

Enhancing Capacity and Rate Performance of Lamellar V_2O_5 Cathode Materials by Modulating Vanadium 3d Orbital Splitting

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Magnesium-ion batteries (MIBs) are promising next-generation energy storage devices. Vanadium oxides are promising cathode materials for MIBs due to their rich chemical valences and versatile structures. However, vanadium oxide cathodes face challenges such as low structural stability, slow Mg^{2+} diffusion kinetics, and low electrical conductivity. The work reported herein used hydrothermal synthesis to pre-intercalate H_2O molecules and Mg^{2+} into V_2O_5 interlayers to stabilize the lamellar structure and modulate V 3d orbital splitting, leading to a $Mg_{0.2}V_2O_5 \cdot 1.5H_2O$ cathode (MVOH1). The V 3d orbital splitting facilitates electron hopping between V^{4+} and V^{5+} cations, leading to the enhanced conductivity of MVOH1; it also makes it easier for V atoms to acquire and lose electrons during discharging and charging, leading to high capacity and high rate capability of MVOH1. Consequently, the MVOH1 cathode exhibited a high specific capacity of 300 mA h g^{-1} at a current density of 0.05 A g^{-1} and retained a specific capacity of 85 mA h g^{-1} at 10 A g^{-1} ; the capacity and rate capability surpass those of previously reported V_2O_5 cathode materials. The aqueous MIB based on MVOH1 demonstrated an ultralong lifespan of 11 000 cycles, which is significantly longer than that of previously reported aqueous MIBs. This study highlights the synergistic effect of regulating interlayer spacing and V 3d orbital splitting on electrochemical performance, which is crucial for developing more efficient and more durable energy storage systems.

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I. INTRODUCTION

Lithium-ion batteries power a wide range of devices, from smartphones to electric vehicles [1]. However, their development is limited by the high cost of lithium and safety concerns [2,3]. Magnesium-ion batteries (MIBs) offer a promising alternative, with benefits such as abundant resources, low cost, and high safety due to inhibited dendrite formation [4,5]. Despite the potential of MIBs,

their development faces challenges. The high charge density of divalent Mg^{2+} leads to its strong interactions with host materials, hindering Mg^{2+} diffusion and causing structural collapse. These issues result in reduced cycling life and specific capacity for MIBs [6–9].

Vanadium-based compounds have attracted substantial attention as cathode materials due to their rich vanadium chemical valences (+2 to +5) and facile distortion of V—O octahedra [10–12]. The presence of multiple oxidation states of vanadium enables a broader range of redox variation and higher specific capacity when vanadium-based materials are used for Mg^{2+} intercalation. In addition, vanadium plays a crucial role in achieving local electroneutrality by the changing of its oxidation states, which helps stabilize the crystal structure and optimize the Mg^{2+} diffusion process [13,14]. Vanadium pentoxide (V_2O_5) is the most promising vanadium oxide cathode material used in MIBs because its weak van der Waals

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forces in V—O bonds provide tunable interlayer spacing for Mg^{2+} insertion, thereby exhibiting a high theoretical specific capacity of 589 mA h g^{-1} [15]. However, the actual capacity and cycling stability of V_2O_5 are still inadequate for large-scale energy applications mainly due to the small layer spacing of V_2O_5 and structural damage caused by the dissolution of vanadium species with low electrical conductivity during Mg^{2+} insertion and extraction [16]. Therefore, molecular and/or metal-cation pre-intercalation has been proposed as an effective strategy to modify the structure and electronic state of V_2O_5 . Pre-intercalating H_2O molecules into interlayers can remarkably expand the interlayer spacing of V_2O_5 and inhibit electrostatic interactions between Mg^{2+} cations and host materials, increasing the diffusion kinetics of Mg^{2+} cations [17]. In addition, H_2O molecules can act as “pillars” in the interlayers to stabilize the layered structure of V_2O_5 . Similarly, pre-intercalating metal ions (M^{2+}) into the interlayers of V_2O_5 can increase its interlayer spacing to enhance the diffusion kinetics of inserted Mg^{2+} cations and stabilize the lamellar structure. More importantly, metal ions in the pre-intercalated V_2O_5 interlayers interact with V—O chains through $M\ 3d$ – $\text{O}\ 2p$ covalent bonds, reducing the band gap. The overlap between $M\ 3d$ and $\text{O}\ 2p$ orbitals and the splitting of $3d$ orbitals promotes electron transfer, which promotes highly stable redox reactions of electrode materials [18,19]. Therefore, designing vanadium-based oxide materials containing intercalated water and metal cations is an ideal strategy to achieve stable Mg^{2+} insertion and extraction and high capacity of MIBs. However, different contents of metal ions and H_2O molecules intercalated in interlayers may have differing coupling effects on host materials [20].

Here we study two vanadium oxide cathode materials pre-intercalated with Mg^{2+} and H_2O molecules: $\text{Mg}_{0.2}\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ (MVOH1) and $\text{Mg}_{0.5}\text{V}_2\text{O}_5 \cdot 2.3\text{H}_2\text{O}$ (MVOH2). These two compositions were selected from a broader range of tested precursor ratios to illustrate the effects of moderate versus excessive pre-intercalation. MVOH1 exhibited a well-balanced interlayer spacing and electronic structure, while MVOH2 enabled the analysis of overintercalation effects on structural reversibility and conductivity. The mixed valence states of vanadium (V^{4+} and V^{5+}) facilitate $3d$ electron hopping, enhancing the electronic conductivity of the cathode materials and increasing the magnesium-storage capacity of the corresponding batteries. Pre-intercalation of H_2O molecules into V_2O_5 interlayers expands their spacing, which further increases as more H_2O molecules are added. However, once the interlayer spacing becomes sufficiently large, pre-intercalation of Mg^{2+} results in a contraction of the layer spacing due to strong electrostatic interactions of Mg^{2+} with VO_x layers. First-principles calculations indicated that the pre-intercalation of H_2O molecules and Mg^{2+} into V_2O_5 interlayers induced the splitting of V $3d$ orbitals,

reducing the band gap. This substantially enhanced the electron-acquiring ability of vanadium atoms, resulting in a low charge-transfer resistance R_{CT} of $0.68\ \Omega$ and high magnesium-ion diffusion coefficient of $4.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for MVOH1. *Ex situ* X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) revealed a highly reversible structural evolution of MVOH1 during the discharging-charging process. Consequently, MVOH1 exhibited an outstanding discharge capacity of 300 mA h g^{-1} at a current density of 0.05 A g^{-1} and excellent high-rate performance (85 mA h g^{-1} at 10 A g^{-1}). An aqueous MIB with the MVOH1 cathode demonstrated an exceptionally long cycling life of 11 000 cycles with a capacity retention of 62%.

II. METHODS

A. Materials

V_2O_5 (purity of 99.5% or greater, Macklin), magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; purity of 99.0% or greater, Sigma-Aldrich], magnesium trifluoromethanesulfonate [$\text{Mg}(\text{CF}_3\text{SO}_3)_2$; purity of 99.0% or greater, Macklin], polyethylene glycol 400 (purity of 99.0% or greater, Aladdin), and perylene-3,4,9,10-tetracarboxylic anhydride (PTCDA; purity of 99.9% or greater, Macklin) were used as received without additional purification.

B. Preparation of MVOH1 and MVOH2 nanobelts

The typical procedure for synthesizing MVOH1 nanoribbons includes the following steps: V_2O_5 (0.18 g) and $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ (0.77 g) are added to 60 ml of deionized water and stirred vigorously in a magnetic stirrer for 1 h to make a thorough mixture. The mixed solution is transferred into a 100 ml Teflon-lined stainless-steel autoclave, and then placed in a blast drying oven at 180°C for 24 h. Then, the precipitation product undergoes three washes with anhydrous ethanol and deionized water, followed by drying in a vacuum drying oven at 80°C for 12 h. Finally, the tan powder sample of MVOH1 is collected. The synthesis steps for MVOH2 were similar to those for MVOH1, with the difference that the amounts of V_2O_5 and $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ used for synthesis of MVOH2 were 4 and 15.38 g, respectively. The synthesis parameters for MVOH1 and MVOH2 were chosen on the basis of preliminary optimization experiments and prior studies on hydrated vanadium oxides. Various $\text{Mg}^{2+}:\text{V}^{5+}$ molar ratios (e.g., $\text{Mg}_{0.1}\text{V}_2\text{O}_5$, $\text{Mg}_{0.2}\text{V}_2\text{O}_5$, $\text{Mg}_{0.3}\text{V}_2\text{O}_5$, and $\text{Mg}_{0.4}\text{V}_2\text{O}_5$) were initially tested. $\text{Mg}_{0.2}\text{V}_2\text{O}_5$ (MVOH1) and $\text{Mg}_{0.5}\text{V}_2\text{O}_5$ (MVOH2) were selected for detailed study as they represent compositions with distinct interlayer structures and electrochemical behaviors: MVOH1 showing optimal performance and MVOH2 highlighting the effect of overintercalation. These representative samples

illustrate the impact of Mg content on orbital splitting and Mg^{2+} storage kinetics.

C. Material characterization

The as-prepared samples underwent powder XRD analysis using Cu $K\alpha$ irradiation ($\lambda = 0.1514178$ nm) with a Rigaku D/Max 2500 PC diffractometer. The composition of the samples was quantitatively determined by inductively coupled plasma optical emission spectroscopy (PerkinElmer 8300). Thermogravimetry–differential thermal analysis (Netzsch STA 449C) was used to determine the molecular formulas of these samples at a heating rate of $15^\circ\text{C min}^{-1}$. The Raman spectra were obtained with a LabRAM HR Evolution system equipped with a 532 nm laser and a confocal objective. A Nicolet iS50 spectrometer was used to acquire Fourier transform infrared (FTIR) spectra over a wavelength range of 400–4000 cm^{-1} with a resolution of 0.09 cm^{-1} . XPS with an ESCALAB 250Xi instrument was used to analyze the oxidation and reduction states of Mg, V, and O. A Quattro S scanning electron microscope was used to examine the microstructure of the prepared samples. TEM and high-resolution TEM (HRTEM) analyses were conducted with a Talos F200S transmission electron microscope to obtain detailed information about the nanostructure and crystal lattices of MVOH1 and MVOH2.

D. Electrochemical measurements

The electrochemical characterizations of MVOH1 and MVOH2 were conducted with a conventional standard three-electrode electrochemical cell. Platinum foil was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The fabrication of the working electrode involved the mixing of the active material (MVOH1 or MVOH2), acetylene black, and polyvinylidene fluoride in a weight ratio of 7:2:1 in *N*-methyl-2-pyrrolidone solvent to create a slurry. After thorough mixing, the slurry was spread onto carbon fiber cloths ($1 \times 1.5\text{ cm}^2$) and then dried in a vacuum oven at 80°C overnight to form the electrodes. The active material of each electrode had a mass loading of approximately $2\text{--}3\text{ mg cm}^{-2}$. The study used an electrolyte solution comprising a $2M$ aqueous solution of $\text{Mg}(\text{CF}_3\text{SO}_3)_2$. To analyze the electrochemical properties of the systems, a Chenhua CHI660E electrochemical workstation was used. This instrument facilitated the measurement of critical parameters, including cyclic voltammetry (CV), galvanostatic charging and discharging (GCD), and electrochemical impedance spectroscopy (EIS) curves. The impedance measurements were performed across a frequency range of 10^{-2} to 10^5 Hz. The diffusion coefficient D_{Mg} of Mg^{2+} ions can be determined with Eqs. (1) and (2):

$$D_{\text{Mg}} = 0.5(RT/n^2F^2AC_{\text{Mg}}A_w)^2, \quad (1)$$

$$Z' = R_s + R_{\text{CT}} + A_w\omega^{-1/2}, \quad (2)$$

where R stands for the gas constant, T represents room temperature, n denotes the number of electrons transferred (in this case, $n = 1$), F represents the Faraday constant, A represents the electrode's surface area, C_{Mg} represents the concentration of Mg^{2+} , and A_w represents the slope of Z' plotted against $\omega^{-1/2}$ [21]. Here, Z' denotes the real impedance, and ω represents the angular frequency.

The assembled PTCDA/MVOH1 full cell had a mass ratio of active materials of approximately 3(PTCDA):1(MVOH1) in atmospheric air. The electrolyte was $2M$ $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ solution prepared by the mixing of deionized water and polyethylene glycol in a volume ratio of 1:1. Additionally, a Whatman grade GF/A glass fiber separator was used. The electrochemical performance of the full cell was evaluated by CV and GCD measurements. CV tests were conducted with the Chenhua CHI660E electrochemical workstation, while the galvanostatic charge-discharge tests were performed with a multichannel battery testing machine (CT4008A, Neware) across different current densities within the potential range of 0–1.7 V. The energy density (E ; Wh kg^{-1}) and power density (P ; W kg^{-1}) of the full cell were obtained by analysis of the galvanostatic charge-discharge curves with the use of the following equations:

$$E = \int_{t_1}^{t_2} UIdt, \quad (3)$$

$$P = \frac{E}{t}, \quad (4)$$

where t_1 and t_2 represent the start and end times (seconds) of the discharge, respectively, Δt is the difference between t_2 and t_1 (seconds), I is the discharge current (amperes), and U is the voltage range (volts). In this case, the specific capacity, energy density, and power density are calculated by considering the mass of the cathode as the reference parameter.

E. Computational methods

Density functional theory (DFT) calculations were conducted with the Vienna Ab initio Simulation Package [22]. To optimize the crystal structure and compute the density of states, we used projector augmented wave potentials with the Perdew–Burke–Ernzerhof exchange–correlation functional [23]. In addressing the significant electron correlation effects inherent to transition metal V, our calculations also incorporated the DFT + U method with $U = 3.25\text{ eV}$ [24]. A Γ -centered Monkhorst-Pack $\mathbf{k}$ -point grid with dimensions of $2 \times 7 \times 2$ was applied for Brillouin zone sampling, with a cutoff energy of 500 eV. Convergence was achieved by optimization of the structures until the forces on each individual atom fell below

0.01 eV Å⁻¹. The crystal structure was visualized and analyzed with VESTA [25].

III. RESULTS AND DISCUSSION

A. Characterization of the lamellar V₂O₅ cathode

H₂O molecules and Mg²⁺ cations were pre-intercalated into V₂O₅ interlayers by a hydrothermal method with

vanadium pentoxide and magnesium nitrate hexahydrate as raw materials, producing two materials, MVOH1 and MVOH2, with different raw material ratios [see Sec. II and Fig. 1(a)]. Figure 1(b) shows the XRD patterns of the two materials, which exhibit distinct (001) reflections that are indicative of lamellar turbostratic ordering. Additionally, the observed pattern closely resembles that of previously reported pre-intercalated vanadium oxide

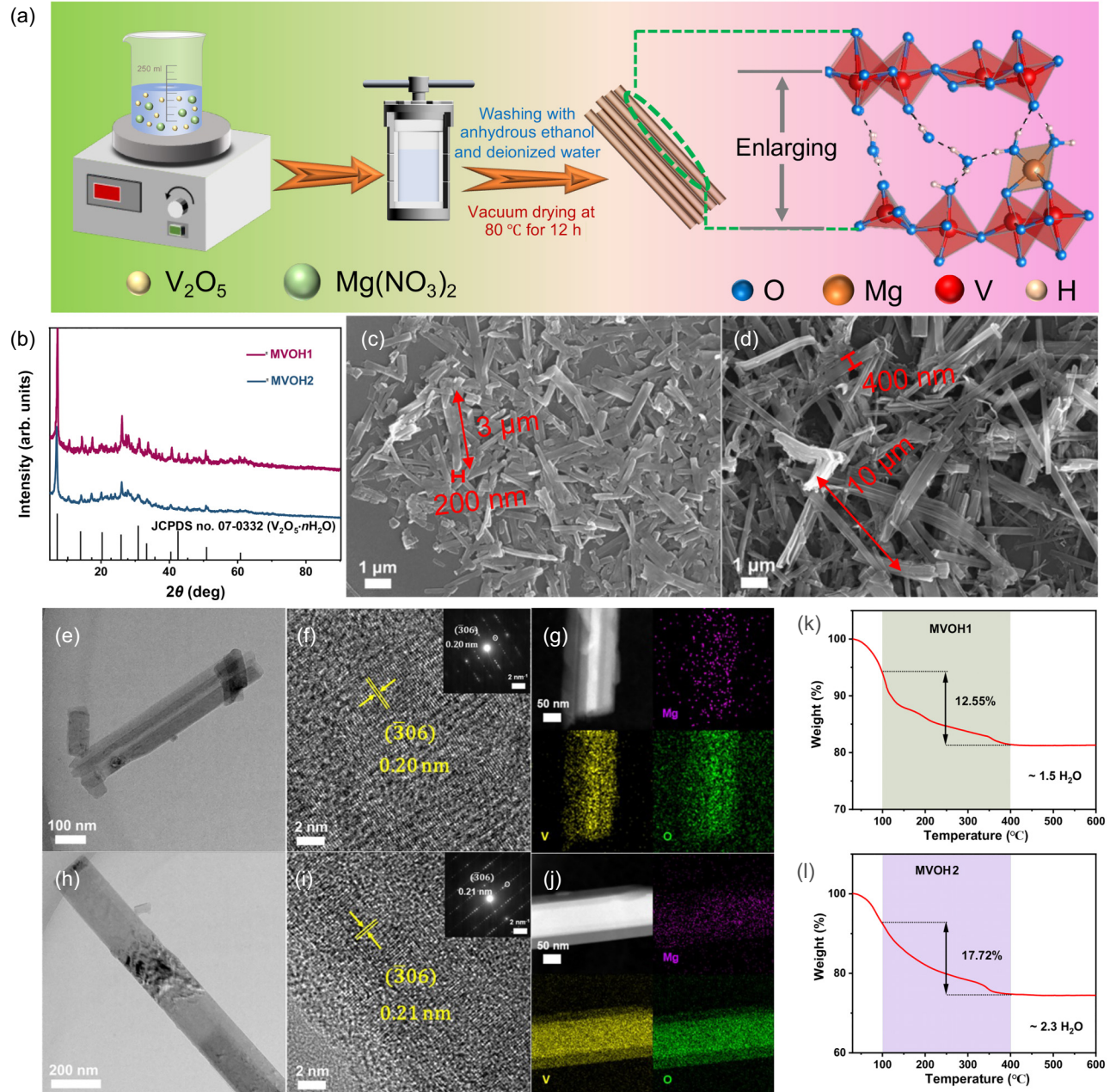


FIG. 1. Characterization results for MVOH1 and MVOH2: (a) Process for preparing MVOH. (b) XRD patterns of MVOH1 and MVOH2. (c),(d) SEM images of MVOH1 and MVOH2, respectively. (e) TEM image of MVOH1. (f) HRTEM image of MVOH1 (the inset shows the SAED pattern). (g) STEM-EDS elemental mappings of MVOH1. (h) TEM image of MVOH2. (i) HRTEM image of MVOH2 (the inset shows the SAED pattern). (j) STEM-EDS elemental mappings of MVOH2. (k),(l) Thermogravimetric analysis curves for MVOH1 and MVOH2, respectively.

materials derived from the parent compound $V_2O_5 \cdot nH_2O$ (JCPDS no. 07-0332) [12,26,27]. On the basis of the position shift of the (001) peak, the interlayer distances of MVOH1 and MVOH2 were calculated to be 12.3 and 12.5 Å, respectively. Compared with the interlayer spacing of $V_2O_5 \cdot nH_2O$ (12.1 Å), those of MVOH1 and MVOH2 were considerably wider due to the intercalation of Mg^{2+} cations and structural H_2O molecules, which favor Mg^{2+} insertion and extraction. Scanning electron microscopy (SEM) was used to investigate the morphology of MVOH1 and MVOH2 [Figs. 1(c) and 1(d)], which show nanobelts. MVOH1 has a nanobelt width of 100–300 nm and a nanobelt length of several micrometers, whereas MVOH2 has a nanobelt width of about 200–500 nm and an average nanobelt length exceeding 10 µm. The crystal structures of MVOH1 and MVOH2 nanobelts were further characterized by TEM [Figs. 1(e)–1(g)]. HRTEM images showed clear lattice fringes in the MVOH1 nanobelts with a spacing of 0.20 nm, corresponding to the (306) planes of MVOH1 [Fig. 1(f)].

The inset selected-area electron diffraction (SAED) pattern shows the single-crystal nature of MVOH1, with labeled spots attributed to the (306) planes. Scanning transmission electron microscopy–energy-dispersive x-ray spectroscopy (STEM-EDS) mapping confirmed that Mg, V, and O were uniformly distributed in MVOH1 [Fig. 1(g)]. Figure 1(i) shows the lattice spacing of MVOH2 to be 0.21 nm, corresponding to the (306) planes, as verified by the inset SAED pattern. The STEM-EDS mapping images of MVOH2 demonstrate a uniform distribution of Mg, V, and O [Fig. 1(j)].

Inductively coupled plasma optical emission spectroscopy was used to determine the Mg and V contents in MVOH1 and MVOH2, revealing Mg:V molar ratios of 0.2:2 and 0.5:2 in MVOH1 and MVOH2, respectively [21]. Thermogravimetric analysis [Figs. 1(k) and 1(l)] indicated that MVOH1 showed a weight loss of 12.55%, while MVOH2 exhibited a weight loss of 17.72% due to crystal water loss. This indicated crystal water contents of 1.5 and 2.3 molecules in MVOH1 and MVOH2, respectively. Consequently, the chemical formulas of MVOH1 and MVOH2 were represented as $Mg_{0.2}V_2O_5 \cdot 1.5H_2O$ and $Mg_{0.5}V_2O_5 \cdot 2.3H_2O$, respectively. The average V valency in MVOH1 was 4.8, while that in MVOH2 was 4.5. Raman spectroscopy demonstrated that MVOH1 and MVOH2 inherited the layered structure of V_2O_5 [21]. The peak at 155 cm^{-1} corresponds to the bending vibrations of the —O—V—O—V— chain, characteristic of the vanadium oxide layered structure [28–30]. The signals at 266 and 323 cm^{-1} originated from the bending vibrations of the V=O bond, while the peaks at 513, 703, and 1018 cm^{-1} are attributed to the stretching vibrations of V—O—V [31,32]. The weak peak at 857 cm^{-1} is attributed to the stretching vibrations of the V—OH₂ bond, indicating the presence of structural water [27,33]. FTIR spectra of MVOH1 and

MVOH2 exhibited typical features of the $V_2O_5 \cdot nH_2O$ structure [21]. The signals at 3421 and 1624 cm^{-1} correspond to the stretching vibrations of the O—H bond and the bending vibrations of H—O—H, respectively, confirming the presence of crystalline water [34,35]. The signal at 1006 cm^{-1} corresponds to the stretching vibration mode of the V=O bond. The signal at 852 cm^{-1} is associated with the stretching vibration of the V—O bond, while the signals at 525 and 728 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of the V—O—V bond, respectively [36–38]. XPS was conducted to further investigate the chemical composition of MVOH1 and MVOH2 [21]. The O 1s spectra of both samples exhibited three fitted signal peaks attributed to different forms of O²⁻ bonding in V—O (530.1 eV), Mg—O (531.2 eV), and H₂O (532.9 eV) [39]. The peaks at 517.4 and 524.8 eV are attributed to the V 2p_{3/2} and V 2p_{1/2} levels of V⁵⁺, while the peaks at 516.1 and 523.4 eV correspond to the V 2p_{3/2} and V 2p_{1/2} levels of V⁴⁺. Peak deconvolution revealed that 80% of V in MVOH1 existed as V⁵⁺ and 20% as V⁴⁺, resulting in an average V valency of +4.8, consistent with the chemical formula $Mg_{0.2}V_2O_5 \cdot 1.5H_2O$. Similarly, in MVOH2, 57% of V was in the form of V⁵⁺ and 43% in the form of V⁴⁺, resulting in an average V valency of +4.5, consistent with the chemical formula $Mg_{0.5}V_2O_5 \cdot 2.3H_2O$. The presence of V⁴⁺ indicates that Mg^{2+} had been chemically pre-inserted into V_2O_5 interlayers, leading to a partial reduction of V [40]. In MVOH1 and MVOH2, the coexistence of V⁵⁺ and V⁴⁺ facilitated the movement of 3d electrons from the 3d orbital of V⁴⁺ to the vacant 3d orbital of V⁵⁺, enhancing electronic conductivity and boosting rate capability [41–43].

B. Regulation of V 3d orbital splitting

To investigate the effect of pre-intercalation of H_2O molecules and Mg^{2+} cations on the properties of MVOH1 and MVOH2, *ab initio* calculations based on density functional theory were conducted. Different numbers of H_2O molecules (zero, two, four, and six) were pre-intercalated into the interlayer of V_2O_5 , together with the simultaneous pre-intercalation of six H_2O molecules and one Mg^{2+} cation. The corresponding lattice structures were relaxed, and the stable crystal structures are provided in Supplemental Material [21]. According to this constructed structure model, we simulate its XRD pattern, and it matches well with the standard XRD pattern of $V_2O_5 \cdot nH_2O$ (JCPDS no. 07-0332) at low diffraction angles, which also agrees well with the experimentally determined XRD patterns of MVOH1 and MVOH2 at low diffraction angles [21]. Without Mg^{2+} , as the amount of pre-intercalated H_2O molecules increases, they combine via hydrogen bonds, forming H_2O chains in the interlayer of V_2O_5 . This increases the interlayer spacing from 6.32 Å for V_2O_5 to 12.5 Å for $V_2O_5 \cdot 6H_2O$ [21]. When one Mg^{2+}

cation is pre-intercalated with six H_2O molecules, the interlayer H_2O chain is disrupted [21]. Instead, the Mg^{2+} cation binds with two O atoms in the lower V—O layer and coordinates with two H_2O molecules. One of the coordinated H_2O molecules forms a hydrogen bond with the O atom in the upper V—O layer, creating a bonding chain of V (lower)—O—Mg—O—H—O—V (upper). Because of the reduced interlayer spacing, the pre-intercalated H_2O can also directly coordinate with V in the lower V—O layer and generate a bonding chain with the upper V—O layer via H_2O molecule bridges. These bonding chains between the upper and lower V—O layers reduce the interlayer spacing to 11.0 Å. This indicates that H_2O molecules and Mg^{2+} cations have opposing effects on the interlayer spacing: H_2O molecules tend to expand the interlayer spacing of V_2O_5 , whereas pre-intercalated Mg^{2+} can contract the interlayer spacing when it becomes too large. This explains the similar interlayer spacing observed in synthesized MVOH1 and MVOH2.

Furthermore, the variation in the electronic structure of V_2O_5 with the pre-intercalation of H_2O molecules and Mg^{2+} cations was explored. The projected density of states (PDOS) of the V $3d_{xy}$ orbital in each pre-intercalated vanadium oxide cathode material is shown in Fig. 2. Further, the PDOS of other V $3d$ orbitals and the total PDOS of V are shown in Supplemental Material [21]. When two H_2O molecules are pre-intercalated into V_2O_5 interlayers,

symmetric PDOS distribution curves appear for spin-up and spin-down channels of the d_{xy} orbital [Fig. 2(b)]. When four H_2O molecules are pre-intercalated, the PDOS of the d_{xy} orbital exhibits a new peak, indicating orbital splitting that generates a new localized band at lower energies [Fig. 2(c)]. As the number of pre-intercalated H_2O molecules increases to six, another new peak appears in the PDOS of the d_{xy} orbital, implying further orbital splitting [Fig. 2(d)]. However, the PDOS value at the Fermi level remains almost zero when two to six H_2O molecules are pre-intercalated. When six H_2O molecules and one Mg^{2+} cation are simultaneously pre-intercalated into V_2O_5 interlayers, the PDOS of the d_{xy} orbital splits into four distinct peaks in the energy range of 0–1.0 eV, indicating more pronounced orbital splitting [Fig. 2(e)]. Meanwhile, the PDOS is distributed in the negative energy range, implying the development of magnetization and predominant electron occupation in the spin-up channel in the high-energy valence bands (VBs). The VBs overlap with the conduction bands (CBs) at the Fermi level, and the lowest distribution in the CBs has an energy as low as 0.25 eV, indicating excellent electronic conductivity and high electron-acquiring ability. Therefore, the simultaneous pre-intercalation of H_2O molecules and Mg^{2+} cations is an effective strategy to enhance the capacity and rate capability of vanadium oxides. The PDOS of the V $3d_{xy}$ orbital in MVOH1 and MVOH2 is shown in Figs. 2(e)

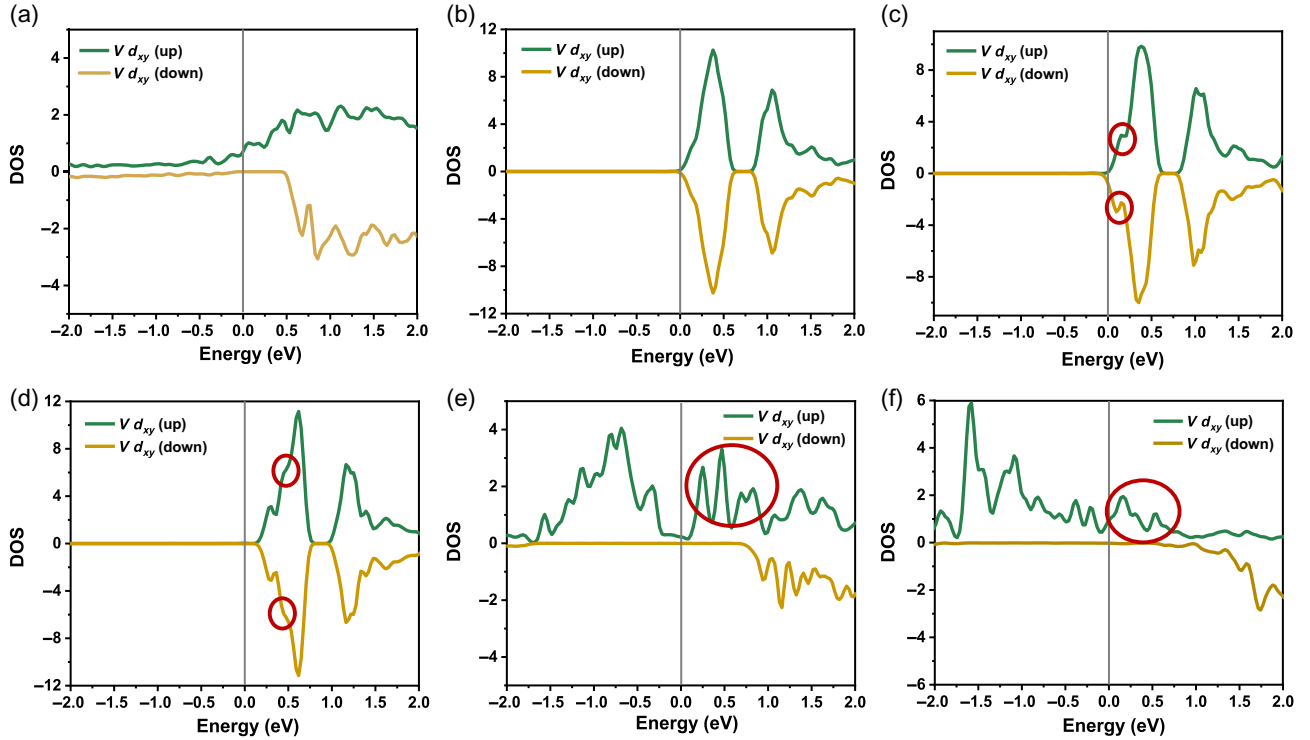


FIG. 2. PDOS of V $3d$ orbitals for different vanadium oxide structures: (a) V_2O_5 ; (b) $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$; (c) $\text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$; (d) $\text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$; (e) $\text{Mg}(\text{V}_2\text{O}_5)_4 \cdot 6\text{H}_2\text{O}$ (approximating MVOH1); and (f) $\text{Mg}_2(\text{V}_2\text{O}_5)_4 \cdot 9\text{H}_2\text{O}$ (approximating MVOH2).

and 2(f), indicating substantial splitting. Because of the larger amount of pre-intercalated H_2O molecules and Mg^{2+} cations, more severe splitting of the V $3d_{xy}$ orbital occurs in MVOH2. The VBs and CBs of MVOH1 and MVOH2 overlap at the Fermi level, implying enhanced electronic conductivity. However, the VBs and CBs of MVOH1 are composed mainly of the d_{xy} orbital [21]; the PDOS of the d_{xy} orbital is distributed in the energy range of -1.4 to -0.5 eV in the valence band and in the energy range of 0.2 – 0.8 eV in the conduction band. Meanwhile, the valence band of MVOH2 is composed mainly of the d_{xy} orbital, while its conduction band is composed primarily of the d_{yz} orbital [21]. The former is distributed in the energy range of -1.7 to -0.9 eV and the latter is distributed in the 0.8 – 1.8 eV range. The energy gap between the VBs and CBs is substantially larger in MVOH2 than in MVOH1, leading to lower electronic conductivity and electron-acquiring ability of MVOH2. Quantitative analysis results for V $3d$ orbital splitting show that the relative conductivity σ_{rel} of MVOH1 is 2.879, which is indeed higher than that of MVOH2 (1.736) [21]. The electronic conductivity of MVOH1 is determined to be 5.21 mS m^{-1} while that of MVOH2 is 4.46 mS m^{-1} , further verifying the enhanced electronic conductivity provided by V $3d$ orbital splitting. Consequently, poorer rate capability and lower discharge capacity are expected for MVOH2. These calculation results reveal that excessive pre-intercalation of H_2O molecules and Mg^{2+} cations is disadvantageous for improving the charge storage performance of vanadium oxides. Although previous studies explored the intercalation of metal cations (Mg^{2+} , Mn^{2+} , Zn^{2+} , etc.) into V_2O_5 , such cations can only enlarge the interlayer spacing or modulate the electronic structure [12,30,44]. Previous work revealed that interlayer H_2O molecules can facilitate the diffusion of Mg^{2+} in the interlayer spacing and stabilize the lamellar structure [17]. In contrast, the co-intercalation strategy leverages the complementary roles of H_2O and Mg^{2+} : H_2O facilitates expanded spacing and diffusion kinetics, while Mg^{2+} tunes the local electronic structure by inducing stronger orbital splitting and band gap reduction. This dual-modulation approach offers a more effective pathway to simultaneously optimize structural integrity, electronic conductivity, and Mg^{2+} transport kinetics.

C. Electrochemical performance of the lamellar V_2O_5 cathode

Since the electronic structure substantially influences the electrochemical performance of electrode materials, the Mg^{2+} storage capabilities of the MVOH1 and MVOH2 nanobelts as cathodes were investigated in three-electrode cells assembled with $2M \text{ Mg}(\text{CF}_3\text{SO}_3)_2$ aqueous electrolyte. Platinum and a SCE were used as the counter and reference electrodes. The CV curves of the two cathodes

at a scan rate of 1 mV s^{-1} in a voltage window of -0.6 to 1.0 V (vs SCE) are shown in Fig. 3(a). Both electrodes exhibit two distinct redox peaks, indicating multiple processes and high Mg^{2+} insertion-extraction reversibility. The redox reactions of MVOH1 occur at potentials of -0.30 and -0.10 V and 0.22 and 0.33 V , while those of MVOH2 occur at -0.31 and -0.12 V and 0.23 and 0.31 V . The peak currents are larger in MVOH1 than in MVOH2, signifying a larger capacity for MVOH1. The GCD curves of MVOH1 and MVOH2 at various current densities exhibit multiple distinct voltage plateaus during the charging and discharging processes, which is consistent with the two pairs of redox peaks observed in the CV curves [Fig. 3(b)]. At a current density of 0.05 A g^{-1} , MVOH1 exhibits a discharge capacity of 300 mA h g^{-1} , while MVOH2 shows a discharge capacity of 260 mA h g^{-1} [Fig. 3(c)]. The high capacity of MVOH1 surpasses the capacity of other reported MIB cathodes [21]. As the current density increases from 0.05 to 10 A g^{-1} , the discharge capacity of MVOH1 is determined to be $300, 183, 155, 129, 111, 109, 101, 95, 91, 88,$ and 85 mA h g^{-1} , respectively [Fig. 3(d)]. MVOH2 exhibits a discharge specific capacity of 260 mA h g^{-1} at 0.05 A g^{-1} and 39 mA h g^{-1} at 10 A g^{-1} [Fig. 3(e)], indicating poor rate capability. Figure 3(c) clearly shows the superior rate performance of MVOH1 compared with MVOH2. When the current density returns to 0.05 A g^{-1} , the discharge capacity of MVOH1 rapidly recovers to 298 mA h g^{-1} , retaining 99.3% of the initial capacity and demonstrating excellent rate performance [Fig. 3(d)]. In contrast, the discharge capacity of MVOH2 recovers only 54.5% of its initial value when the current density returns to 0.05 A g^{-1} . The cycling performances of MVOH1 and MVOH2 at 4 A g^{-1} are illustrated in Fig. 3(f). The MVOH1 cathode shows an initial capacity of 100 mA h g^{-1} with a high capacity retention ratio of 75% after 100 cycles, whereas the capacity retention ratio of the MVOH2 cathode is only 36%. Therefore, the MVOH1 cathode demonstrates superior Mg^{2+} storage performance, including higher discharge capacity, better rate capability, and longer cycling lifespan. These results correlate well with the appropriate splitting extent of the V $3d$ orbital in MVOH1. Although MVOH2 has a larger interlayer spacing than MVOH1, the less favorable splitting of the V $3d$ orbital in MVOH2 leads to its poorer Mg^{2+} storage performance.

The Mg^{2+} storage kinetics of MVOH1 and MVOH2 were investigated through CV measurements at scan rates of 0.2 – 1.0 mV s^{-1} . The similar shapes and redox peaks observed indicated rapid migration kinetics and highly reversible Mg^{2+} insertion and extraction. The peak current i and sweep rate v relationship followed the power-law equation $i = av^b$, where a and b are adjustable parameters. Regression analysis of the peak current and sweep rate for peaks 1–4 in Fig. 4(a) yielded b values of $1.00, 0.83, 0.97,$ and 0.95 [Fig. 4(b)], indicating

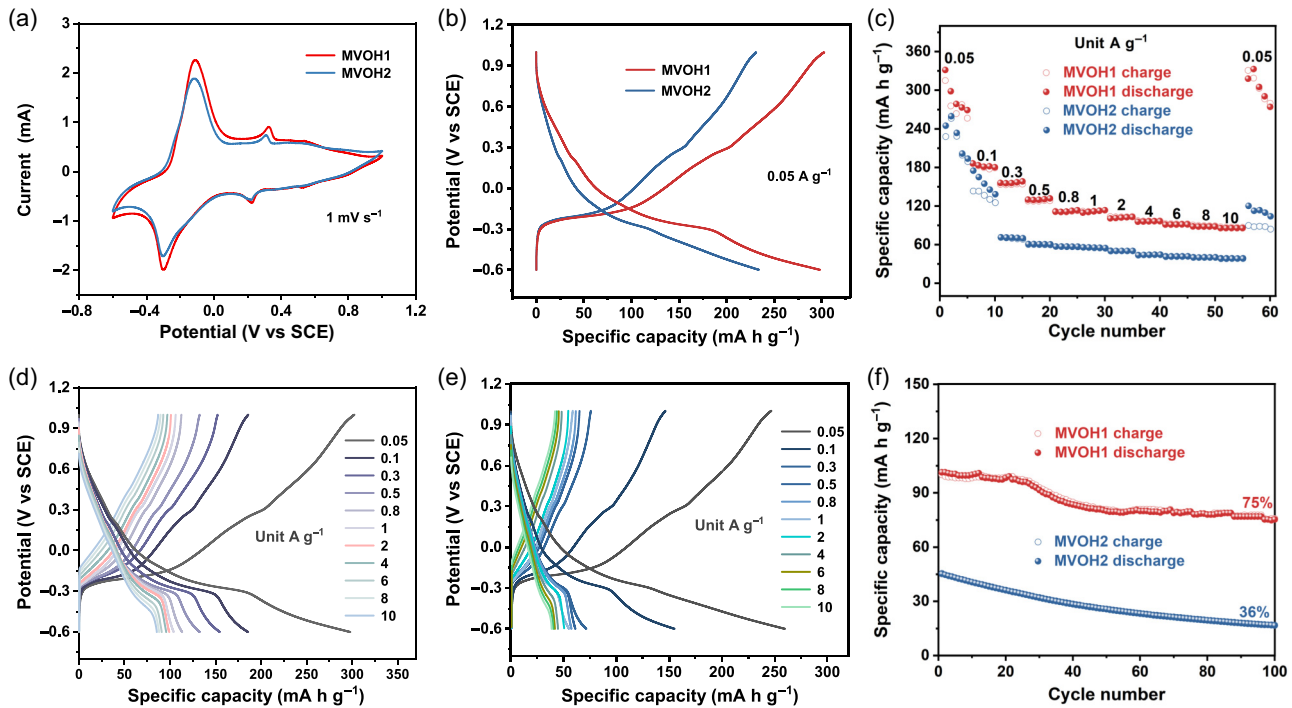


FIG. 3. Electrochemical characterization of MVOH1 and MVOH2: (a) CV curves. (b) Charge-discharge profiles. (c) Rate capability. (d) Charge-discharge profiles at different rates for the MVOH1 electrode. (e) Charge-discharge profiles at different rates for the MVOH2 electrode. (f) Cycling performance of the MVOH1 and MVOH2 electrodes at 4 A g⁻¹.

that MVOH1's charge storage ability resulted primarily from surface pseudocapacitive reactions. In addition, the equation $i(V) = k_1 v + k_2 v^{1/2}$ was used to quantitatively evaluate the contribution of pseudocapacitance $k_1 v$ and diffusion $k_2 v^{1/2}$ to the specific capacity of MVOH1, where $i(V)$ represents the current at a specific voltage V . As the scan rate increased from 0.2 to 1.0 mV s⁻¹, the calculated pseudocapacitive contribution for MVOH1 increased from 76.5% to 86.36% [Figs. 4(c) and 4(d)], indicating favorable diffusion kinetics of Mg²⁺ during charging and discharging. For MVOH2, the regressed b values for peak currents and sweep rates were 0.83, 0.77, 0.89, and 0.79 in the same scan rate range [Figs. 4(e) and 4(f)], implying contributions from surface pseudocapacitance and diffusion to the capacity [45]. The pseudocapacitance contribution ratio of MVOH2 increased from 68.43% at 0.2 mV s⁻¹ to 80.57% at 1.0 mV s⁻¹ [Figs. 4(g) and 4(h)], which are lower values than those for MVOH1, indicating more sluggish Mg²⁺ insertion and extraction kinetics in MVOH2. The high pseudocapacitance contributions of MVOH1 and MVOH2 are attributed to the increased inter-layer spacing, the improved electronic conductivity due to the splitting of the V 3d orbitals, and the presence of a large number of electrochemically active sites associated with the hydrated lamellar structure. These features facilitate surface redox reactions and rapid charge transfer, which jointly promote pseudocapacitive behavior. EIS was used

to further examine the Mg²⁺ migration kinetics in MVOH1 and MVOH2 [21]. The diffusion coefficient of Mg²⁺ D_{Mg} for MVOH1 was calculated to be 4.0×10^{-12} cm² s⁻¹, higher than that for MVOH2 (1.9×10^{-13} cm² s⁻¹) and other reported aqueous MIB cathode materials [21], indicating faster migration kinetics of Mg²⁺ in MVOH1. The R_{CT} values of MVOH1 and MVOH2 were determined to be 0.68 and 0.83 Ω , respectively, signifying rapid Mg²⁺ migration at the cathode-electrolyte interface in MVOH1, which aligns with its higher electric conductivity and greater electron-acquiring ability of V with more pronounced 3d orbital splitting. The remarkably high capacity and excellent rate capacity of MVOH1 were attributed to the fast bulk migration and interface crossing of Mg²⁺ ions.

D. Crystal structure evolution of the lamellar V₂O₅ cathode

Ex situ XRD measurements were performed to elucidate the crystallographic structure evolution of MVOH1 and MVOH2 during the first two discharge-charge cycles [Fig. 5(a)]. No new diffraction peaks appeared, and the peak intensities changed slightly during the insertion and extraction of Mg²⁺, indicating no phase transition and a typical intercalation reaction mechanism [Fig. 5(b)]. The (001) peak of MVOH1 at 7.2° corresponded to a

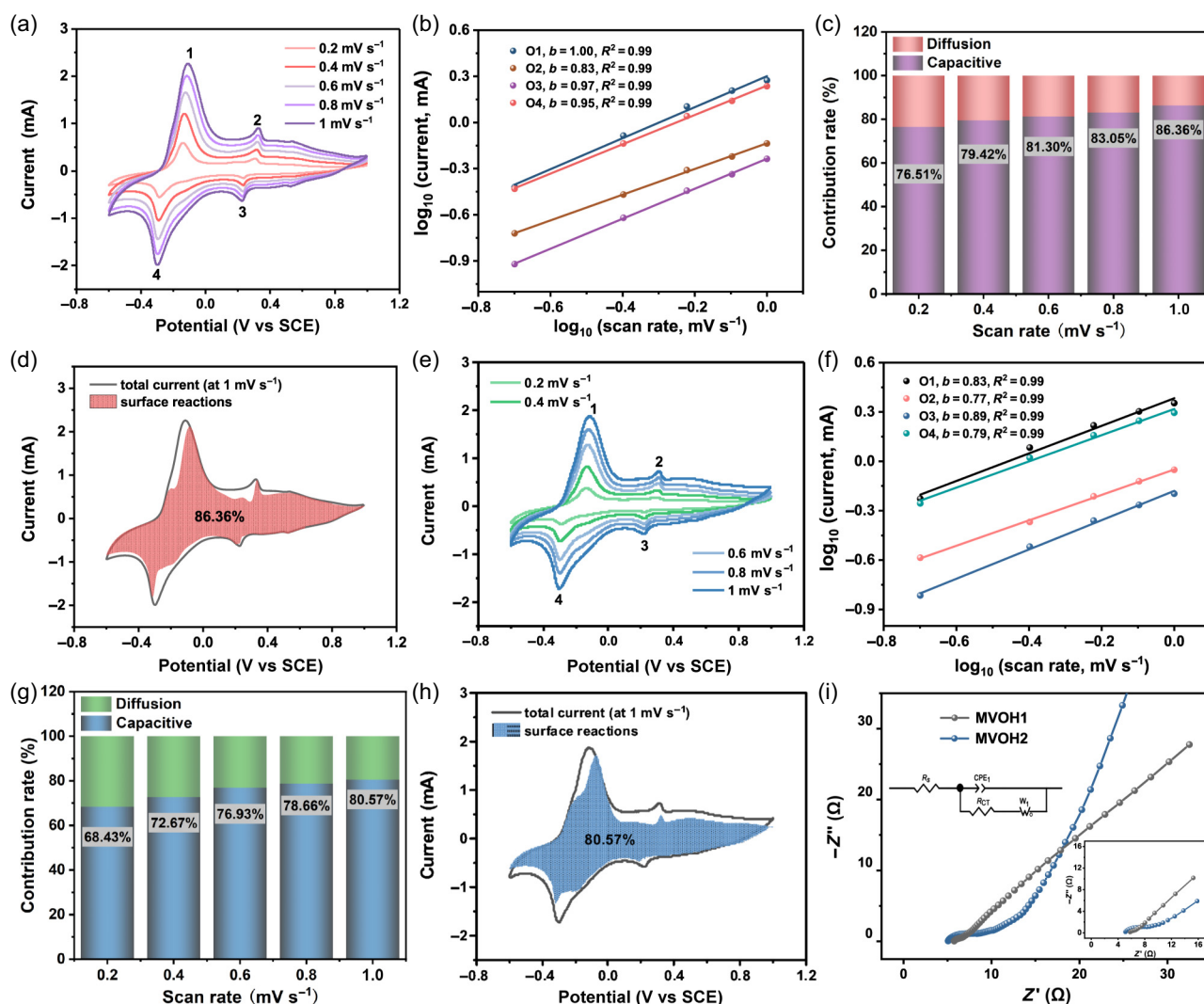


FIG. 4. Electrochemical kinetics of the MVOH1 cathode: (a) CV curves at different scan rates; (b) b values corresponding to four redox peaks; (c) capacity contribution ratio at different scan rates; (d) capacitance separation at 1 mV s⁻¹. Electrochemical kinetics of the MVOH2 cathode: (e) CV curves at different scan rates; (f) b values corresponding to four redox peaks; (g) capacity contribution ratio at different scan rates; (h) capacitance separation at 1 mV s⁻¹. (i) EIS spectra of MVOH1 and MVOH2. CPE₁ refers to constant phase element, and W_1 denotes Warburg diffusion impedance.

layer spacing of 12.3 Å, which shifted to 7.7° at the first discharge event (at -0.6 V) (points A–D), indicating a decrease in layer spacing to 11.5 Å due to electrostatic interactions between inserted Mg²⁺ and V–O layers. When the cathode was charged to 1.0 V (points D–H), the (001) peak shifted to 7.3°, corresponding to a recovery of layer spacing to 12.1 Å. After that, the XRD pattern followed the same rule in the second cycle (points H–L–P), indicating the highly reversible nature of Mg²⁺ insertion and extraction in MVOH1. The MVOH2 cathode also showed the same intercalation reaction mechanism without new XRD peaks [21]. As Mg²⁺ cations are inserted, the (001) diffraction peak gradually shifts from 7.1° (layer spacing 12.5 Å) to 7.6° (layer spacing 11.6 Å) in the initial discharge process. However, no substantial shift of

the (001) diffraction peak is observed in the subsequent charge process, indicating irreversible changes in the initial discharge process. This demonstrates that the excessive pre-intercalation of Mg²⁺ in the V₂O₅ interlayer hinders the reversible insertion and extraction of newly inserted Mg²⁺. These results were further confirmed by *ex situ* TEM characterizations [Fig. 5(c)]. In the initial state, the interlayer spacing of MVOH1 is 0.20 nm, corresponding to the (306) planes of MVOH1. When MVOH1 is discharged to -0.6 V, the lattice spacing of the (306) planes decreases to 0.17 nm and recovers to 0.20 nm when MVOH1 is fully charged to 1.0 V, demonstrating the intercalation reaction mechanism and excellent reversibility of Mg²⁺ insertion and extraction. In contrast, the MVOH2 cathode undergoes a contraction of the lattice spacing from 0.21 nm in the

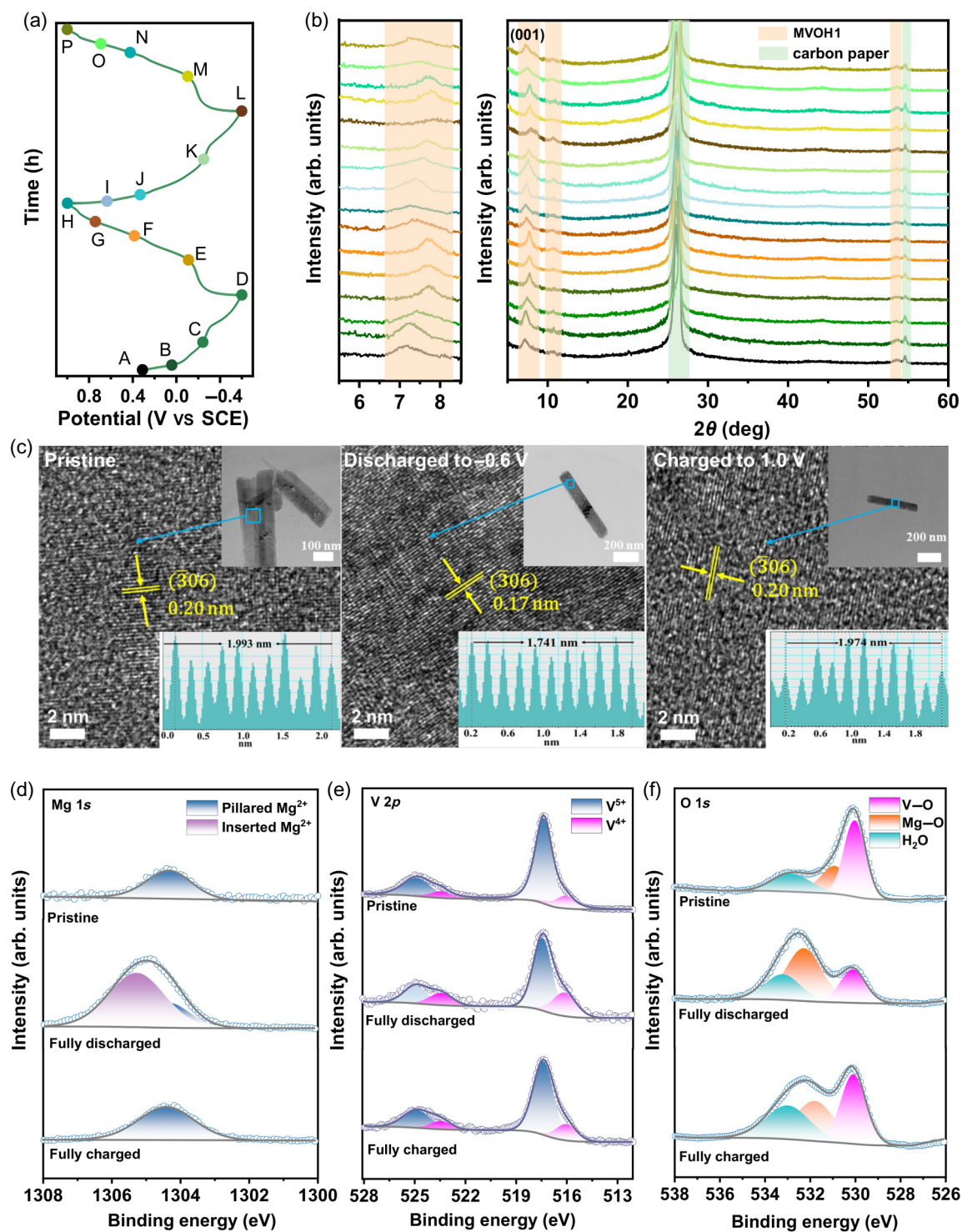


FIG. 5. Electrochemical reaction mechanism of the MVOH1 cathode: (a) Charge-discharge curves in selected states during the first and second cycles at 0.05 A g^{-1} . (b) *Ex situ* XRD patterns, and (c) *ex situ* HRTEM images in the pristine, discharged to -0.6 V , and charged to 1.0 V states. (d)–(f) *Ex situ* high-resolution XPS spectra in the pristine, fully discharged, and fully charged states: (d) Mg 1s core level, (e) V 2p core level, and (f) O 1s core level.

initial state to 0.19 nm after a full discharge [21]. However, in the fully charged state, the reduced lattice spacing recovers only to 0.20 nm , indicating irreversible changes in

MVOH2 during the initial discharge process and poor Mg^{2+} storage performance. Furthermore, the STEM-EDS images show the uniform distributions of Mg, V, and O

in MVOH1 and MVOH2 in each charged and discharged state [21]. The Mg distribution images of MVOH1 in the pristine, fully discharged, and fully charged states demonstrate the reversible insertion and extraction of Mg^{2+} in MVOH1 [21]. In contrast, those of MVOH2 display the noticeable residue of newly inserted Mg^{2+} after a full charge, indicating irreversible insertion and extraction of Mg^{2+} in MVOH2 [21].

Ex situ XPS measurements were performed to investigate the valence changes of Mg, V, and O in the MVOH1 and MVOH2 cathodes in different states. As shown in Fig. 5(d), the signal at 1304.2 eV in pristine MVOH1 is attributed to pre-intercalated Mg^{2+} . In contrast, a new signal is observed at a higher energy level of 1304.2 eV when the cathode is fully discharged to -0.6 V, which is attributed to the newly inserted Mg^{2+} during the discharging process. When MVOH1 is charged to 1.0 V, the signal of the inserted Mg^{2+} disappears, and the Mg 1s signal returns to being that of pristine MVOH1, demonstrating the high reversibility of Mg^{2+} insertion and extraction. For the V 2p core level [Fig. 5(e)], pristine MVOH1 shows a small amount of V^{4+} produced by the pre-intercalation of Mg^{2+} in the interlayer. When MVOH1 is discharged to -0.6 V, the content of V^{4+} rapidly increases. In contrast, the corresponding V^{5+} content decreases, resulting in a decrease in the $\text{V}^{5+}:\text{V}^{4+}$ ratio from 4:1 to 2:1. This indicates that the reduction of V^{5+} occurs during Mg^{2+} insertion. After MVOH1 has been charged to 1.0 V, the $\text{V}^{5+}:\text{V}^{4+}$ ratio returns to the initial state of 4:1, illustrating the highly reversible insertion and extraction of Mg^{2+} in MVOH1. Figure 5(f) displays the O 1s core levels of MVOH1, revealing three distinct O atoms: O atoms in the VO_x -polyhedra layers (V—O, 530.4 eV), O atoms coordinated with Mg^{2+} (Mg—O—V and Mg—OH₂, 531.7 eV), and O atoms in structural water in the interlayer (H₂O, 533.1 eV). When MVOH1 is fully discharged, the signal of Mg—O bonds is enhanced, indicating that the newly inserted Mg^{2+} cations coordinate with O atoms during discharging. The signal of H₂O molecules moves to higher binding energy, indicating that the interlayer structural H₂O molecules are in a free physical adsorption state rather than a chemically bound state [46]. In the fully charged state, the O signals in MVOH1 are similar to those in the pristine state, indicating a reversible intercalation mechanism involving the redox of V atoms. For the MVOH2 cathode, the Mg 1s core level spectrum of pristine MVOH2 has one signal at 1304.4 eV attributed to pre-intercalated Mg^{2+} [21]. MVOH2 fully discharged to -0.6 V exhibits a new signal at 1305.1 eV, corresponding to the newly inserted Mg^{2+} during discharging. The signals of pre-intercalated Mg^{2+} and newly inserted Mg^{2+} remain the same in MVOH2 fully charged to 1.0 V, signifying the irreversibility of Mg^{2+} extraction. This is further verified by the signals of the V 2p core level and the O 1s core level [21]. Compared with pristine MVOH2,

MVOH2 discharged to -0.6 V has a $\text{V}^{5+}:\text{V}^{4+}$ ratio of 1.3:1.0 due to the V^{5+} reduction accompanied by Mg^{2+} insertion. Still, the $\text{V}^{5+}:\text{V}^{4+}$ ratio recovers only to 1.1 after full charge at 1.0 V, implying the residue of newly inserted Mg^{2+} . Similarly, the signal of O atoms coordinated with Mg^{2+} becomes more intense in the fully discharged state than in pristine MVOH2, while the signal of V—O bonds becomes weaker. When MVOH2 is fully charged to 1.0 V, the Mg—O and V—O signals change slightly and do not recover to those of the pristine state, signifying the irreversible insertion of Mg^{2+} in MVOH2. Thus, the excellent electrochemical performance of MVOH1 stems from the high reversibility of Mg^{2+} insertion and extraction.

Ex situ XRD, SEM, and TEM analyses after extended cycling further confirm the structural integrity of MVOH1 [21], validating its long-term stability under repeated Mg^{2+} intercalation and extraction cycles. To further verify the ionic species involved in the energy storage process and evaluate the possibility of proton intercalation, time-of-flight secondary ion mass spectrometry characterization was conducted for MVOH1 electrodes in fully discharged and fully charged states, respectively [21]. The H⁺ signal remained low and did not show a significant change between the discharged and charged states, indicating that proton intercalation was negligible during discharging and charging [47]. In contrast, the MgOH^+ and MgVO^+ signals exhibited a clear increase in the discharged state and returned to the lower intensity upon charging, confirming the reversible insertion and extraction of Mg^{2+} as the dominant charge carrier. These results demonstrate that the co-intercalated lamellar structure of MVOH1 effectively suppresses the parasitic H⁺ insertion, ensuring that the electrochemical reactions are governed by Mg^{2+} intercalation, which is critical for maintaining structural integrity and electrochemical stability in aqueous electrolytes.

E. Electrochemical performance of the full MIB

To further explore the outstanding performance of MVOH1 nanobelts, they are used as the cathode, with PTCDA serving as the anode, to assemble a full MIB [Fig. 6(a)]. The electrolyte used is a 2M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ solution prepared with a polyethylene glycol to H₂O volume ratio of 1:1. The CV curves in Fig. 6(b) display the performance of the full cell within the potential range of 0–1.7 V at scan rates from 1 to 5 mV s⁻¹. Redox peaks are observed at 0.43 and 0.80 V, corresponding to the insertion and extraction of Mg^{2+} cations in the MVOH1 cathode. These redox peaks shift slightly with increasing scan rates, indicating high reversibility of Mg insertion and extraction and excellent rate capability of the full cell. The GCD curves of the PTCDA/MVOH1 full cell at different current densities are shown in Fig. 6(c), with the rate performance depicted in Fig. 6(d). The full cell delivers a high specific discharge capacity of 125 mA h g⁻¹

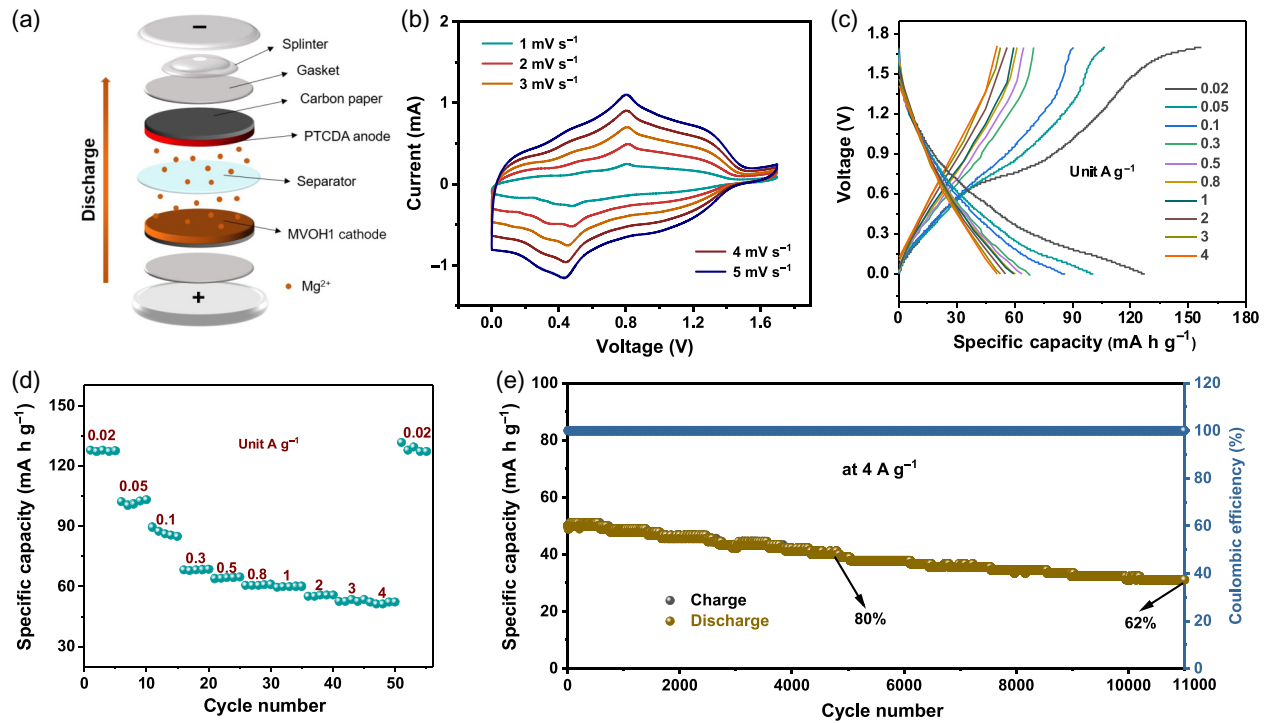


FIG. 6. Electrochemical performance of the PTCDA//MVOH1 full cell: (a) Full cell with an MVOH cathode and a PTCDA anode. (b) CV curves at different scan rates. (c),(d) GCD curves and rate capability at different current densities. (e) Cycling stability at 4 A g⁻¹.

at 0.02 A g⁻¹ and maintains a capacity of 47 mA h g⁻¹ even at 4 A g⁻¹, demonstrating excellent rate capability. When the current density returns to 0.02 A g⁻¹, the discharge capacity recovers to 124 mA h g⁻¹, highlighting the exceptional cycling stability. The GCD curves exhibit plateaus at approximately 0.8 V during charging and at around 0.3 V during discharging, which maintain similar shapes across different current densities, indicating excellent rate capability. Remarkably, the full cell exhibits an ultralong lifespan of 11 000 cycles, retaining 61.6% of its initial capacity at 4 A g⁻¹ [Fig. 6(e)]. In addition, a high average Coulombic efficiency of approximately 99% is achieved throughout the entire lifespan, indicating exceptionally high reversibility of Mg²⁺ insertion and extraction in the PTCDA//MVOH1 full cell. This ultralong lifespan surpasses that of previously reported aqueous MIBs [21]. The PTCDA//MVOH1 full cell also demonstrates a maximal energy density of 58 W h kg⁻¹ and a maximal power density of 2.3 kW kg⁻¹. The excellent electrochemical performance of the full cell assembled with MVOH1 signifies its promising potential for practical use in energy storage devices and favorable prospects for future applications.

IV. CONCLUSIONS

Herein, the strategy of simultaneous pre-intercalation of H₂O molecules and Mg²⁺ is proposed to enhance the Mg²⁺ storage performance of V₂O₅ interlayers by

modulating the V 3d orbital splitting. Pre-intercalating various amounts of H₂O molecules and Mg²⁺ cations into V₂O₅ interlayers induces different degrees of V 3d orbital splitting. The simultaneous pre-intercalation of H₂O molecules and Mg²⁺ causes substantial splitting of the V 3d orbital, increasing the electronic conductivity and electron-accepting capability of V₂O₅, resulting in a substantially enhanced rate capability. Further V L-edge x-ray absorption spectroscopy would be helpful for a rigorous experimental analysis of the V 3d orbital splitting, which will be done in a future study. In addition, the pre-intercalation of H₂O molecules and Mg²⁺ cations enlarges the interlayer spacing to a suitable value, providing favorable migration kinetics for Mg²⁺ while maintaining a stable lamellar structure. Compared with the single intercalation of either H₂O or metal cations, this dual-intercalation strategy provides a more comprehensive modulation of the structural and electronic properties of the host material. The synergistic effect of expanded interlayer spacing and reinforced V 3d orbital splitting enhances both Mg²⁺ diffusion kinetics and charge-transfer capability, leading to the excellent rate capability and cycling stability. The as-prepared MVOH1 cathode exhibited a discharge specific capacity of 300 mA h g⁻¹ at a current density of 0.05 A g⁻¹ with excellent rate performance; a specific capacity of 85 mA h g⁻¹ was retained even when the current density was increased to 10 A g⁻¹. The assembled PTCDA//MVOH1 full cell demonstrated a specific

capacity of 125 mA h g^{-1} at 0.02 A g^{-1} and a capacity retention rate of 62% after 11 000 cycles. This study offers a promising avenue for enhancing the electrochemical behavior of other vanadium-based layered cathodes. Moreover, this approach could be extended to the cathode design for other multivalent ion batteries such as Zn^{2+} and Ca^{2+} batteries, where sluggish ion diffusion and structural instability also pose major challenges. Therefore, this study has provided valuable insights into the rational design of advanced electrode materials for a wide range of next-generation energy storage technologies.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [48].

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