

Reversible multivalent carrier redox exceeding intercalation capacity boundary

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Compared with widely established monovalent-ion batteries, aqueous multivalent-ion batteries promise higher capacity release by achieving multiple electron-transfer events per ion intercalation in the host material. Despite plausibility, this high-capacity dream is untenable with the total tolerable redox charge-transfer limit of the host material for all carrier species equally, which is historically assumed to depend on the material rather than the guest carrier itself, and the kinetic hysteresis induced by larger charge/radius ratios induced kinetic hysteresis further enlarges the divide. Herein, we report that copper carrier redox in vanadium sulfide (VS₂) exceeds the intrinsic intercalation capacity boundary, with the highest capacity release as 675 mAh g⁻¹ at 0.4 A g⁻¹ among all VS₂ cathodes previously reported. *Operando* X-ray absorption spectroscopy, *operando* synchrotron X-ray diffraction and composite ex situ characterization jointly demonstrated that intercalated divalent copper is preferentially involved in redox afforded extra electron transfer to form reversible monovalent copper pillars, thus not only ensuring stable topological de/intercalation with high capacity but also sustaining fast migration kinetic paths through reconfigurable pillar effects. Intercalated carrier redox reported here emphasizes the interlayer variable valence advantage of multivalent ions, providing insights into high-performance multivalent-ion storage chemistry in aqueous batteries.

Rechargeable batteries are indispensable for intermittent energy storage towards renewable energy sources, allowing ions to be reversibly stored in layers of material to provide conversion of chemical and electrical energy^{1–4}. Monovalent (alkaline) ions represented by lithium ion are currently dominant especially in mobile electronics and electric vehicles^{1,5}, but rising safety and cost buzz has prompted the emergence of aqueous multivalent-ion batteries (AMBs) as a complement to large-scale energy storage, which can plausibly utilize accessible metal anodes such as zinc^{6,7} or aluminium⁸ and

nonflammable aqueous electrolytes^{9–11}. However, the large charge/radius ratios of multivalent ions present a critical challenge to the cathode in AMBs, as the inherent high surface charge density of carriers and predictably tough kinetics in solid-phase diffusion hinder capacity release and reversibility in intercalation chemistry^{3,12,13}. With such consideration, the design of cathode materials and intercalation chemistries is particularly essential, and more efforts are required to enable high-capacity and stable cathodes for multivalent-ion intercalation in AMBs.

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Conventionally, it has been theoretically expected that multivalent-ion chemistry can provide greater capacity release to cathodes than monovalent-ion intercalations, based on the fact that multivalent ions can provide multiple electron transfer events in each carrier intercalation at first glance^{14–17}. In contrast, monovalent ions provide only one electron transfer per carrier intercalation^{18,19}. However, this perspective fundamentally relies on the shaky assumption that the host material can hold the same number of carriers in the interlayer regardless of the type of carrier. Palacín²⁰ and Yao¹² contend that, in practical mechanistic considerations, the theoretical capacity boundary of any intercalated compound actually depends on the total number of electrons that can be transferred to the variable-valence redox centres of the host, which is the material endowment property, implying that over-expectations for multivalent-ion intercalation are not feasible. Therefore, in the framework of the intercalation mechanism, the theoretical capacity release boundary of the cathode material in the multivalent-ion system would not be better—if not worse—than that in the monovalent-ion system, especially considering the poor kinetics^{19,21}. As a typical case, layered vanadium sulfide (VS₂) has been demonstrated to provide only 180 mAh g⁻¹ in zinc batteries²¹, which is much lower than that reported in sodium batteries (~500 mAh g⁻¹) at the same specific current⁵. Exploring novel cathode chemistries to truly take advantage of the multiple charge carriers of multivalent ions shuttling in the electrolyte remains desirable but challenging.

Beyond established experimental exploration and insights into multivalent-ion chemistry, the potential of multivalent-ion carriers in the valence state^{22,23}, i.e., the redox capability, has long been neglected in intercalated electrodes, although preliminary investigations have been conducted in liquid-flow batteries (electrolyte redox)^{24–27} and elemental electrodes (conversion)²⁸; for example, Wu et al. proposed that copper ions can be used as redox charge carriers in sulfur conversion to achieve high capacity²⁹, and the phenomenon was extended to other conversions^{11,30–33}. Exploration of electroplating/stripping and redox utilizing electrolytes is also in progress^{22,34}. It can be expected that, compared to monovalent carriers acting only as charge carriers in intercalation, the high valence state of intercalated multivalent carriers in host as redox centres endows the possibility to afford extra charge transfer, permitting a fundamental breakthrough in the intrinsic capacity boundary of the electrode material. Moreover, the redox of intercalated multivalent carriers inside the host considerably affects the electronic structure and interlayer ion transport dynamics of the host material^{7,21}, which thus contributes to the deep intercalation of multivalent ions by overcoming kinetic disadvantages and the inherent trade-off between stability and capacity. Predictably, intercalated carrier redox offers apparent benefits in multivalent-ion storage and will undoubtedly advance in-depth research to exceed the established mechanism framework, yet such research is still incipient.

Herein, we report intercalated multivalent-ion redox reaction in VS₂ cathode using divalent copper-ion carriers to exceed the theoretically reversible capacity boundary. *Operando*/ex situ X-ray absorption fine structure spectroscopy (*o*-XAFS), *operando* synchrotron X-ray diffraction (*o*-XRD), and composite ex situ characterization jointly confirmed that copper carriers were stored as monovalent forms through redox in interlayers at the early stage of intercalation, thus not only doubling the reversible capacity release to 675 mAh g⁻¹ but also realizing the predicted sustainable kinetic advantages with stable operation for 7000 cycles at 10 A g⁻¹ through monovalent copper-ion pillar effects which can be reconfigured by copper-ion de/intercalation. Employing in zinc batteries with decoupled configurations, the VS₂ cathode with copper carriers delivers an energy density of 773 Wh g⁻¹ (based on the mass of the VS₂ cathode) and the ability to operate for 1000 cycles, providing a substantial boost in stability and energy supply. High-load (7.03 mg cm⁻²) and scaled-up watt-hour level cells (1.1 Wh) are also built to provide a total charge storage of 0.91 Ah.

Initiating carrier redox provides insights into aqueous battery chemistry and represents a kind of high-performance intercalated electrodes.

Intercalated carrier redox mechanism

Conceptually formalized VS₂ (*f*-VS₂) secondary particles were synthesized via a one-step hydrothermal method and assembled from micrometre-sized hierarchical nanosheets (Supplementary Figs. 1–3)^{11,35}, which were well-indexed to hexagonal-stacked 2H-VS₂ (PDF#89-1640) belonging to the P-3m1(164) space group (Fig. 1a, Supplementary Figs. 4–6),³⁶ and the elemental components were as expected (Supplementary Figs. 7–12)^{4,37–39}. Structural investigations of several ion intercalations revealed that, unlike the multivalent ion carriers that have been disclosed such as magnesium and zinc, the Cu-S bonds formed by intercalated copper-ions have shorter bond lengths compared to the V-S bonds in VS₂ host, implying that stronger interactions may enable the capture of additional electrons from the host to trigger the intercalated carriers redox (Fig. 1b). Previous reports have shown that VS₂ delivers an intercalation capacity release of <200 mAh g⁻¹ as cathode in multivalent-ion batteries^{40,41}. Realizing copper-ion intercalation with carrier redox is expected to break this long-standing inherent limitation^{42,43}. Thus, when copper ions are used as carriers, the *f*-VS₂ cathode has a capacity of up to 675 mAh g⁻¹ at 0.4 A g⁻¹ (Fig. 1c, d). This capacity record considerably exceeds all VS₂ cathodes revealed in ion batteries to date (Fig. 1e, Supplementary Table 1)^{6,8,18,21,43–60}, suggesting the possibility of novel redox mechanisms that have yet to be identified, permitting stable operation for 7000 cycles at high specific current of 10 A g⁻¹ with a Coulombic efficiency (CE) of ~100% and capacity retention of 82.4% (Fig. 1f). Therefore, the valence evolution of the vanadium centre of *f*-VS₂ obtained via *o*-XAFS analysis was first investigated (Fig. 1g). An *operando* approach was taken to capture the XAFS data in fluorescence mode with minimized X-ray attenuation. The near-edge structure of the normalized V K-edge showed a distinct shift in the V state at 5482 ~ 5485 eV towards lower energy during intercalation, suggesting a decrease in the vanadium valence state during redox (Fig. 1h). The V state in full discharge *f*-VS₂ remains far from the standard V foil (V⁰), ruling out conversion reactions (Supplementary Fig. 13). When the current is reversed, the edge reversibly moves to higher energy and returns to the pristine state at full charge (Fig. 1i), indicating the complete retrieval of intercalated ions. The Fourier transformed (FT) K-edge extended X-ray absorption fine structure (EXAFS) spectra of the V K-edge were further analysed to clarify the local structure around V during intercalation (Fig. 1j). The strongest main peak corresponded to the nearest-neighbour V-S coordination shell located at ~1.9 Å (no phase correction)⁶¹. Insignificant V-S bond elongation (<0.12 Å) occurs during the discharge process and vice versa, implying a robust in-plane structure during intercalation. Changes in V-S coordination can also be identified from the peak profiles of ex situ tender-energy S K-edge X-ray absorption near edge structure (XANES) in the range of 2465–2475 eV⁶², but no extra anionic redox was found since no offset of the main sulfur peak was observed (Supplementary Fig. 14)^{63,64}.

Nevertheless, from theoretical electron transfer number calculations based on VS₂, vanadium centre evolution alone, which does not involve conversion reactions, cannot provide the observed high discharge capacity. The reasonable inference of carrier redox prompted further investigation of the valence evolution of copper during intercalation. Eighteen *f*-VS₂ electrodes were extracted from one cycle with different charge/discharge states, and their copper content was quantified (Fig. 2a), with duplicates for the fully discharged state. The apparent emergence of Cu 2p peaks in X-ray photoelectron spectroscopy (XPS) clearly indicates copper intercalation (Supplementary Fig. 15, Supplementary Fig. 16), and the maximum copper content (fully discharged state) is close to 1.0 Cu per VS₂. The corresponding

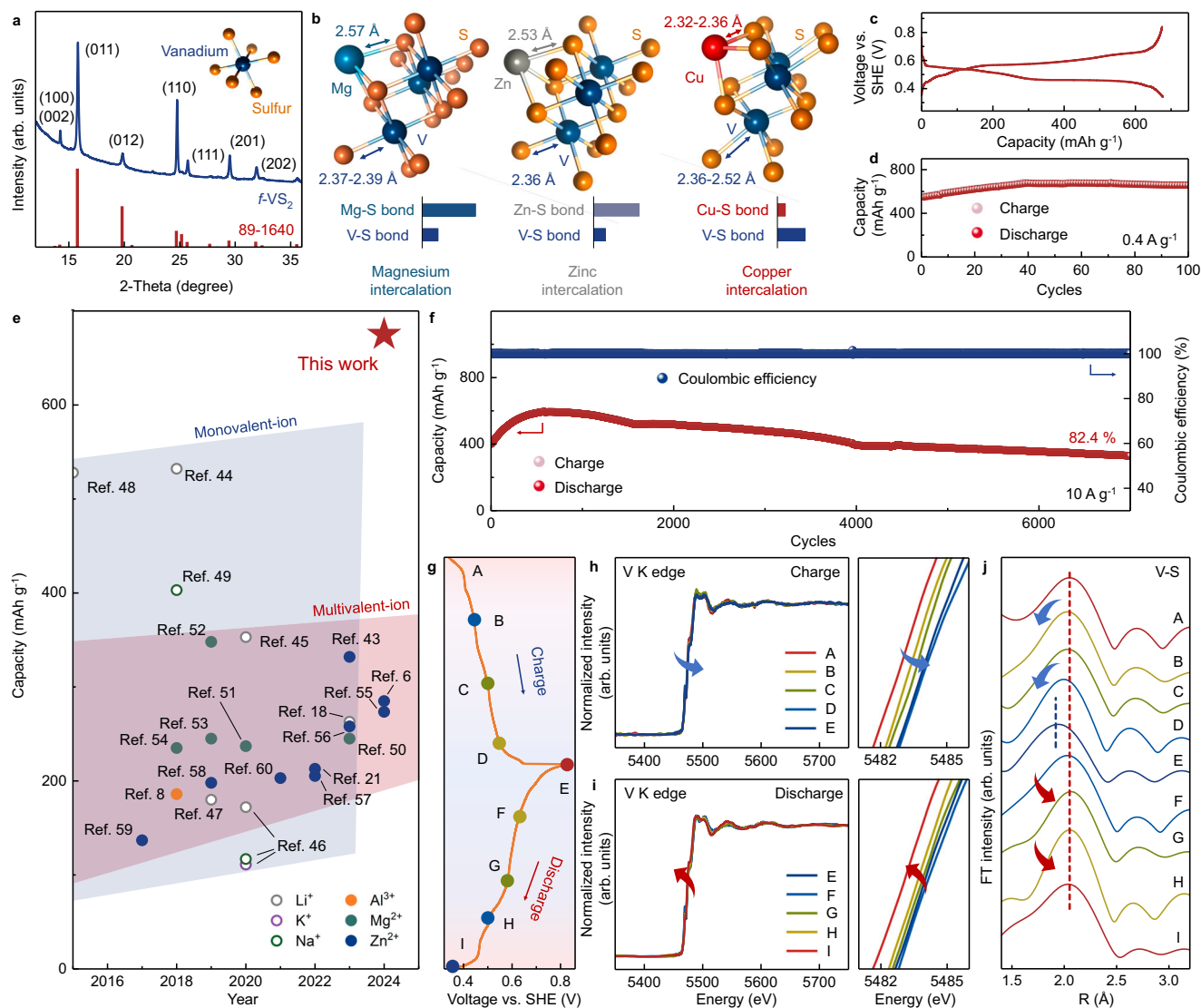


Fig. 1 | Copper-ion intercalation in VS₂. **a** XRD pattern of VS₂. **b** Structural investigations of ion intercalations, including magnesium, zinc, and copper. **c** Galvanostatic charge-discharge (GCD) curve and **(d)**, cycling performance of *f*-VS₂ electrodes with copper intercalation at 0.4 A g⁻¹. **e** Comparison with the capacity of reported VS₂ cathodes to date. VS₂ cathodes for monovalent-ion batteries and multivalent-ion batteries are distinguished by blue and red colour blocks,

respectively. **f** Cycling performance of *f*-VS₂ electrodes with copper intercalation at 10 A g⁻¹. **g** GCD curves and corresponding V K-edge *o*-XAFS data in **(h)**, deintercalation (charging) and **(i)**, intercalation (discharging). The right-side images show the magnified XANES region. **j** EXAFS evolution inferred from *o*-XAFS data. The red and blue dashed lines mark the V-S peak positions for the fully discharged and fully charged states, respectively.

XPS Cu 2*p* core spectra are shown in Fig. 2b and Fig. 2c. The Cu 2*p*_{3/2} peak and the Cu 2*p*_{1/2} peak increased in intensity as the discharge process proceeded. Notably, during the first half of intercalation (before the sixth discharge spectrum), a copper content of ~0.75 per VS₂, only isolated Cu 2*p*_{3/2} (932.7 eV)/Cu 2*p*_{1/2} (952.6 eV) peaks were identified, implying the presence of monovalent copper species. As the depth of intercalation proceeded, additional Cu²⁺ peaks with signature satellite peaks (located at 943/962 eV) emerged, indicating the presence of Cu²⁺ species. Similar observations for bulk VS₂ corroborate the conclusions (Supplementary Fig. 17). Therefore, considering that Cu²⁺ species dominate the type of copper carriers in the electrolyte, carrier redox should occur at the early stage of intercalation, i.e., Cu²⁺ carriers are first redox-converted to Cu⁺ species after intercalation to remain in the interlayer, whereas Cu²⁺ carriers intercalate and migrate at the later intercalation stage, and vice versa. When the current is reversed during charging, similar inverse processes are observed, and copper ions are almost completely extracted from the interlayer, confirming the reversibility of the proposed mechanism.

The collection of XAFS spectra for specific discharge states (states I, II, III, and IV) demonstrated similar results (Fig. 2d). In states I and II, the copper species in VS₂ have almost unchanged overlapping edge positions, indicating that a low copper valence state coincides with the monovalent copper position (Cu^I, inferred from Cu₂S). Upon further discharging (states III and IV), a shift of the absorption edge towards higher energies (Cu^{II}, inferred from CuS) is observed, indicating an increase in the average valence state of the intercalated copper ions. Finally, the average copper valence state reached 1.27. The redox of copper carriers in the interlayer was hence indeed triggered at the beginning of intercalation⁶⁵, which is consistent with the XPS evidence. For comparison, a monovalent copper-ion (Cu^I) electrolyte was prepared on the basis of the stability of the Cu⁺ ions in acetonitrile to exclude the effect of the redox of the copper carriers (Fig. 2e). At the same specific current, *f*-VS₂ in the Cu^I electrolyte provides only 97 mAh g⁻¹ capacity (rate performance shown in Supplementary Fig. 18), which is ~14% of the capacity of *f*-VS₂ in the Cu^{II} electrolyte. In addition, a 41.6% capacity was obtained after 1000 cycles, which is far

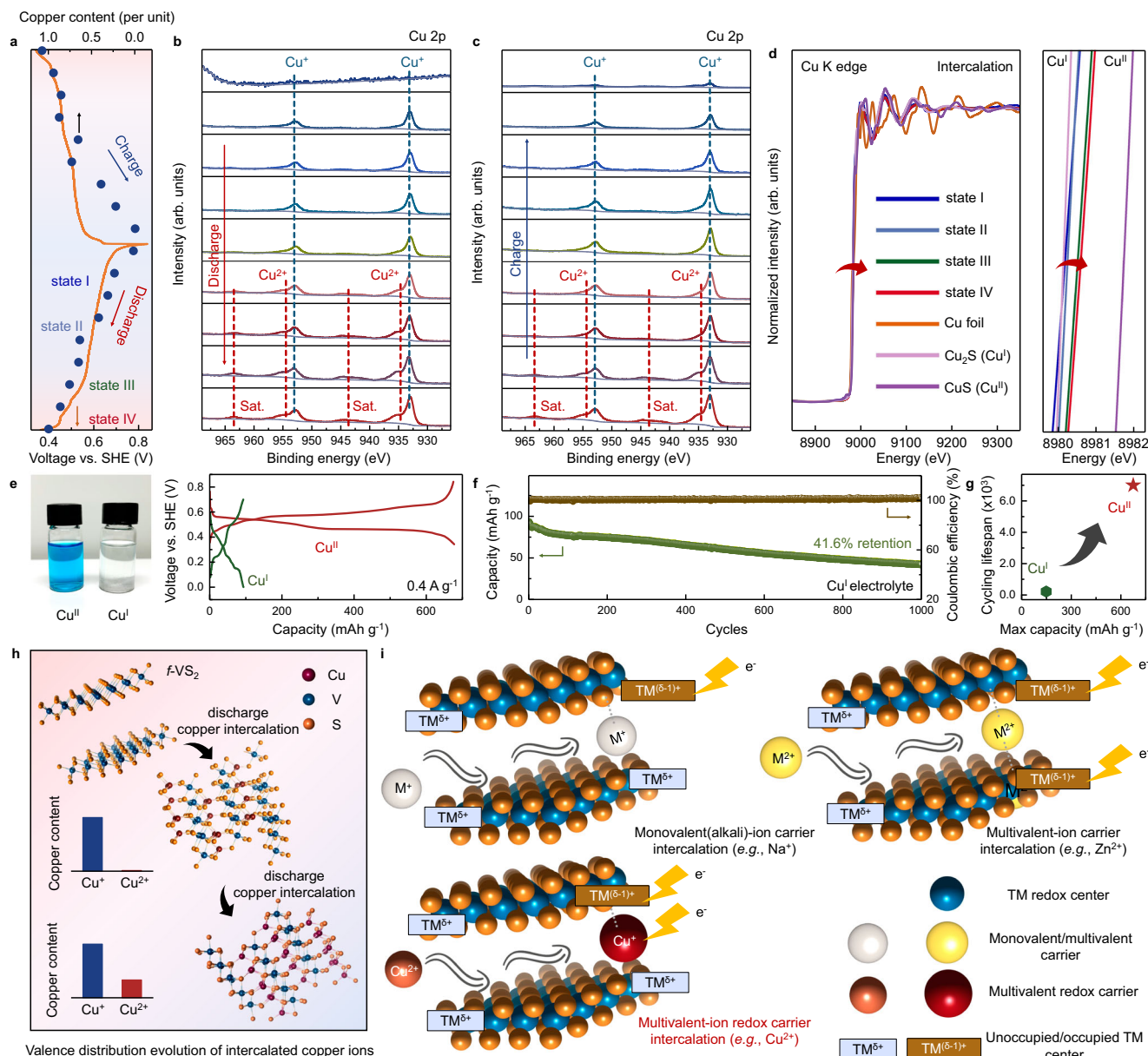


Fig. 2 | Carrier redox mechanism. **a** GCD curves, evolution of the copper content quantified from the XPS spectra, and corresponding Cu 2p XPS data in **(b)**, intercalation (discharging) and **(c)**, deintercalation (charging). **d** XAFS data for specific discharge states and corresponding XANES region amplification. **e** Optical images of the Cu^{II} and Cu^I electrolytes and GCD curves of f-VS₂ in the corresponding systems. See Methods for the configuration of the Cu^I electrolyte. **f** Cycling performance of f-VS₂ using the Cu^I electrolyte. **g** Comparison of the maximum capacity and cycling lifespan of f-VS₂ in the Cu^{II} and Cu^I electrolyte systems. **h** Schematic of

the valence distribution of the intercalated copper ions in the discharge. Monovalent copper resulting from carrier redox appears at the beginning of intercalation, whereas divalent copper appears at the final stage of intercalation. **i** Schematic of the intercalation process of monovalent-ion, multivalent-ion, and multivalent-ion redox carriers. Intercalation of multivalent-ion redox carriers can improve the charge transfer capacity while occupying a limit number of transition metal (TM) redox sites.

inferior to that of f-VS₂ in the Cu^{II} electrolyte (Fig. 2f), highlighting the composite enhancement of stability and capacity by intercalated carrier redox (Fig. 2g). Therefore, it can be concluded that the copper carriers and vanadium centres involved in the redox process are plausibly jointly contributing to the high reversible capacity of f-VS₂ (Fig. 2h), which implies that interlayer carrier redox may optimize the intercalation kinetics and reversibility in host materials. The FT-EXAFS analysis also revealed stable bond structures and an increase in the Cu-Cu ligand content (Supplementary Fig. 19), data that coincide with the insights extracted from the V K-edge. This first-revealed redox of intercalated carriers could bring intrinsic advantages to multivalent-ion batteries (Fig. 2i). Compared with monovalent carriers, multivalent

carriers are generally believed to possess a greater potential capacity because they can carry multiple charges at once for redox charge transfer with host materials. However, this expectation is actually strictly constrained by the total number of electron transfers that can be provided by the redox centre in host materials, which theoretically treats all types of carriers equally. Therefore, multivalent carriers would instead be mediocre by occupying more redox centres. In this regard, the use of intercalated multivalent copper ions as redox centres can afford extra electron transfer to form monovalent copper ions, thus increasing the capacity based on limited redox centres in the host, which is difficult to achieve in monovalent-ion batteries. The evolution of intercalated multivalent carriers (Cu^{II}, ionic radius = 57

pm) to monovalent carriers (Cu^+ , ionic radius = 60 pm) also leads to an increase in the ion size, thus maintaining sound layer spacing, and the effect of such endogenous carrier-dependent interlayer interactions on the intercalation capability was subsequently revealed via structural research.

Reversible pillar effects in structural evolution

The structural evolution caused by the reversible storage of ions in $f\text{-VS}_2$ was further investigated through $o\text{-SXR}$ D. The evolution of several major characteristic peaks of $f\text{-VS}_2$ during two continuous charging and discharging processes (Fig. 3a), including the (011), (002), and (110) planes (Fig. 3b) is shown. The peak shifts towards smaller angles are considerable in the initial stages of copper-ion intercalation, inducing simultaneous in-plane and out-of-plane lattice expansions that subsequently become moderate. When the electron transfer number reaches $\sim 2.2\text{e}^-/\text{VS}_2$, the SXR pattern can plausibly be indexed to the $\text{Cu}_{0.75}\text{VS}_2$ species (Supplementary Fig. 20), indicating the presence of an extra redox centre providing more electron transfer processes, which is consistent with the results of the spectroscopic analysis. Until the fully discharged state was reached, a maximum of 3.08% in the (002) plane and 2.77% in the (110) plane was observed, corresponding to a volume expansion of less than 10%, which coincided with the macroscopic cross-sectional view (Supplementary

Fig. 21). The characteristic peaks move similarly but in opposite trends during charging, eventually returning to the pristine peak position at the completion of charging. No additional peak generation/vanishing or tendency breaks were recognized, confirming a reliable intercalation mechanism, and the structure of VS_2 fully recovered after deintercalation. Further $o\text{-SXR}$ D was performed after 50 cycles (Fig. 3c), and overlapping de/intercalation processes were noted (Fig. 3d). Quantification of the expansion of the characteristic lattice for both $o\text{-SXR}$ D measurements reveals that $f\text{-VS}_2$ maintains a stable reversible intercalation mechanism (Fig. 3e). Notably, the most significant lattice expansion ($\sim 2\%$ according to the (002) plane) occurs at the beginning of intercalation, when the copper ions are transformed from divalent copper (Cu^{2+}) to monovalent copper (Cu^+) in the interlayer. The larger monovalent copper ions act as pillars to stabilize the interlayer structure and reduce the degree of lattice expansion following ion intercalation ($<1\%$ according to the (002) plane) (Fig. 3f). Previous reports have shown that intercalated interlayer pillars can mitigate lattice distortion and retain plausible ion diffusion paths that favour intercalation kinetics through the so-called pillar effect; however, the demonstrated pillars are usually retained in the interlayer and do not deintercalated, thus permanently altering the material structure. In contrast, copper ions with intercalated carrier redox not only ensure reversible stable intercalation with promising decent kinetics but also

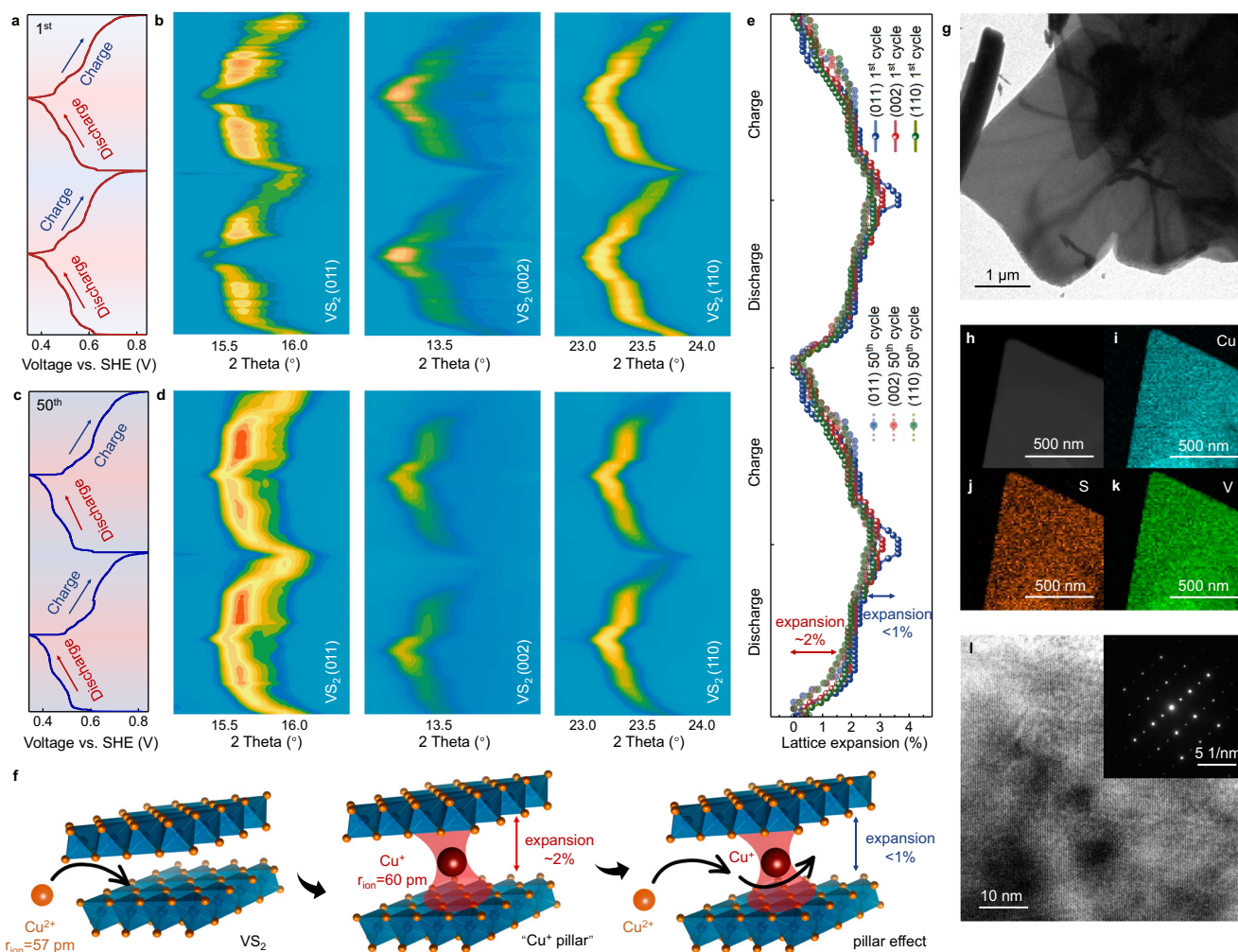


Fig. 3 | Pillar effects in structural evolution. **a** GCD curves and **(b)** corresponding $o\text{-SXR}$ D patterns of typical characteristic Bragg peaks in the initial two cycles. **c** GCD curves and **(d)** corresponding $o\text{-SXR}$ D patterns of typical characteristic Bragg peaks in the two cycles after cycling. **e** Quantized lattice expansion during the measured

cycles. **f** Schematic of the pillar effects of copper carrier redox during the intercalation process. **g** TEM observation, **(h)** HAADF image, and the corresponding **(i)**, **(j)**, **(k)**, **(l)** elemental mapping of full-discharged product. **l**, HRTEM image and SAED pattern of full-discharged product.

contribute to desirable capacity enhancement, allowing reconfiguration in layers via reversible de/intercalation. Transmission electron microscopy (TEM; Fig. 3g) and scanning electron microscopy (SEM) observations (Supplementary Fig. 22) of the fully discharged products were performed, and the ultrathin nanosheet morphology with a ten-micrometre horizontal size was well preserved. The uniform elemental distribution with copper intercalation (Fig. 3h–k, Supplementary Fig. 23) and the inherited microstructure (Fig. 3l) similarly support the stable de/intercalation mechanism with reversibility.

The pillar effects of copper carrier redox during the intercalation process are illustrated via density functional theory (DFT) analysis. Calculations of density of states (DOS) distributions for species in initial (VS_2 , Fig. 4a), intermediate ($\text{Cu}_{0.75}\text{VS}_2$, Fig. 4b), and fully intercalated ($\text{Cu}_{1.0}\text{VS}_2$, Fig. 4c) states show that a continuous conduction

band without energy gaps is maintained near the Fermi energy level (E_F), suggesting that the high conductivity of materials is guaranteed by intercalated copper ions. The highest and sub-highest electron-filling intensities near E_F are occupied by V and Cu in the intermediate state, and the sulfur intensity edge is far from the profile, which is consistent with the observation that no anion redox occurs in the experiments. Thermodynamic analysis on the basis of the Gibbs free energy further revealed the feasibility of intercalation (Supplementary Fig. 24). The absorption and migration of copper at the VS_2 interface were also examined via first-principles calculations (Fig. 4d). All the possible adsorption sites with optimized structures for copper adsorbed on VS_2 and $\text{Cu}_{0.75}\text{VS}_2$ were considered (Supplementary Fig. 25, Supplementary Table 2). A comparison of the copper adsorption energies for the top (-2.71 eV) and hollow (-2.53 eV) potential sites indicated that

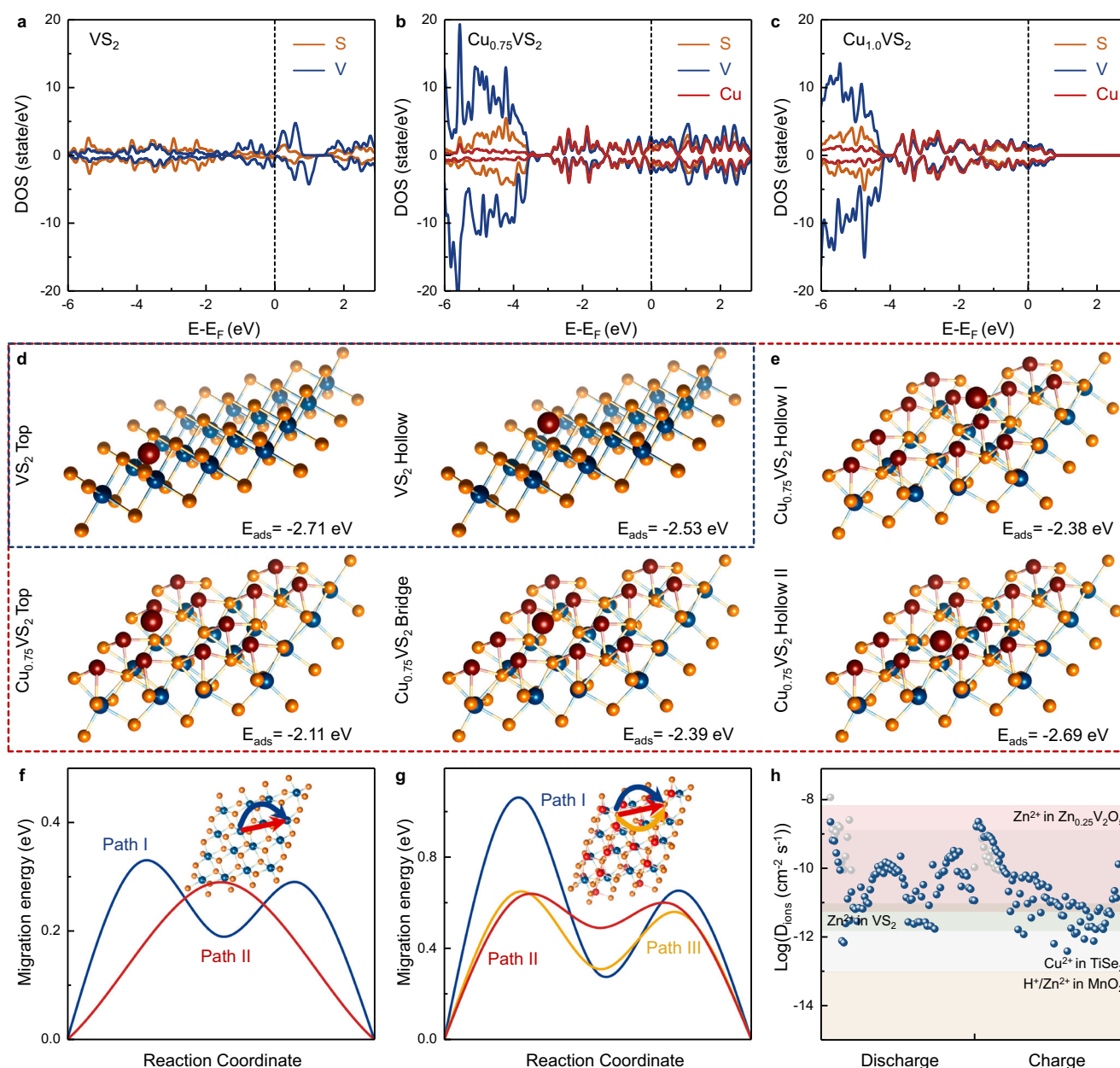


Fig. 4 | Theoretical calculations and kinetics. a DOS in different intercalated states: pristine state VS_2 , **(b)** intermediate state $\text{Cu}_{0.75}\text{VS}_2$ and **(c)** fully intercalated state $\text{Cu}_{1.0}\text{VS}_2$. The dotted lines mark the positions of the Fermi energy levels. **d** Adsorption energy of copper at accessible top sites and hollow sites of VS_2 . **e** Adsorption energy of copper at accessible top sites, hollow sites (multiple), and

bridge sites of $\text{Cu}_{0.75}\text{VS}_2$. The blue, orange, and red atoms represent the vanadium, sulfur, and copper elements, respectively. **f** Migrated energy barriers on the VS_2 and **(g)** $\text{Cu}_{0.75}\text{VS}_2$ surfaces corresponding to plausible diffusion paths. **h** Ion diffusion coefficients of VS_2 with copper intercalation. Cu^I in acetonitrile (grey) as reference.

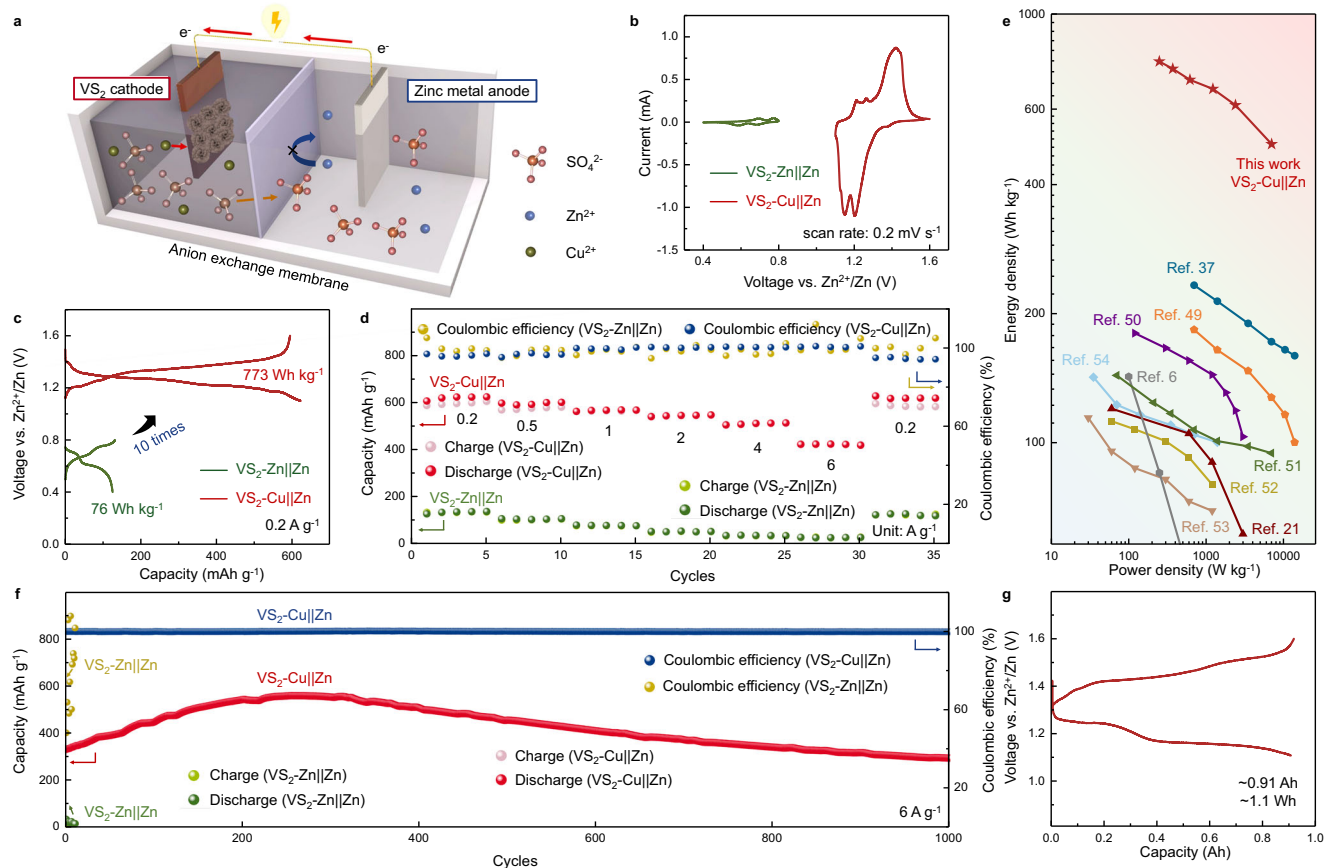


Fig. 5 | Energy storage applications. **a** Schematic of the established decoupled cell configurations with *f*-VS₂ cathodes and copper carrier redox mechanisms. **b** CV curves at 0.2 mV s⁻¹ and **(c)** GCD curves at 0.2 A g⁻¹ of *f*-VS₂ in the VS₂-Cu||Zn cell and VS₂-Zn||Zn cell. **d** Rate performance of *f*-VS₂ in the VS₂-Cu||Zn cell and VS₂-

Zn||Zn cell. **e** Comparison of the record reported here with the performance of all known VS₂ cathodes in zinc batteries. **f** Long-term cycling of *f*-VS₂ in a VS₂-Cu||Zn cell at 6 A g⁻¹. **g** GCD curves of the scale-up 1.1 Wh cell at 50 mA g⁻¹.

copper was susceptible to capture at the interface. Nonetheless, the energy difference across sites is not considerable, and both sites can act as adsorption sites to initiate redox processes. At the intermediate state of intercalation (Cu_{0.75}VS₂), the hollow site becomes the dominant site (top -2.11 eV, hollow -2.69 eV (II)/-2.38 eV (I), bridge -2.39 eV; Fig. 4e). The intercalated copper pillar does not considerably change the adsorption energy, maintaining the appreciable interfacial adsorption kinetics of VS₂ during intercalation. Migration barriers as low as 0.29 eV were obtained when copper diffused along the top-top path, which enabled unimpeded access of copper to all possible kinetic storage sites (Fig. 4f). The migration barriers of the intermediate state of the intercalation also remain at a low hindering level of 0.63 eV (Fig. 4g). The galvanostatic intermittent titration technique (GITT) provides experimental evidence. Generally, ions that have been intercalated will occupy favourable sites leading to slow kinetics of subsequent intercalation, as shown by the rapid decrease in diffusion coefficients for Cu^I (Supplementary Fig. 26) or zinc-ion intercalation without redox. The *f*-VS₂ with copper carrier redox provides an average ion diffusion coefficient $D_{\text{ions}} \sim 10^{-10.62} \text{ cm}^2 \text{ s}^{-1}$ (Fig. 4h), which is comparable to the recognized high-speed intercalation cathode Zn_{0.25}V₂O₅ in aqueous batteries and an order of magnitude greater than the diffusion of zinc carriers without redox in *f*-VS₂ (Supplementary Fig. 27, Supplementary Fig. 28). Therefore, benefitting from the reversible pillar effects of copper carrier redox in the intercalation process, the advantage of fast and reliable kinetics is maintained throughout the de/intercalation process, which is important for obtaining high performance.

Demonstration of high-performance VS₂-Cu||Zn cell with carrier redox

Aqueous zinc batteries with decoupled configurations and *f*-VS₂ cathodes were established to take advantage of the copper carrier redox mechanisms (Fig. 5a). The Cu^I electrolyte is not suitable for such systems, thus cells with zinc carriers without carrier redox were also established for comparison. When *f*-VS₂ cycles in the VS₂-Zn||Zn cell (Fig. 5b) - note that here using VS₂-M||N to define the specific battery system, where M is the carrier involved in redox at the cathode and N is the anode - results in a capacity lower than 125 mAh g⁻¹ (Fig. 5c). In contrast, when copper ions are used as carriers (VS₂-Cu||Zn), the performance is drastically improved, as shown in the cyclic voltammetry (CV) curve (Fig. 5b). At 0.2 A g⁻¹, *f*-VS₂ in the VS₂-Cu||Zn cell provides a capacity release of 623 mAh g⁻¹ and an energy supply of 773 Wh kg⁻¹, which is 10 times greater than that of the cell using zinc carriers at the same specific current (all calculated on the basis of the VS₂ mass), as shown in the GCD curves. Even if the specific current is increased to 0.5, 1, 2, 4, and 6 A g⁻¹, capacities of 600, 567, 547, 508, and 423 mAh g⁻¹ can be obtained, respectively (Fig. 5d). The energy efficiency ranged from 80% ~ 96%. When the specific current is returned to 0.2 A g⁻¹, a capacity of 617 mAh g⁻¹ is recovered, demonstrating favourable robustness to current abuse (Supplementary Fig. 29), which is far superior to that of *f*-VS₂ in the VS₂-Zn||Zn cell (Supplementary Fig. 30). Compared with all the VS₂ cathodes used in zinc batteries reported to date, the *f*-VS₂ cathode in the VS₂-Cu||Zn cell offers more than twice the energy density advantage (Fig. 5e)^{6,21,43,55-60}. Further long-term cycling measurements were performed at 6 A g⁻¹ (Fig. 5f).

The capacity retention of 88.7% (compared with the pristine cell) confirms the stability of $f\text{-VS}_2$ with a CE of $\sim 100\%$. With facile optimization of the zinc anode, the cell lifespan can be further extended to 1800 cycles (Supplementary Fig. 31). After long cycles, retained flower-like clusters are observed at the electrodes (Supplementary Fig. 32), which corroborates the reliable stability. In stark contrast, $f\text{-VS}_2$ using zinc as a carrier is constrained by slow kinetics and rapidly degrades to a capacity below 15 mAh g^{-1} within 10 cycles, two orders of magnitude lower than that of $f\text{-VS}_2$ in the $\text{VS}_2\text{-Cu}||\text{Zn}$ cell in terms of energy density and lifespan (Supplementary Fig. 33). The established advantages have driven the build-up of a high-load (7.03 mg cm^{-2}) and scale-up 1.1 Wh cell (Fig. 5g), which can deliver 581 mAh g^{-1} capacity and 690 Wh kg^{-1} energy density (calculated on the basis of $f\text{-VS}_2$ loading), enabling 0.91 Ah reversible charge storage and an energy efficiency of 81.7% (Supplementary Fig. 34).

Discussion

Driven by resource sustainability and reserve advantages in the Earth's crust, interest in multivalent-ion batteries, which cover several ion carriers from zinc to aluminium. The taken-for-granted anticipation of the prospect of multivalent ion batteries promises high-capacity availability, which is invoked by the fact that single ion can carry multiple charges: Multivalent ions such as zinc enable more than one charge equivalents transfer per mole of the metal carriers, leading to a higher specific capacity than that of monovalent metal-ion batteries. However, this motivation is untenable for host electrodes employed in ion storage such as intercalation-type VS_2 cathodes, due to the limitation of the total number of redox centers. Beyond the upper limit of the total number of transferable electrons per mole of material, the bond–lattice structure of the material irretrievably collapses, depending not on the type of carrier but on the number of redox sites in the material itself. Given these considerations, the most important advantage of multivalent ion carriers may be the variable valence property, whereby the intercalated carriers act as redox centres to undertake electron transfer to break through the upper limit of the total number of electrons that can be transferred in the material itself, which is clearly beyond the reach of monovalent carrier systems. Inspired by the mixed valence of copper minerals in nature, the redox reaction of divalent copper has been developed and applied in many different battery systems. The exploitation of copper elements as anchored redox centers in electrodes has been demonstrated in lithium and zinc batteries^{66,67}, and initiating the deposition of copper ions from the electrolyte to the electrode interface or liquid-flow-type redox as well as conversion in sulfur group element electrodes have shown in several novel battery prototypes^{22,29,32,68}. These established deposition/conversion reactions clearly result in copper carrier redox, however the possibility and mechanism of carrier redox within the intercalated host material is long neglected. Apparently, for the capacity enigma that continues to loom over multivalent-ion intercalation chemistry, realizing the redox of intercalated multivalent-ions with insights into the electronic structure and interlayer ion transport dynamics of the host material in reaction is a desirable starting point. In this work, we report carrier redox in an intercalation-type $f\text{-VS}_2$ cathode, which provides the highest recorded capacity among VS_2 cathodes of 675 mAh g^{-1} and enables stable operation for 7000 cycles at 10 A g^{-1} . Composite *operando/ex situ* characterization and first-principles calculations revealed that the preferential redox of intercalated copper ions in the interlayer not only provides extra capacity for $f\text{-VS}_2$ but also maintains a fast kinetic advantage via the reversible pillar effect, conferring a 773 Wh kg^{-1} energy supply in aqueous zinc-decoupling batteries. We also found that the similar intercalated carrier redox mechanism is present in niobium disulfide (Supplementary Fig. 35). Carrier redox during intercalation provides a potential pathway to truly utilize the multicharge-carrying advantages of multivalent

carriers, which is promising for stimulating fervour for research on multivalent-ion batteries.

Methods

Materials

To prepare $f\text{-VS}_2$, first, 2 mmol of NH_4VO_3 was added to a mixture of 30 mL of deionized water and 2 mL of ammonium hydroxide. Then, 20 mmol of thioacetamide was added to the above mixture and stirred for 4 h at room temperature in an atmosphere. The autoclave was sealed and kept at 180°C for 20 h and then cooled to room temperature. The product was washed with deionized water and ethanol several times and then dried at 60°C overnight in a vacuum oven. $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (99.9%), $\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$ (99.9%), copper foil (99%), and zinc foil (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. NbS_2 were purchased from Nanjing MKNANO Tech. Co., Ltd. and were used directly without further purification.

Electrodes and electrolytes

$f\text{-VS}_2$ was mixed with carbon black and polyvinylidene fluoride at a weight ratio of $7:2:1$ in 1-methyl-2-pyrrolidinone (i.e., active material as $70 \text{ w.t.}\%$), and then, the slurry was pasted on carbon paper and dried under vacuum at 60°C for 10 h . Typical thickness of the electrodes is $150 \mu\text{m}$ (including the collector) for a 6 mm diameter disc (area 28.3 mm^2). The typical mass loading of the active materials was $1\text{--}1.5 \text{ mg cm}^{-2}$. Preparation of NbS_2 electrodes followed the same protocol. All metal electrodes were polished with 800 grit silicon carbide sandpaper and cleaned with ethanol before use. 1 M CuSO_4 in H_2O (for the $\text{VS}_2\text{-Cu}||\text{Zn}$ cell) and 1 M ZnSO_4 in H_2O (for the $\text{VS}_2\text{-Zn}||\text{Zn}$ cell and $\text{VS}_2\text{-Cu}||\text{Zn}$ cell) were prepared or obtained in stoichiometric ratios. In addition, a Cu^I electrolyte was used: $0.2 \text{ M Cu}(\text{ClO}_4)_2$ was dissolved in anhydrous acetonitrile, the cleaned copper foils were incubated overnight, and the solution eventually became colourless because of the reduction of Cu^{2+} in the solution.

Electrochemical evaluation

Electrochemical energy storage tests are carried out in an air-conditioned room with the temperature of the AC set at 27°C , affected by the ambient air temperature with a variation of 2°C . All the specific energy/energy density values and the specific power/power density values reported in the manuscript are calculated based on the mass of VS_2 . For all cells, significantly excessive metal anodes are used ($\sim 80 \text{ mg cm}^{-2}$, $\text{N:P} > 10$). As previously defined, the cells are named $\text{VS}_2\text{-M}||\text{Zn}$, where $f\text{-VS}_2$ is the cathode material and M is the carrier in the cathode chamber reacting with $f\text{-VS}_2$, i.e., Cu or Zn . Specifically, for the $\text{VS}_2\text{-Cu}||\text{Zn}$ cell, an ion-selective membrane (anion exchange membrane, AEM typed as FAB-PK-130 and commercially obtained from FUMATECH BWT GmbH) is used to divide the complete cell into two chambers, referred to as the cathode chamber and the anode chamber. Since AEMs can block cations (e.g., Zn^{2+} and Cu^{2+}) from crossing over but allow anions (SO_4^{2-}) to traverse freely, the cathode and anode chambers can be filled with aqueous sulfate solutions containing different cations without worrying about electrolyte mixing (normally 2 mL due to cell size). In the case of $f\text{-VS}_2\text{-Cu}||\text{Zn}$, for example, the cathode chamber is filled with a 1 M CuSO_4 solution, and $f\text{-VS}_2$ coated on carbon paper is used as the cathode submerged in the solution. Similarly, the anode chamber was filled with an equal amount of 1 M ZnSO_4 solution, and zinc metal was used as the anode. Owing to the confinement of the AEM, Zn ions do not diffuse to the cathode side to disturb the de/intercalation of Cu ions, and SO_4^{2-} ions are allowed to shuttle between the two chambers to balance the charge. All energy densities in the manuscript are calculated on the basis of the VS_2 material in the cathode. The GCD and GITT tests were performed with a LANHE CT2001A (Wuhan Land Electronic Co., Ltd.) battery testing system, with cycling in the voltage range of $1.1\text{--}1.6 \text{ V vs. Zn}^{2+}/\text{Zn}$ (for

the $\text{VS}_2\text{-Cu}||\text{Zn}$ cell) and 0.4–0.8 V *vs.* Zn^{2+}/Zn (for the $\text{VS}_2\text{-Zn}||\text{Zn}$ cell), and were precycled at a low specific current (0.5 A g^{-1}) for 5 cycles to activate the electrodes before formal testing. When copper foil is used as an anode, a 1 M CuSO_4 solution (Cu^{II}) or a Cu^{I} electrolyte is used as the electrolyte without an AEM. Electrochemical evaluation of NbS_2 electrodes followed the same protocol. CV tests were performed with a CHI 760E (Chenhua Instrument Company, Shanghai, China) electrochemical workstation, and the voltage range was consistent with that used in the GCD cycling.

Characterization

The VS_2 samples/electrodes were characterized via SEM (Carl Zeiss Gemini SEM 300), XPS (Kratos Analytical Axis UltraDLD), TEM (JEM-F200), and Raman spectroscopy (RENISHAW inVia Basis; 532 nm). The XRD experiments were performed on beamline BL02U2 (X-ray wavelength of 0.6887 Å) at the Shanghai Synchrotron Radiation Facility (SSRF). The S XAFS experiments were performed on beamline BL16U1 at the SSRF, and the Cu XAFS experiments were performed on beamline BL13SSID at the SSRF. The position of the absorption edge was calibrated with S powder or Cu foil, and the obtained data were analysed with the ATHENA software package. For *ex situ* measurements of the VS_2 cathodes, the batteries were first charged/discharged to the specific potential with a LAND workstation and opened in air to collect the cathodes. The prepared cathodes were washed with deionized water and anhydrous ethanol three times and dried at room temperature for 10 min for further measurements. *o*-SXRD experiments were performed on beamline BL02U2 (X-ray wavelength of 0.6887 Å or 0.695 Å) at the SSRF. The beam size was confined by horizontal and vertical slits to $\sim 0.3 \times 0.3 \text{ mm}^2$. The two-dimensional XRD signal was obtained by a PILATUS3S 2M detector and integrated with Fit2D software. In addition, a special coin cell was designed for the *o*-SXRD study. There were two observation holes with radii of $\sim 2 \text{ mm}$ in the middle of both sides of the cell, guaranteeing that X-rays penetrated through the active material during operation. The special *operando* cell observation holes were sealed with polyimide tape. The same cell but with an observation hole (5 mm) was also used to perform *V o*-XAFS measurements at beamline BL17B1 at the SSRF. The position of the absorption edge was calibrated with V foil, and the obtained data were analysed with the ATHENA software package. During the test, the batteries were cycled at 0.3 A g^{-1} .

Calculation

Calculations were conducted using spin-polarized DFT within the Vienna *ab initio* simulation package (VASP). Projector-augmented wave (PAW) pseudopotentials were employed to describe the core–valence interactions, whereas the exchange–correlation functional was based on the generalized gradient approximation (GGA) within the PBE framework. The cut-off energy for the plane wave basis was set to 520 eV. All the bulk structures (VS_2 , $\text{Cu}_{0.75}\text{VS}_2$, and $\text{Cu}_{1.0}\text{VS}_2$) were optimized. The *k*-points were set to $8 \times 8 \times 1$ for the VS_2 bulk structure and $3 \times 3 \times 1$ for the $\text{Cu}_{0.75}\text{VS}_2$ and $\text{Cu}_{1.0}\text{VS}_2$ bulk structures in the Gibbs free energy calculations. The convergence criteria for energy and force were set to $1 \times 10^{-5} \text{ eV/atom}$ and 0.02 eV/Å , respectively. A total of $4 \times 4 \times 4$ supercells with 3 atomic layers were selected for the VS_2 slabs, whereas a 2×2 unit-cell with four atomic layers was selected for the $\text{Cu}_{0.75}\text{VS}_2$ surface. A $2 \times 2 \times 1$ *k*-points were set for all optimized slabs. To avoid interactions between periodic images, a vacuum layer over 15 Å was set in the *z* direction. The climbing image nudged elastic band (CI-NEB) method with the quasi-Newton algorithm was employed to calculate the diffusion barrier of a Cu atom on the surface of a monolayer VS_2 . The vibrational frequencies of the optimized structures were computed via the finite difference method with a step size of 0.02 Å. Three types of sites were considered for the adsorption of Cu on a single-layer $\text{VS}_2/\text{Cu}_{0.75}\text{VS}_2$, including the top, bridge and hollow sites. The energy for the Cu-chemisorbed state was calculated via the formula

$E_{\text{ads}} = E_{\text{Cu-VS}_2} \text{ or } \text{Cu-Cu}_{0.75}\text{VS}_2} - E_{\text{Cu}} - E_{\text{VS}_2} \text{ or } \text{Cu}_{0.75}\text{VS}_2}$. $E_{\text{Cu-VS}_2} \text{ or } \text{Cu-Cu}_{0.75}\text{VS}_2}$ is the energy of the Cu atom adsorbed on the VS_2 or $\text{Cu}_{0.75}\text{VS}_2$ surface, respectively. $E_{\text{VS}_2} \text{ or } \text{Cu}_{0.75}\text{VS}_2}$ represents the energy of single-layer VS_2 or $\text{Cu}_{0.75}\text{VS}_2$. E_{Cu} is the energy of the isolated Cu atom.

Data availability

The authors declare that all data supporting the findings of this study are available within the paper and its supplementary information files.

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Author contributions

D.Z. conceived the project. Y.S. and D.Z. developed the concept. Y.S. and H.S. conducted the experiments and data analysis. R.Q. performed the calculations. Q.L. and J.Z. analyzed the absorption spectrum data. W.Z., H.L., and M.L. performed the cycling tests. W.W. and Y.G. contributed to the calculations. Y.S., and D.Z. wrote the manuscript. X.L., C.Z., and D.Z. supervised the project. All authors discussed and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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