefficient value (D) can be calculated from EIS using the following equation:

$D = 0.5(RT/An^2F^2C\sigma)^2$

where *D* represents the diffusion coefficient (cm² s⁻¹), *R* represents the gas constant, *T* represents the absolute temperature, *A* represents the surface area of the anode (cm²), *n* is the number of electrons transferred electrochemical reaction, *F* is the Faraday constant, *C* represents the concentration of ions and σ is the Warburg factor relative to $Z_{\rm re}$ [44]. From the following equation, σ can be obtained (Fig. S7).

$$Z_{\rm re} = R_{\rm D} + R_{\rm L} + \sigma \omega^{-1/2}$$

Under the same condition, the ions diffusion coefficients at room temperature are inversely proportional to the σ^2 . The σ calculated from EIS to be 977.3 and 1265.5 for the VS₂-GO and VS₂, respectively, indicating the VS₂-GO has better Li⁺ diffusion ability. The graphene layers on the surface of VS₂ layers effectively reduce the impedance, resulting in enhanced electrochemical performance of VS2-GO. Fig. S8a shows the typical charge and discharge curves of VS₂-GO|APC-LiCl|Mg hybrid battery (0.5–2 V), VS₂-GO|1 M LiPF₆/EC + DMC + EMC (volume ratio of 1:1:1)|Li LIB (1.2-2.7 V) and VS2-GO|APC|Mg MIB (0.5-2 V) at the same current density of 0.5 C. Similar charge and discharge curves of the VS2-GO|APC-LiCl|Mg hybrid battery and VS2-GO|1 M LiPF₆/EC + DMC + EMC (volume ratio of 1:1:1)|Li LIB confirm that Li+ intercalation/deintercalation dominates the cathode reaction in MLIBs. The slight difference could be related to the different Li⁺ intercalation/deintercalation properties in different electrolyte systems. However, it is difficult for Mg²⁺ intercalation in pure APC electrolyte due to the sluggish kinetics of Mg²⁺ in VS₂. Fig. S8b shows the cycling performance of these three battery systems, the specific capacities of hybrid MLIB and VS2-GO/Li battery are well maintained. However, the VS₂-GO cathode shows little capacity in the VS₂-GO|Mg battery even after 100 cycles activation.

The electrochemical tests of the electrodes prepared by mixing the active materials, acetylene black and PTFE in a weight ratio of 8:1:1 were conducted (Fig. S9). A discharge capacity of 228 mA h g⁻¹ can be obtained at 0.5 C, and the capacity keeps well after 100 cycles. These results show similar superior performances with the electrodes in the weight ratio of 6:3:1, demonstrating that the electrodes still have enhanced electrochemical performances while improving the ratio of the active materials. The excellent electrochemical performances can be attributed to the following advantages of this material. Firstly, the unique layered crystal structure provides an advantaged condition for fast Li⁺ diffusion. Secondly, the graphene provides a conductive net-



Fig. 4. (a) *Ex-situ* XRD patterns during galvanostatic charge and discharge at 0.5 C. HRTEM images of VS₂-GO. (b) Discharged to 0.5 V. (c) Charged to 2.0 V. (d) The respective *ex-situ* V 2p XPS spectra of the VS₂-GO electrode at the denoted states.

work for electronic transport, improving the electrical conductivity of the electrode. We also synthesized the VS₂/GO composites with different amount of GO to optimize the ratio of graphene coating. The morphology of these samples is shown in Fig. S3. According to C-S analyzers (Table S2), the graphene contents of the samples are 6.10%, 9.36% and 19.48%, respectively. The composites are in turn marked as VS₂-GO, VS₂-GO-1 and VS₂-GO-2. Fig. S10 displays the cycling performance of these samples, the results show that VS₂-GO with lowest carbon contents has the highest capacity. This is mainly due to that the GO in this battery almost does not provide capacity, the capacity decreases with the increase of graphene contents (Fig. S5). On the other hands, the large amount of graphene decreases the accessible surface area and diffusion rate of ions [45].

To further investigate the charge storage behavior of the VS₂-GO cathode during Li⁺ insertion/extraction, ex-situ XRD, TEM, XPS and EDS mappings are performed (Fig. 4). Fig. 4a shows the XRD patterns of the selected states. The pristine electrode (state a) shows hexagonal VS₂ phase. When the electrode was discharged to 1.3 V (state b), the phase is still VS₂ but with weaker intensity. Further discharging the cell to 1.0 V and 0.5 V (states c and d), the (001) reflection of VS₂ is weakening along with the appearance of two new peaks at 10.1° and 20.2°, indicating the formation of a new phase. This typical phase transition may result from the insertion of Li⁺ into the VS₂ layers (VS₂ + x Li^+ + x $e^- \rightarrow \text{Li}_x \text{VS}_2$) (x = 2.0, According to S1, Supporting information) [38]. The charge process is fully reversible and the electrode can be converted back to VS₂. As a comparison, the ex-situ XRD (Fig. S11) of electrode in LIBs is also performed. The result exhibits the similar structure changes during discharge and charge process, which confirms that the electrochemical reaction is dominated

by Li⁺ intercalation/deintercalation. To further understand the mechanism of VS₂ during the discharge and charge process, ex-situ HRTEM measurements were employed to analyze the structure of the lithiated and delithiated VS₂ electrodes. When the electrode discharged to 0.5 V, the typical HRTEM image (Fig. 4b) shows a clear expanded interplanar distance of 6.69 Å, indicating the intercalation of Li⁺. The electrode still keeps a well layered structure similar to the pristine VS_2 . When the electrode charged to 2.0 V, the HRTEM image (Fig. 4c) shows a clear lattice space of 5.76 Å, corresponding to the (001) plane of VS_2 and the structure recovers. The large interlayer spacings of VS₂ are stable and beneficial for ion diffusion and thus improve Li⁺ storage performance. The ex-situ EDS mappings (Fig. S12) clearly show that C, V, S well keep the original structure during discharge and charge process, while Mg is nearly undetectable, which confirms that it is difficult for Mg²⁺ to intercalate into the VS₂ during the electrochemical process. Besides, the energy storage mechanism is more evident via tracking the variations of the V 2p peaks during the discharge/charge process. As shown in the ex-situ XPS spectra (Fig. 4d), the V⁴⁺ peaks are located at 524.2 and 516.9 eV in fresh electrode [48], respectively, which originate from VS₂. When the electrode is further discharged to 0.5 V, the V⁴⁺ signals are weak, the peaks for V^{3+} can be observed at 522.8 and 515.8 eV [49,50], indicating the charge transfer in vanadium during the Li⁺ insertion process. The V 2p peaks of V⁴⁺ are clear in the spectrum when the electrode charged to 2.0 V. The change of the vanadium valence state further demonstrates the insertion/extraction mechanism.

At a high current density of 5 C, capacity of 146 mA h g^{-1} can be retained even after 10,000 cycles (Fig. 5a). Flexible pouch batteries based on this system were further fabricated to verify the possibility of



Fig. 5. (a) Cyclic performance of VS₂-GO at a current density of 5.0 C. (b) The lighted LED lamp ring and the corresponding flexible pouch-type battery. (c) Average voltage versus reversible capacity and (d) comparison of energy density at various current densities of the state-of-the-art intercalation cathodes for various reported Mg^{2+}/Li^{+} hybrid battery systems with low voltage (≤ 2.0 V) (Mo_6S_8 [20], TiS₂ [21], TiO₂ [22], Li₄Ti₅O₁₂ [23], MoS₂ [41], MoO₂ [46], d-Ti₃C₂T_x [47]).

commercial application. The obtained pouch-type batteries (10×8 cm) are capable of lighting the LED lamp ring (Fig. 5b). Average voltage versus reversible capacity and energy density versus current density for the state-of-the-art intercalation cathodes in various reported Mg²⁺/Li⁺ hybrid battery systems with low voltage (< 2.0 V) are compared (Fig. 5c and d). Since the salt in electrolyte participates the overall reaction, we calculated the theoretical specific capacity as 239 mA h g⁻¹ and specific energy density as 359 W h kg⁻¹ for this battery system, considering 1.5 V as the average discharge voltage (see Supporting information S1 for the calculation details) [51]. Experimentally, we demonstrated the energy density of 353 W h kg⁻¹, standing out among those in previous MLIBs systems. Most of cathodes in the MLIBs show low-rate capability while the VS₂-GO in this work demonstrates the best

electrochemical performance. These advantages make the VS_2 as one of the most promising candidates among currently studied cathode materials for rechargeable energy storage.

4. Conclusion

A novel class of high-performance and safe hybrid magnesiumbased batteries have been successfully fabricated using Mg anode, VS₂-GO cathode and APC-LiCl dual salt electrolyte. The highly stable VS₂ framework and graphene wrapped structure provide more active sites, larger electrode-electrolyte contact area, rapid ion diffusion and electron transport, leading to superior electrochemical performance in MLIBs. The VS₂-GO cathodes deliver a high reversible discharge capacity of 235 mA h g⁻¹ and specific energy density up to 353 W h kg⁻¹. Outstanding high-rate capability (129 mA h g⁻¹ at 80 C, discharge/charge in 32 s) and ultra-long cycle life (146 mA h g⁻¹ capacity remains even after 10,000 cycles at 5 C) are also obtained, which stands out among those of the previous state-of-the-art electrodes of hybrid MLIBs in coin cells. The impressive electrochemical performance demonstrates that the VS₂-GO is a highly promising cathode for commercial hybrid magnesium-based batteries. Besides, our findings provide the opportunity to these types of materials as viable electrode candidates for MLIBs, which represent a great direction for advanced rechargeable electrode materials.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ensm.2017.11.012.

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