

Interconnected Lamellar 3D Semiconductive PCP for Rechargeable Aqueous Zinc Battery Cathodes

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Two-dimensional electronically conductive porous coordination polymers/metal-organic frameworks (2D EC-MOFs) of M-HHTPs (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene; M = Co, Ni, Cu, etc.) have received extensive attention due to their ease of preparation, semiconductive properties, and tunability based on the choice of metal species. However, slight shifts between layers attenuate their specific surface area and stability. In this study, we have newly adopted the metal-ion bridge strategy and synthesized a vanadyl counterpart of M-HHTP, with a chemical formula of $(VO)_3(HHTP)_2$, hereafter referred to as VO-HHTP. The semiconductor VO-HHTP has a vertically interconnection by octahedral VO_6 chains and exhibits a relatively high specific surface area (ca. $590\text{ m}^2\text{ g}^{-1}$) compared to other 2D EC-MOFs. Motivated by its redox activity and porous nature, VO-HHTP was applied as the cathode material in rechargeable aqueous zinc batteries (RAZBs). VO-HHTP demonstrated a high capacity of 240 mAh g^{-1} and excellent rate capability, even with a reduced amount of conductive agent, surpassing the performance of the previous EC-MOFs. Furthermore, its stable structure ensures long-term cycling stability, addressing a common issue in previous EC-MOFs. Our work contributes to the development of new concepts in both the design of π -conjugated EC-MOFs and the study of cathode materials for RAZBs.

1. Introduction

Benefitting from porous structure, electrically conductive porous coordination polymers/metal-organic frameworks (EC-PCPs/EC-MOFs) ^[1], have attracted widespread attention for electrochemical applications, including electrocatalysis ^[2], electrochemical energy storage systems ^[3], and electrochemical sensors ^[4]. Among EC-MOFs, two-dimensional (2D) π -conjugated EC-MOFs (2D EC-MOFs) are highly regarded as potential advanced materials

due to their semiconductive properties, open porous structures, and abundant active sites. In particular, honeycomb-like 2D EC-MOFs, constructed from square-planar metal cores (MX_4 ; $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$; $\text{X} = \text{O}, \text{N}, \text{S}$) and trigonal organic linkers (such as tetrahydroxy-1,4-benzoquinone (THQ), hexaaminobenzene (HAB), and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP)) have been systematically developed and studied because of their diverse channel sizes and electronic structures (**Figure S1** and **Table S1**)^[5]. These characteristics arise from the extended π - d conjugated network layers and the stacking structure through π - π interaction^[5a].

Over the past decade, there have been significant advancements in the use of EC-MOFs in various electrochemical applications. However, research on their applications in rechargeable aqueous zinc batteries (RAZBs) is still in its early stages and relatively limited^[6,7]. RAZBs are considered as a promising solution for large-scale energy storage systems due to their high energy density and efficiency, safety, low cost, and environmental friendliness. They can help stabilize the variable energy output from renewable sources such as wind and photovoltaic power generation. Therefore, the development of RAZBs is a critical issue for the widespread adoption of clean, renewable energy, which could ultimately address energy and environmental challenges. Previously, the 2D EC-MOF $\text{Cu}_3(\text{HHTP})_2$ as the cathode material in the RAZB achieved a high capacity of 228 mAh g^{-1} at 0.05 A g^{-1} ^[6a], with most of this capacity delivered through the redox reaction of the HHTP ligand. A one-dimensional (1D) π - d conjugated EC-MOF called Cu-BTA-H was synthesized and produced its batteries with a very high capacity of 330 mAh g^{-1} at 0.2 A g^{-1} ^[6b]. However, previously reported MOF cathodes face the challenge of unsatisfactory cycling stabilities, attributed to the variable 1D and 2D framework structure.

Typically, the 2D EC-MOFs adopt the AB stacking structure, where each layer slightly shifts relative to the neighboring layer^[5a, 5d]. This layer shifting can lead to a reduced specific surface area and hindered pore accessibility^[8]. In addition, their 2D structures sometimes undergo substantial structural changes during certain electrochemical processes. For instance, the insertion of cations causes structural shrinkage^[6a]. This effect would influence the performances and the stability, particularly during prolonged cycles of violent electrochemical reactions. A nitrogen-containing 4,4'-bipyridyl (BPY) molecules into the interlayers of the 2D EC-MOF functions as a pillar connecting the layers of $\text{Cu}_3(\text{THQ})_2$, to form a three dimensional (3D) structure with an extended conjugated layer while retaining the advantages of a 2D EC-MOF^[8], and increasing specific surface area and double-layer capacitance. We hypothesize that introducing additional interactions around the metal cores between each layer can enhance the stability and the acceptability of the porous structure^[9].

In this context, we have designed a novel 2D EC-MOF, $(\text{VO})_3(\text{HHTP})_2$ or VO-HHTP, by strategically combining VO^{2+} ions with the HHTP ligand. Our design features planar coordination between vanadium and HHTP, with out-of-plane coordination of oxygen in VO^{2+} facilitating additional interlayer interactions among neighboring layers^[10] (**Figure 1a**). The metal-ion bridge strategy minimizes the effect on layer spacing, instead of the organic molecule bridge like BPY^[8]. This unique layer-connecting structure not only reinforces the framework stability but also significantly enhances surface area and pore accessibility, offering promising potential as a cathode material for RAZBs (**Figure 1b**). VO-HHTP achieved a high capacity of 240 mAh g⁻¹ along with exceptional rate capability, even when employing a reduced amount of conductive agent. Furthermore, it demonstrated remarkable long-term stability, surpassing the performance of previous MOF materials. We also delved into the redox mechanisms through FT-IR and XAFS measurements, revealing a two-step redox reaction involving the ligand and vanadium, respectively, which is different from that in the previous report on Cu-HHTP. Our comprehensive characterizations and electrochemical tests provide valuable insights into the structure, conductivity, electrochemical performance, redox kinetics, and redox reaction mechanisms, thereby advancing the field of energy storage and materials science.

2. Results and Discussion

The MOF VO-HHTP was synthesized by reacting the 2:1 mixture of vanadyl sulfate and HHTP in water under the reflux condition for 48 hours, resulting in the formation of a black-color powder (see supporting information for the synthetic detail). The scanning electron microscopy (SEM) images revealed the uniform rod-shaped morphology of the obtained VO-HHTP, with a diameter ranging from 10 to 20 nm and a length of approximately 500 nm (**Figure 2a**). The crystal structure of VO-HHTP was further analyzed using synchrotron powder X-ray diffraction (PXRD) ($\lambda = 0.7995879 \text{ \AA}$). The PXRD pattern of VO-HHTP was well-fitted with a trigonal system ($P\bar{3}c1$) with a unit cell of $a = b = 21.37 \text{ \AA}$ and $c = 6.85 \text{ \AA}$ (**Figure 2b**, **Table S2**, see supporting information for the fitting detail), indicating VO-HHTP has a similar structure with other M-HHTP compounds. The presence of a strong and sharp 002 diffraction peak at 13.30° ($d_{\text{hkl}} = 3.43 \text{ \AA}$) indicates a well-ordered stacking along the c -axis (**Figure S2a**). The two most prominent diffraction peaks at 2.46° and 4.92° correspond to the crystal planes (100) and (200). These peaks are characteristics of the periodic network structure commonly observed in honeycomb-like 2D EC-MOFs (**Figure S2b and S2c**)^[11].

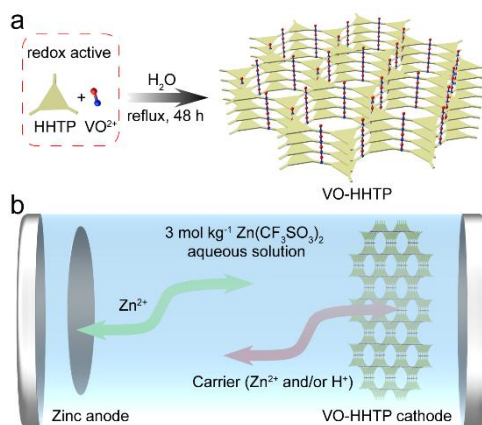


Figure 1. Concept schemes of VO-HHTP. a) The designed interconnected lamellar 3D structure by HHTP and VO^{2+} . b) Schematic illustration of the (-) Zn | $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (3 mol kg^{-1}) | VO-HHTP (+) cell.

The high-resolution transmission electron microscopy (HRTEM) images further support the formation of a honeycomb-like network structure (**Figure 2c and 2d**). Lattice fringes of the crystal plane (100) are clearly observed from the [010] direction on the side of the hexagonal prism, with the spacing measured at approximately 1.86 nm, matching the (100) d_{hkl} value (18.50 Å) in the proposed structure (Figure S2b). Furthermore, the bright-field image pattern in Figure 2d clearly reveals a regular honeycomb-like porous structure on the top side of the hexagonal prism. This pattern can be well-fitted with a simulated image from [001] direction, indicating a match in the unit cell dimensions for both a and b -axes. In addition, the high brightness suggests unobstructed channels, which negates the possibility of fully staggered stacking and confirms reduced layer slippage.

As mentioned earlier, we anticipated enhanced interactions between neighboring honeycomb layers due to the interactions among V=O cores, as is often observed in V-O-V interconnected structures in octahedral VO_6 -based compounds ^[10]. To identify this characteristic structure, we carried out the Raman spectroscopy measurements (**Figure 2e**). The sharp band with a peak at 988 cm^{-1} (1) corresponds to the stretching vibration of $\text{V}_1=\text{O}_1$ ^[10a, 12]; peaks (3) (689 cm^{-1}) and (4) (522 cm^{-1}) belong to the stretching vibration of $\text{V}_1-\text{O}_{2,4}$ and $\text{V}_1-\text{O}_{3,5}$, respectively ^[12]. The presence of a V-O-V chain is suggested by peak (2) (887 cm^{-1}) and (5) (403 cm^{-1}), which represent the asymmetric and symmetric $\text{V}_1-\text{O}_6-\text{V}_2$, respectively ^[12b]. In addition, the presence of an obvious G band (6) and a weaker D band (7) also indicate the planar structure of the honeycomb layers.

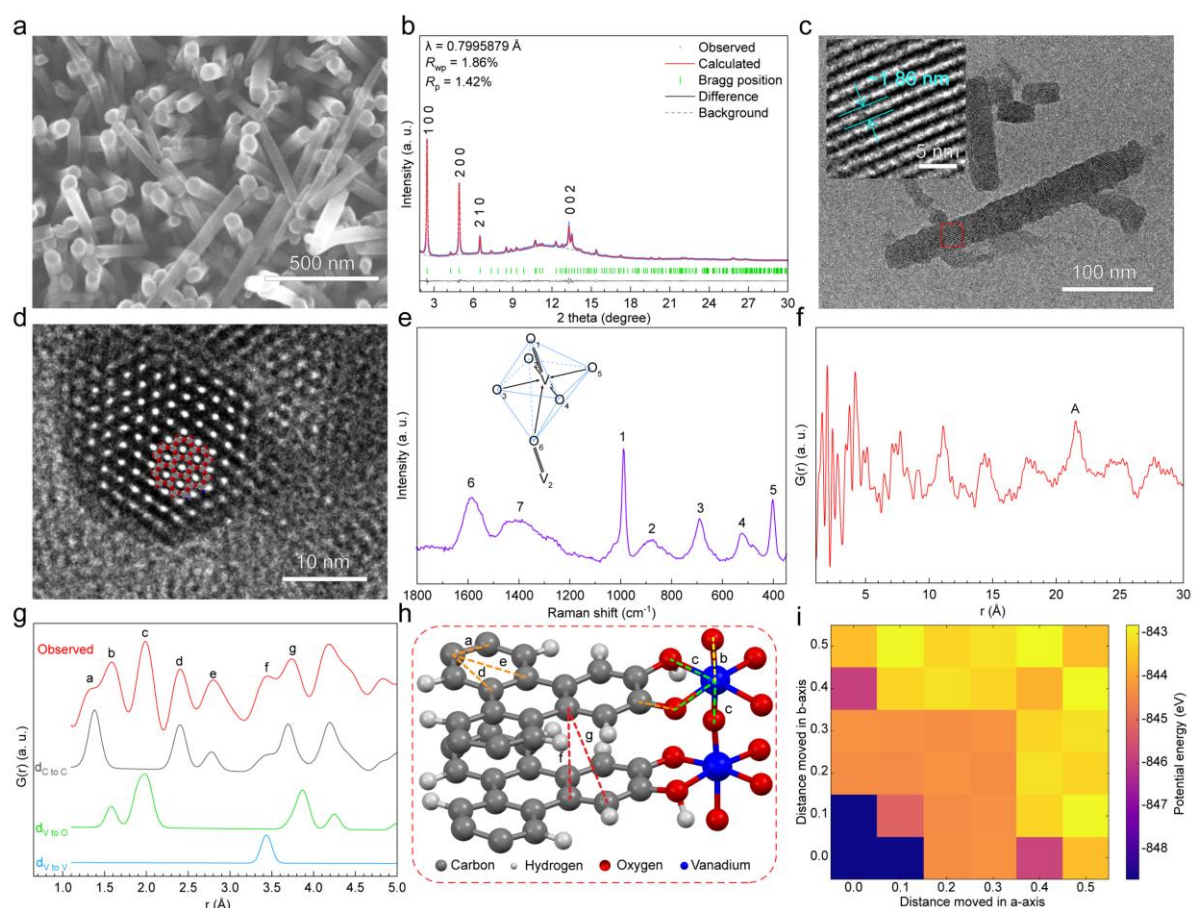


Figure 2. Structural studies of VO-HHTP. a) SEM image of as-prepared VO-HHTP. b) A profile plot of the Pawley refinement to synchrotron PXRD data collected at Spring-8 BL02B2 ($\lambda = 0.7995879$ Å). The experimental data is represented by blue open circles, the simulation by red, the difference by gray, and Bragg reflection markers by green. c, d) HRTEM images viewed from [010] (c) and [001] (d) direction, inset is latticing spacing images. e) Raman spectrum of as-prepared VO-HHTP. f, g) PDF curves, calculated using PDFgetX3 software. h) Detailed structural model. i) Potential energy color map of structural models with varying layer positions.

To gain deeper insights into the structure and layer stacking manner in VO-HHTP, we carried out the X-ray total scattering measurements using synchrotron radiation, to analyze the pair distribution function (PDF) (**Figure 2f**)^[13]. The PDF curve can be roughly divided into two length scales: very sharp peaks in the short-distance range (under 5 Å, **Figure 2g**) correspond to distances between specific atom pairs within the structure; while broad peaks in the long-distance range (above 10 Å) correspond to overall pair distances within the symmetric porous framework^[14]. As shown in Figure 2g and h, the distances of atom pairs in HHTP correspond to peaks a, d and e^[14b], while peak c indicates the atom pairs between the metal

center and oxygen ($d_{V\text{ to }O}$). These atom pairs are similar to those present within 2D Cu-HHTP MOFs (**Figure S3a**). In comparison to Cu-HHTP, an additional peak b appears at 1.59 Å. This distance corresponds to the common bond length of $V=O$ ^[13a], which is the characteristic atom pair within $V=O$ core in VO-HHTP. The peak f includes the atom pairs of all $d_{V\text{ to }V}$ and part of $d_{C\text{ to }C}$, and the distance of 3.45 Å conforms to the d_{hkl} value (3.43 Å) of (002) crystal planes, which corresponds to the layer spacing. Therefore, peak f indicates aligned atom-pairs in adjacent layers, and the matching distance values suggest eclipsed stacking along the *c*-axis (**Figure 2h**). The misaligned atom-pairs in adjacent layers (distance g in Figure 2h) display larger distances, corresponding to peak g (3.74 Å) in **Figure 2g**. As a comparison, Cu-HHTP was reported to exhibit face-to-face stacking (**Figure S3c**) ^[8], and the PDF curve displays similar peaks f and g in Figure S3a. Furthermore, the PDF curve of VO-HHTP displays low-frequency peaks in the range above 10 Å, suggesting a simple framework (Figure 2f), in which peak A (21.52 Å) conforms the values of the unit cell dimensions *a* and *b* (21.37 Å). Thus, peak A characterizes the overall distances between atoms in the parallel walls of the honeycomb-like structure (**Figure S3d**). Compared to Cu-HHTP in **Figure S3b**, the higher intensity of the peak A suggests a high order in the layer arrangement ^[15c]. The local structure is further supported by the radial distribution function (RDF) centered around vanadium. As shown in **Figure S4a**, oxygen atoms constitute the first shell at homologous distances according to the PDF. Additionally, the distance between the vanadium atoms also corresponds to that observed in the PDF.

Finally, we further assessed the layer stacking in VO-HHTP through theoretical calculations using MatlantisTM ^[15]. In this computation, we extracted two layers to explore potential parallel slipping and compared the potential energies of 36 models by adjusting the relative positions of the *ab*-plane for these layers (for calculation details, refer to Supporting discussion 1). **Figure 2i** presents a color-coded potential energy map, with the horizontal and vertical axes representing these relative positions (fractional coordinates), where *a* = 0, *b* = 0 corresponds to the initial eclipsed stacking configuration. The potential energy map revealed that the eclipse and minor slipping stacking structures achieve the lowest potential energy due to the formation of V-O-V bonds between layers. In fact, the structural optimization of the layer-slipped models under fixed unit cell conditions ultimately stabilizes them into the eclipse stacking configuration. These results further support the presence of eclipse-type stacking in the VO-HHTP structure with the formation of V-O connecting structures.

Motivated by the suggested eclipsed stacking structure of VO-HHTP, we conducted a thermal stability investigation using thermogravimetric (TG) analysis and the variable

temperature (VT)-PXRD measurements. As shown in **Figure S5a**, VO-HHTTP experienced a mass drop during the initial heating to 100 °C, indicating the release of guest water. In comparison, the sample activated under 100 °C for 10 h under a N₂ atmosphere displays sluggish mass loss during the testing process. The structural stability during the water release process was also studied by VT-PXRD patterns as shown in **Figure S5b**. The as-prepared VO-HHTTP exhibited consistent PXRD patterns throughout the heating process, and the release of guest water did not lead to significant structural variation. This resilience can be attributed to its interconnected structure.

Since we observed clear porous channels, we anticipated that VO-HHTTP would have a high specific surface area. To assess the specific surface area, we conducted gas sorption isotherm measurements using nitrogen (N₂) as the probing gas at 77K as shown in **Figure S6**. We obtained a relatively high Brunauer-Emmett-Teller (BET) surface area of 590 m² g⁻¹, which exceeds the values reported for other 2D EC-MOFs with the HHTTP ligand (BET of 490, 425 or 348 m² g⁻¹ for M-HHTTP with M = Co²⁺, Ni²⁺, or Cu²⁺, respectively) [5c, 5d]. This result is attributed to the benefits of the eclipsed stacking structure, which provides an enlarged layer spacing and reduces layer-slipping.

To evaluate the oxidation states of the metal and the ligand in VO-HHTTP, we conducted X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR) (**Figure S7** and **Figure S8**). In Figure S7a, the O1s core level XPS spectrum was fitted into three distinct chemical environments. These three peaks are attributed to the C-O group in the original HHTTP, with a higher binding energy of approximately 533 eV, the V=O group in VO²⁺ at a lower binding energy of around 531 eV [16], and the C=O group with a binding energy of around 532 eV, indicating the oxidized state of the HHTTP ligand. The presence of the C=O group is further supported by ATR FT-IR in Figure S8. This suggests the HHTTP ligands in VO-HHTTP were partially oxidized, as illustrated in the insert of Figure S7a, which is consistent with the findings of the previous study on Cu-HHTTP [6a]. Regarding the oxidation state of vanadium, we studied the valence state of vanadium in VO-HHTTP by XPS V2p core level spectrum and X-ray absorption fine structure (XAFS) analysis. The V2p XPS spectrum indicates the vanadium valence state of around 4+ (Figure S7b). In **Figure S9a**, the normalized XAFS spectrum of vanadium in the as-prepared sample exhibits a clear pre-edge peak related to the high-degree *d-p* mixing of oxygen and vanadium [17]. The ionization energies of outer orbits, which are related to the valence state of vanadium, were calculated using the center of gravity energies (E_{cog}) in the area from pre-edge to edge, as shown for VO₂ in **Figure S9b** [18]. In **Figure S9c**, V₂O₃, VO₂, and V₂O₅ were used as standard samples

for 3+, 4+ and 5+ valence states, respectively, and the standard curve was linearly fitted by valence and E_{cog} . The valence state of vanadium in VO-HHTP was estimated to be 4.35+, suggesting a slight degree of oxidation during the synthesis process of VO-HHTP.

VO-HHTP is expected to be conductive due to its partial oxidation state and the extended π - d conjugation within its layers. The band gap of VO-HHTP was initially determined through ultraviolet-visible (UV-vis) diffuse reflection spectroscopy. As shown in **Figure 3a**, the band gap was estimated to be <1.55 eV using the Tauc plot in the insert^[19], indicating its semi-conductive nature. The calculated density of states of VO-HHTP also support the semiconducting ground states (**Figure S10**). Furthermore, we tested the electrical conductivities of the pelletized VO-HHTP at various temperatures using electrochemical impedance spectroscopy (EIS) and I-V methods in a two-probe test system (**Figure S11**). **Figure 3b and S12** display the temperature-dependent Nyquist plots, which were well-fitted by an equivalent circuit with parallel capacitance (C_1) and resistance (R_1) as shown in the inset of Figure 3b, suggesting an active carrier hopping conducting mechanism^[20]. The apparent resistance of the material was calculated from R_1 (see the Supporting discussion 2 for detailed explanations). The calculated R_1 values are listed in **Table S3**, and the conductivities (σ) are listed in **Table S4**. At room temperature, the pelletized VO-HHTP exhibits a moderate conductivity of $4.15 \times 10^{-7} \text{ S cm}^{-1}$, confirming its semiconductive behavior as predicted by the optical band gap. Additionally, the temperature-dependent conductivities were analyzed by the Arrhenius plot, indicating the apparent activation energy of 0.52 eV (**Figure 3c**). Simultaneously, the conductivities at different temperatures were also assessed using the I-V method (**Figure S13**), and these results are in agreement with those obtained through the EIS method (Table S4 and **Figure 3d**).

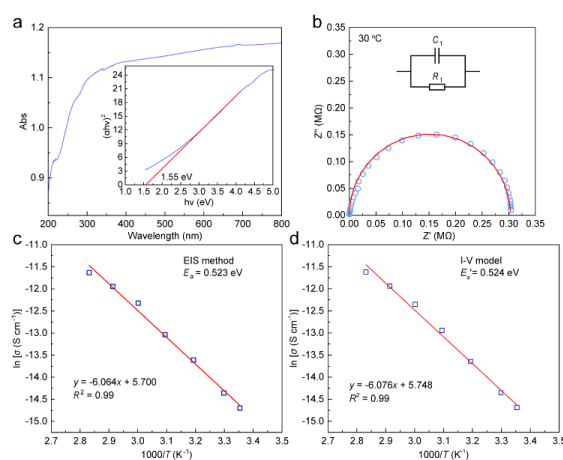


Figure 3. Conductivity studies of VO-HHTP. a). UV-vis diffuse reflection spectrum with Tauc figure inserted. b) The representative fitting of the Nyquist plot with a typical equivalent circuit (inset). c, d) The Arrhenius plots of $\ln(\sigma)$ vs. $1000/T$ of EIS method (c) and I-V method (d).

Due to the presence of both redox-active vanadium ions and HHTP ligands, along with its high surface area^[6a,21], VO-HHTP is indeed a highly promising candidate for the use as a redox-active cathode material in RAZBs. The electrochemical performance of VO-HHTP cathode material was studied in RAZBs with 3 mol kg⁻¹ zinc trifluoromethanesulfonate (Zn(OTf)₂) electrolyte. **Figure 4a** displays the galvanostatic discharge and charge (GDC) curves at various current densities. The VO-HHTP cathode delivers a maximum stable capacity of 240 mAh g⁻¹ at a current density of 0.05 A g⁻¹ with 50 wt% of active material. It exhibits two pairs of voltage plateaus, clearly identified at 0.94/1.03 V and 0.59/0.70 V (vs Zn/Zn²⁺) by the corresponding differential capacity curves (**Figure S14**). The cathode also demonstrates good rate capability, retaining approximately 44% capacity (105 mAh g⁻¹) even with a 160-fold increase in current density to 8 A g⁻¹. Furthermore, at the same or bigger current density gradient, VO-HHTP exhibits higher retention percentages compared to MOF cathodes and some typical conventional cathodes reported in previous studies on RAZBs (**Table S5**)^[6, 22]. We also tested the battery's storage stability using a rest test, as shown in **Figure S15a**. The open circuit voltage decreases slightly during the 8-hour rest due to the initial migration and arrangement of the double-layer charge on the electrodes. The capacities delivered in the subsequent GDC test correspond to the stable capacity shown in Figure 4a (**Figure S15b**). Therefore, VO-HHTP demonstrates stability in the electrolyte and battery without any self-discharge.

Considering the semiconductive nature of VO-HHTP, its weight percentage was increased to 80 wt%, while the content of the conductive agent was reduced to 10 wt% for battery testing. It still maintains good rate capability (**Figure S16**). As shown in **Figure 4b**, the cathode with 80 wt% VO-HHTP exhibits a similar capacity evolution trend with that of 50 wt%, with only slightly lower capacities. This capability to increase the active material percentage significantly benefits the overall specific capacity of the battery. **Figure 4c** demonstrates the long-term cycling stability of the cathode with 80 wt% VO-HHTP under 2 A g⁻¹. Although a capacity drop is observed during the first few cycles, it was stabilized over the subsequent long-term cycling. Specifically, the cathode retains 81% of its initial reversible capacity after 500 cycles, and this retention is still 74% after 1000 cycles. Compared other MOFs in RAZBs, VO-HHTP demonstrates better cycling stability at the same or smaller current density over the same cycle number(**Table S5**)^[6, 22].

We conducted further studies on the electrochemical kinetics of the VO-HHTP cathode in zinc cells. We tested cyclic voltammetry (CV) curves at various scan rates (**Figure 4d**). The relationship between peak currents and scan rates follows the equation of $i = av^b$, where i represents the current and v is the scan rate^[23]. A b value of 0.5 indicates a diffusion-controlled

process, while a b value of 1 represents a non-diffusion process. We calculated the b values for two pairs of redox peaks through linear fitting of $\ln(i)$ and $\ln(v)$ (**Figure S17**). The redox peaks at higher voltages (A_R , A_O) yielded high b values (0.89, 0.82, respectively), while the peaks at lower voltage (B_R , B_O) display medium values (0.71, 0.77, respectively). The calculation of non-diffusion-controlled contribution is further illustrated in **Figure 4e** [24]. The uneven distribution suggests its dominance in the high voltage range, consistent with the b value calculations. **Figure 4f** summarizes the percentages of non-diffusion-controlled under different scan rates, which amount to be 58.4% at 0.4 mV s^{-1} , and increase to 74.3 at 1.8 mV s^{-1} . EIS was performed for the VO-HHTP electrode at various states in a three-electrode cell in situ. **Figure 4g and S18a** show the Nyquist plots at the states labeled in **Figure S18b**. All of them were well-fitted using the Randles equivalent circuit as illustrated in the inset [20]. As the fitting results shows in **Table S6**, larger charge transfer resistance was observed for the low voltage processes (B_R/B_O), indicating gradually hindered reaction kinetics due to crowded cations in the structure.

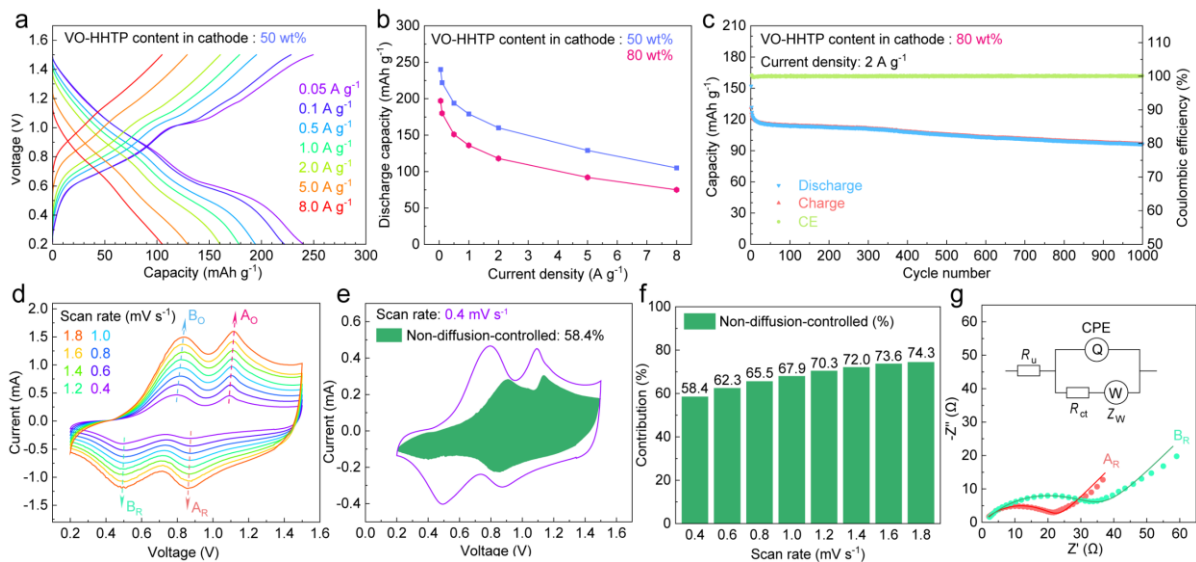


Figure 4. Electrochemical performances of the VO-HHTP cathode in RAZBs. a) GDC curves under various current densities. b) Reversible discharge capacities under various current densities with 50 wt% and 80 wt% of VO-HHTP in cathode. c) Long-term cycling stability at 2 A g^{-1} for 1000 cycles with 80 wt% of VO-HHTP. d) CV curves under various scan rates with 80 wt% of VO-HHTP. e) The non-diffusion-controlled region in the CV curve at 0.4 mV s^{-1} . f) Non-diffusion-controlled capacity contributions at different scan rates. g) Fitting of Nyquist plots at different peaks along discharge (inset shows the equivalent circuit).

To explore the reaction mechanism of VO-HHTP cathode material in zinc cells, we conducted PXRD, FT-IR, and XAFS analyses at the states depicted in Figure S14. **Figure 5a** compares the PXRD patterns of fully discharged and charged cathodes. There were no

noticeable shifts in the major peak positions, indicating the stable framework structure during the redox processes. The asterisk-marked broad peak that appeared after the discharge corresponds to the characteristic peak of the by-product basic zinc salt (BZS). This by-product was also observed on the surface of the discharged cathode under SEM (**Figure S19**). The peak was found to disappear after the recharging process. The reversible formation of BZS suggests the potential insertion of H^+ into the cathode during the discharge process [25].

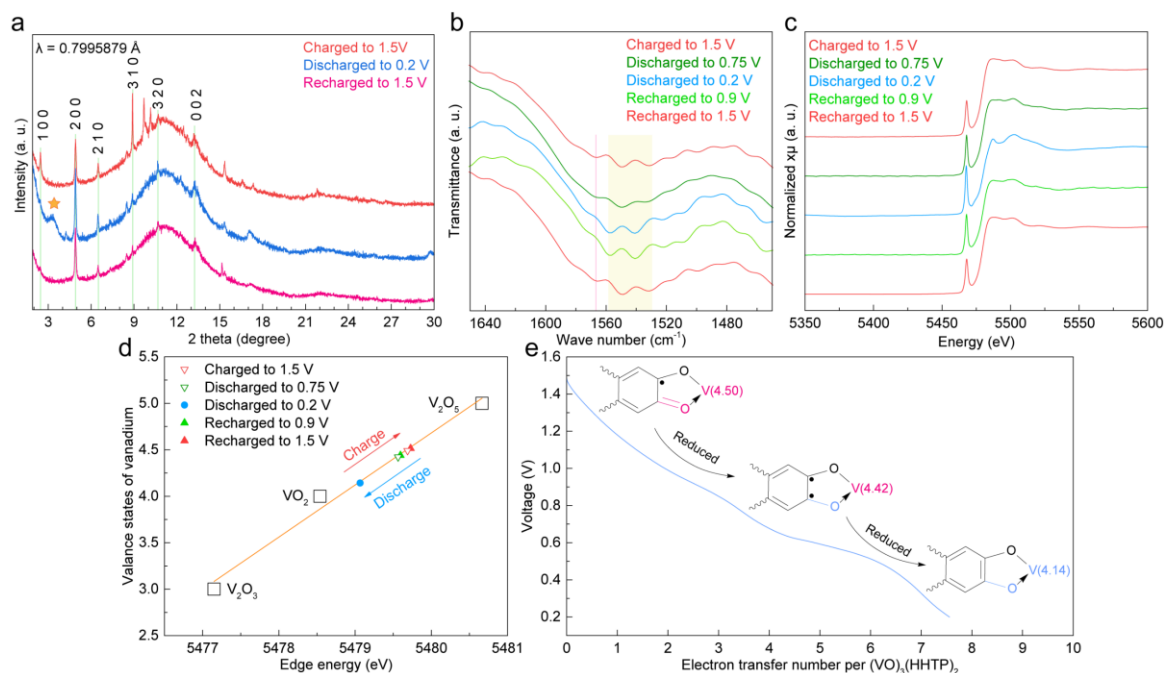


Figure 5. Characterizations of VO-HHTP cathode materials at different states. a) Synchrotron PXRD patterns. b) ATR FT-IR spectra. c) Normalized XAFS spectra. d) Calculated V valence states by using an integral method with standard curve. e) Two-step reduction during the discharge process.

To investigate the mechanisms of redox reactions, we studied the transformation of active sites using ATR FT-IR and XAFS measurements. HHTP is known to be redox active through the reversible transformation between C-O and C=O [6a, 21]. The presence of C=O functional groups was also confirmed by XPS and ATR FT-IR, as mentioned earlier. **Figure 5b** illustrates the progression of the consumption and restoration of C=O absorption band (pink line) with a delayed change in the vibration pattern of the carbon ring (yellow region), indicating a transformation in the conjugated structure. This variation mainly occurs within the high voltage range (corresponding to the redox peaks at 0.94/1.03 V in Figure S14). The consumption of C=O during discharge was studied in detail using O1s XPS. As shown in **Figure S20**, C=O was reduced to both C-OH and C-O⁻/Zn²⁺, indicating its combination with H⁺ and Zn²⁺, respectively. The Zn 2p XPS further confirms the continuous insertion of Zn²⁺ and the formation of basic zinc salts. In VO-HHTP, vanadium is also expected to be redox-active due to variable valences,

and we studied the redox mechanism using XAFS measurements. **Figure 5c** demonstrates the excellent reversibility of vanadium and its coordination environment. We calculated the vanadium valences at different states using an integral method with the standard curve shown in **Figure 5d**. The valence shifts were found to be between 4.51+ and 4.14+. The valence shift is negligible at high voltage; conversely, the redox of vanadium primarily occurs around the pair of redox peaks at 0.70/0.59 V in Figure S14. The valence of vanadium remains above 4+ throughout the electrochemical cycle to ensure proper coordination properties and local structural stabilization. The study of redox mechanisms reveals a two-step redox process involving the HHTP ligand at the high-voltage plateau and the central vanadium at the low-voltage plateau, as illustrated in **Figure 5e** and **Figure S21**.

3. Conclusion

In conclusions, we have succeeded in producing a new HHTP-based MOF, VO-HHTP, using VO^{2+} ions and HHTP, possessing a vertically interconnection formed by octahedral VO_6 chains. This material exhibits an enlarged specific surface area of $590 \text{ m}^2 \text{ g}^{-1}$ and demonstrates semi-conductivity. Furthermore, owing to its high redox activity, stable structure and open channels, VO-HHTP could perform as a useful cathode material in RAZBs, resulting in batteries with a higher reversible capacity (240 mAh g^{-1}). This improved rate capability, and more stable capacity compared to previous studies involving MOF cathodes ^[6]. Thanks to its semiconductive nature, VO-HHTP maintained a high capacity and consistent rate capability even with a reduced amount of inert conductive agent, which is more practically valuable than batteries with an excessive conductive agent.

4. Experimental Section

Materials: All reagents were purchased commercially and used without further purification. 2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP, 95.0%) and vanadyl sulfate hydrate (VOSO_4 , 72%) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$, 98%) was purchased from BLD Pharmatech Ltd. (China). Methanol (99.0%) was purchased from Nacalai (Japan). Graphite foil was purchased from SGL group (Germany). Poly(tetrafluoroethylene) (Teflon [TM] 30B, 60 wt% dispersion, PTFE) was purchased from Polysciences Inc. (U. S. A.). Conductive carbon black super P was purchased from MTI Co. (China). Cu-HHTP was prepared according to a previously reported procedure^[5c].

Characterizations: The phase and crystal structures of all samples were determined by powder X-ray diffraction (PXRD) patterns, which were measured by SPring-8, Japan (beamline BL02B2, $\lambda = 0.79962 \text{ \AA}$). The X-ray total scattering data was obtained at the SPring-8, Japan (beamline BL13XU, $\lambda = 0.353887 \text{ \AA}$) for pair distribution function (PDF) analysis. The high quality XAFS spectra for radial distribution function (RDF) analysis were measured at SPring-8, Japan (Beamline BL14B2). The morphology and structure of the product and cathodes were observed by scanning electron microscope (SEM, Hitachi SU5000, Japan) and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2200FS(HR), Japan). Thermostatic gas adsorption and desorption experiment was carried out by a BET instrument using a surface area analyzer (BEL-mini X, MicrotracBEL Corp., Japan) with N_2 as a probe molecule at 77 K. The thermogravimetric analysis (TGA) curves were obtained from a Rigaku TG 8120 analyzer (EVO2 TG/S-SL, Japan) using a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ under a N_2 flow. Raman spectra were gathered by a Raman spectrometer (Melles Griot, U. S. A.) with laser of 488 nm wavelength. Fourier transform infrared (FT-IR) was performed on FT/IR-6100 (JASCO Corporation, Japan) by attenuated total reflectance method. X-ray photoelectron spectroscopy (XPS) was carried out on JPS 9010TRX (JEOL, Japan). UV-vis diffuse reflection spectra were tested by V-670 UV-vis-near-IR spectrophotometer (JASCO Corporation, Japan). XAFS spectra were measured at Aichi synchrotron radiation center (beamline BL5S2), and at SPring-8 (beamline BL14B2). All electrochemical experiments were carried out on Bio-Logic Vsp-300 (Franch). Temperature-dependent PXRD patterns were measured by Rigaku Smartlab X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), vacuum environment and temperature control were supplied by a gas sorption analyzer (BELSORP MAXII-HPKX, MicrotracBEL Corp., Japan).

Synthesis of $(\text{VO})_3(\text{HHTP})_2$ (VO-HHTP): 324 mg (1 mmol) of HHTP and 453 mg (2 mmol) of VOSO_4 were added to a 100 mL flask containing 50 mL of water. The system was stirred vigorously for 1 h at room temperature. Then, the stirring speed was reduced, and the temperature was increased until reflux was achieved, and this reflux condition was maintained for 48 hours. The solid was separated by centrifugation while hot and then washed with water and methanol sequentially. The product was dried in a vacuum oven at $40 \text{ }^\circ\text{C}$ overnight, and 125 mg of black powder was obtained (yield 30 %).

Conductivity measurements: The conductivity of VO-HHTP was tested by powder pellet in a two-probe test system, as shown in Figure S11. VO-HHTP powder was compressed under 20

MPa for 5 min, resulting in a pellet with a diameter of 5 mm, thickness of 0.346 mm, and weight of 9.91 mg. Two gold cylinder contactors clamped the pellet with springs, and electrodes were connected as shown in Figure S11. The system was placed in an oven to control temperature, and the conductivities at different temperatures were tested by electrochemical impedance spectroscopy (EIS) and I-V methods.

Electrochemical measurements: VO-HHTP electrodes were prepared by mixing VO-HHTP, super P conductive additive, and 10% PTFE binder in deionized water with weight ratios of 5:4:1 and 8:1:1. The slurry was drop-casted onto graphite foil discs with an 11 mm diameter and dried at room temperature overnight. The mass loading of VO-HHTP was around 1.3 mg cm⁻². Galvanostatic discharge/charge (GDC) and cyclic voltammetry (CV) measurements were carried out in two-electrode PFA Swagelok type cells with titanium rods as the current collectors, zinc foil anode and 3 mol kg⁻¹ Zn(OTf)₂ aqueous solution as the electrolyte. In-situ EIS measurements were carried out in T-shaped PFA Swagelok type cells with an additional standard calomel electrode (SCE) for reference. For the preparation of cathode samples for characterizations, batteries with 50% active material ratio were run to different test sites at 0.1 A g⁻¹ to obtain cathodes at various states. All electrochemical tests were carried out after 1 cycle of GDC to exclude extra irreversible capacity caused by the initial migration and arrangement of the double layer charge on the electrodes.

PXRD refinements and structural model: The PXRD pattern of the as-prepared VO-HHTP was refined using the Pawley method. Topas3 software (Bruker AXS) was used for the analysis. Assuming the structural similarity, the space group and the lattice parameters of Cu-HHTP ($P\bar{3}c1$, $a = b = 22.13$ and $c = 6.56$ Å) were used as the starting point of the fitting. The refinement result gave the lattice parameters of $a = b = 21.37$ Å and $c = 6.85$ Å and the cell volume of 2709.05 Å³ with $R_p = 1.42\%$ and $R_{wp} = 1.86\%$. The simulated structure of VO-HHTP was modeled using Materials Studio software, along with the unit cell parameters obtained above. The structure was geometry-optimized by the CASTEP module of the Materials Studio software with the generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE) for use in the PDF analyses.

PDF analyses and simulation: The high-quality X-ray total scattering data was obtained at the SPring-8, Japan (beamline BL13XU, $\lambda = 0.353887$ Å) as **Figure S22a**. The PDF data were analyzed using PDFgetX3 software. Specifically, the scattering data were background

subtracted with background scale value 1 and normalized into a reduced structure function (**Figure S22b**). A r_{poly} value of 0.9 was imposed to let the reduced structure function vibrate around $0 \text{ \AA}^{-1}$. Finally, the reduced structure function was Fourier transformed within the Q range of $0.8 \sim 20 \text{ \AA}^{-1}$ to obtain the PDF curve in Figure 2f. To study the contributions of different atom pairs in the local structure in the PDF curve, a structural model obtained above was employed to calculate simulated PDF curves of atom pairs C to C, V to O, and V to V in Figure 2f, using PDFgui software.

Density of States calculation: A density functional theory (DFT) structure relaxation and DOS calculation have been performed using Vienna Ab Initio Package (VASP). We employed PBE projector-augmented wave (PAW) pseudopotentials with an energy cutoff of 400 eV. Partial occupancies of the Kohn-Sham orbitals were applied using the tetrahedron method with width of 0.05 eV. The electronic relaxation is stopped when energy difference is lower than 1×10^{-4} eV, and geometry relaxation is stopped when forces are smaller than $0.02 \text{ eV \AA}^{-1}$. The geometry optimization is performed by allowing all atoms to relax, while the unit cell is kept fixed, and the k -points sampling used is $8 \times 8 \times 8$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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VO-HHTP, a 2D electronically conductive metal-organic framework (EC-MOF) featuring vanadyl oxide (VO^{2+}) centers and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligands, achieves robust interlayer interactions and organized stacking. This innovative structure significantly boosts its performance as a cathode for rechargeable aqueous zinc batteries, delivering higher capacity, superior rate capability, and enhanced cycling stability, surpassing existing materials.

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Interconnected Lamellar 3D Semiconductive PCP for Rechargeable Aqueous Zinc Battery Cathodes

