

# A high-rate and stable quasi-solid-state zinc-ion battery with novel 2D layered zinc orthovanadate array

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# Advanced Materials

## High-Rate and Stable Quasi-Solid-State Zinc-Ion Battery with Novel 2D Layered Zinc Orthovanadate Array --Manuscript Draft--

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<b>Question</b>	<b>Response</b>
Please submit a plain text version of your cover letter here.  <b>If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here.</b>	Dear Dr. Esther Levy,  Thank you for giving us the opportunity to resubmit our manuscript (adma.201802147). We have revised it according to your and the reviewers' comments. Repeating sentences have been reworded. Reviewers #1 and 3 are quite positive, and Reviewer #2 questions the novelty, which we can defense. We have addressed all the comments by all three referees. A point to point response is provided separately. I would appreciate if you could reconsider our revised manuscript favorably and avoid the potential conflict of interest with Reviewer #2. This manuscript is very timely given the current hotspot of Zn-ion batteries. In fact, we have submitted an Invited Review to Adv Funct Mater (adfm.201802564) which is currently under minor revision.  ----Major novelty of our paper---- <ul style="list-style-type: none"><li>• Three First: For the 1st time, a novel 2D layered zinc orthovanadate array is synthesized and used as cathode material. The first demonstration of intercalation pseudocapacitance in Zn-ion batteries, especially quasi-solid-state ZIBs. And the 1st report on quasi-solid-state ZIB.</li><li>•Metallic Zn nanoflake array on 3D porous conductive support to replace conventional compact Zn foil anode, which significantly suppresses Zn dendrite growth.</li><li>•We demonstrate a high depth of discharge of ca. 100% for cathode and 66% for anode. In contrast, recent reported ZIBs based on Zn foil anode have very low (&lt; 15%) depth of discharge in the anode because of large amount of non-active Zn materials.</li></ul> ----Justification for resubmission---- <p>Referees #1 and 3 suggest minor revisions. The main concern of Referee #2 is the novelty of our cathode part Zn<sub>2</sub>(OH)VO<sub>4</sub> array. He said there already 7 papers about V-based cathode materials. But the Zn<sub>2</sub>(OH)VO<sub>4</sub> (ZOV) reported herein is a novel 2D layered zinc orthovanadate, which is synthesized for the first time and used as metal ions storage electrode in batteries field. This new cathode also gives new Zn ion storage mechanism: In previous reports of ZIBs, most of the V-based cathode materials are phase-change type, so the rate and cycling performances are all mediocre. The open framework of ZOV shows expanded interlayer spacing (0.73 nm versus 0.57 nm for V<sub>2</sub>O<sub>5</sub> and VS<sub>2</sub>, and 0.58 nm for VO<sub>2</sub>), which is perfect for the 2D (b–c plane) fast ion transport.</p> <p>As a result, we also demonstrate higher performance than before. 89 % capacity retention after 2000 cycles at 20 C, and highest ever energy and power densities (115 Wh kg<sup>-1</sup> and 5100 W kg<sup>-1</sup>, based on mass of both cathode, anode, and current</p>

	collectors).  Sincerely,  Hong Jin Fan School of Physical and Mathematical Sciences Nanyang Technological University, Singapore 21 Nanyang Link, Singapore 637371 E-mail: fanhj@ntu.edu.sg
Do you or any of your co-authors have a conflict of interest to declare?	No. The authors declare no conflict of interest.
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<b>Abstract:</b>	Zinc-ion batteries are under current research focus because of their uniqueness in low cost and high safety. However, it is still desirable to improve the rate performance by improving the Zn <sup>2+</sup> (de)intercalation kinetics and long-cycle stability by eliminating the dendrite formation problem. Herein, we construct the first paradigm of a high-rate and ultra-stable flexible quasi-solid-state zinc ion battery from a novel 2D ultrathin layered zinc orthovanadate array cathode, a conductive porous graphene foam supported Zn array anode, and gel electrolyte. The nanoarray structure for both electrodes assures the high rate capability and alleviates the dendrite growth. The flexible Zn-ion battery has a depth of discharge of ca. 100% for the cathode and 66% for the anode, and delivers an impressive high-rate of 50C (discharge in 60s), long-term durability of 2,000 cycles at 20C, and unprecedented energy density ~115 Wh kg <sup>-1</sup> , together with a peak power density ~5.1 KW kg <sup>-1</sup> (calculation includes masses of cathode, anode and current collectors). First principles calculations and quantitative kinetics analysis show that, the high-rate and stable properties are correlated with the 2D fast ion migration pathways and the introduced intercalation pseudocapacitance.

1 **High-Rate and Stable Quasi-Solid-State Zinc-Ion Battery with Novel 2D**  
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3 **Layered Zinc Orthovanadate Array**  
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53 *Zinc array*  
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## Abstracts

Zinc-ion batteries are under current research focus because of their uniqueness in low cost and high safety. However, it is still desirable to improve the rate performance by improving the  $\text{Zn}^{2+}$  (de)intercalation kinetics and long-cycle stability by eliminating the dendrite formation problem. Herein, we construct the first paradigm of a high-rate and ultra-stable flexible quasi-solid-state zinc ion battery from a novel 2D ultrathin layered zinc orthovanadate array cathode, a conductive porous graphene foam supported Zn array anode, and gel electrolyte. The nanoarray structure for both electrodes assures the high rate capability and alleviates the dendrite growth. The flexible Zn-ion battery has a depth of discharge of ca. 100% for the cathode and 66% for the anode, and delivers an impressive high-rate of 50C (discharge in 60s), long-term durability of 2,000 cycles at 20C, and unprecedented energy density  $\sim 115 \text{ Wh kg}^{-1}$ , together with a peak power density  $\sim 5.1 \text{ KW kg}^{-1}$  (calculation includes masses of cathode, anode and current collectors). First principles calculations and quantitative kinetics analysis show that, the high-rate and stable properties are correlated with the 2D fast ion migration pathways and the introduced intercalation pseudocapacitance.

Li-ion batteries have been the dominating commercial power source for portable electronics and has achieved great success in the past decades, the scarce abundance (20 ppm) and increasing higher cost of Li pose challenges for its large-scale application<sup>[1-3]</sup>. Zinc offers significant advantages over lithium in terms of the natural abundance, large-scale distribution, easy processing, and nontoxicity<sup>[4]</sup>. Zinc ion batteries (ZIBs) are promising due to their two-electron redox ( $\text{Zn}^{0/2+}$ ), low cost, high safety, as well as easier to scale up than organic Li-ion batteries<sup>[1, 5]</sup>. One of the issues that that has held back the application of Zn in next-generation batteries lies in its poor cycle life and inferior fast-discharge performance due to the dendrite formation on zinc foil anode<sup>[1]</sup>. Recent reported cathode materials include tunnel-type  $\alpha\text{-MnO}_2$ <sup>[6]</sup>,  $\gamma\text{-MnO}_2$ <sup>[7]</sup>, Prussian blue analogs<sup>[8]</sup>, NASICON structured  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ <sup>[9]</sup>,  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ <sup>[10]</sup>, calix[4]quinone<sup>[11]</sup>, layered-type  $\text{LiV}_3\text{O}_8$ <sup>[12]</sup>,  $\text{Na}_{1.1}\text{V}_3\text{O}_{7.9}$ <sup>[13]</sup>,  $\text{VS}_2$ <sup>[14]</sup>, and metal vanadium oxide bronzes<sup>[5, 15]</sup>. Despite these efforts, the high-rate performance and

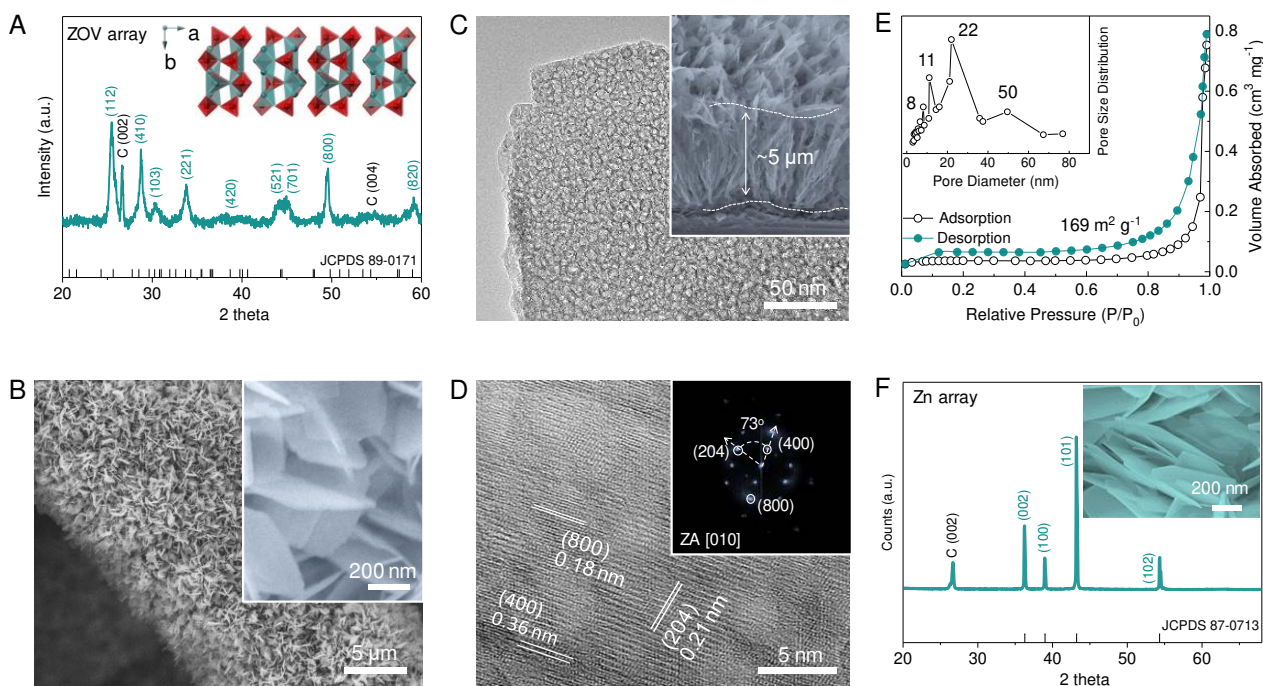
1 cycling sustainability are still relatively poor, probably due to reasons such as elements  
2 dissolution, self-aggregation, and phase change incorporated in  $\text{Zn}^{2+}$  uptake. Therefore, novel  
3 intercalation cathodes with tailored nanoarchitecture design are prerequisite, which can both  
4 provide short and fast  $\text{Zn}^{2+}$  migration channels and sustain the structure integrity without  
5 crystallographic phases change for long-time and high-rate cycling.  
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10 To date, three types of Zn-ion storage mechanisms are being discussed in literature, i.e.  
11 diffusion-controlled faradaic process<sup>[4, 8-12]</sup>, the surface-induced pseudocapacitive faradaic  
12 process, and the nonfaradaic contribution from the electrical double-layer capacity (EDLC)  
13 effect.<sup>[14, 15]</sup> In most cases, the EDLC value ranges between  $10\text{--}50\ \mu\text{F cm}^{-2}$  and is considered  
14 negligible<sup>[16]</sup>. It is difficult to achieve high-rate performance based on the first process due to  
15 the poor mass diffusion of divalent cation  $\text{Zn}^{2+}$  in the bulk lattice. It is expected that the second  
16 process should be able to render fast kinetics that is particularly favorable to  $\text{Na}^+/\text{K}^+/\text{Zn}^{2+}$  ion  
17 batteries with cation sizes larger than  $\text{Li}^+$  <sup>[17, 18, 19]</sup>. Particularly in solid-state battery systems,  
18 the progress on faradic capacitive contribution has been very limited.  
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29 In order to tackle the above issues and achieve high-rate and stable ZIBs, herein we report  
30 our flexible quasi-solid-state Zn-ion battery (QSS-ZIB) by employing a novel layered zinc  
31 orthovanadate as high-performance cathode and zinc nanoflake array as anode. For the anode  
32 part, we synthesized metallic Zn nanoflakes array on a 3D porous conductive support to replace  
33 conventional compact Zn foil. This, together with the use of newly designed quasi-solid-state  
34 electrolyte instead of aqueous electrolyte, Zn dendrite growth is thoroughly eliminated. In the  
35 zinc orthovanadate array cathode side, we show that the thin and mesoporous morphological  
36 features and the associated fast 2D ion migration pathways facilitate a significant intercalation  
37 pseudocapacitive contribution without crystallographic phase change. This flexible all-array  
38 QSS-ZIB enables high rate capability with long-term cycling performance, and delivers  
39 unprecedented maximum energy and power densities as high as  $\sim 115\ \text{Wh kg}^{-1}$  and  $\sim 5100\ \text{W}$   
40  $\text{kg}^{-1}$ , respectively (on the basis of mass from both cathode, anode, and their current collectors).  
41 Our results may stimulate a paradigm shift of ZIB to new  $\text{Zn}^{2+}$  host materials, 3D zinc metal  
42 electrode and solid-state electrolyte, and also afford deeper understanding of the Zn ion  
43 migration processes in such layered host through intercalation pseudocapacitance. Such safe,  
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cost-effective, and high-energy/power density ZIB may be a promising candidate for safer power sources than the dominating LIBs.

## Characterization of electrode materials



**Figure 1 | Morphology and structure of ZOV array cathode and Zn array anode.** (A) XRD pattern of zinc orthovanadate which can be index to orthorhombic  $Zn_2(OH)VO_4$  (PDF #89–0171). Inset A: illustration of the layered crystal structure. (B) SEM image of the ZOV with a homogeneous nanoflake structure. Inset B: high resolution SEM image. (C) TEM image of ZOV showing porous surface of the array. Inset C: cross-section of the arrays on top of the substrate. (D) High resolution TEM image of ZOV array. Inset D: corresponding fast Fourier transform (FFT) pattern along the [010] zone axis. (E)  $N_2$  adsorption/desorption isotherm of the ZOV array. Inset E: corresponding pore size distribution. (F) XRD spectrum of the electrodeposited Zn array that corresponds to the hexagonal Zn (PDF #87–0713). Inset: SEM image showing the Zn flake-array structure.

The flexible graphene foam (GF) supported ZOV array cathode is synthesized using a hydrothermal route (details in the Experimental Section). As shown in Figure 1A, the X-ray diffraction (XRD) spectrum unveils the characteristic pattern of orthorhombic  $Zn_2(OH)VO_4$  structure (space group  $Pnma$ , with calculated lattice parameters of  $a = 14.68 \text{ \AA}$ ,  $b = 5.98 \text{ \AA}$ ,  $c = 8.87 \text{ \AA}$ , JCPDS #89–0171), except for the (002) and (004) peaks from the carbon substrate (JCPDS #75–1621). The special layered crystal structure of ZOV is shown in inset of Figure

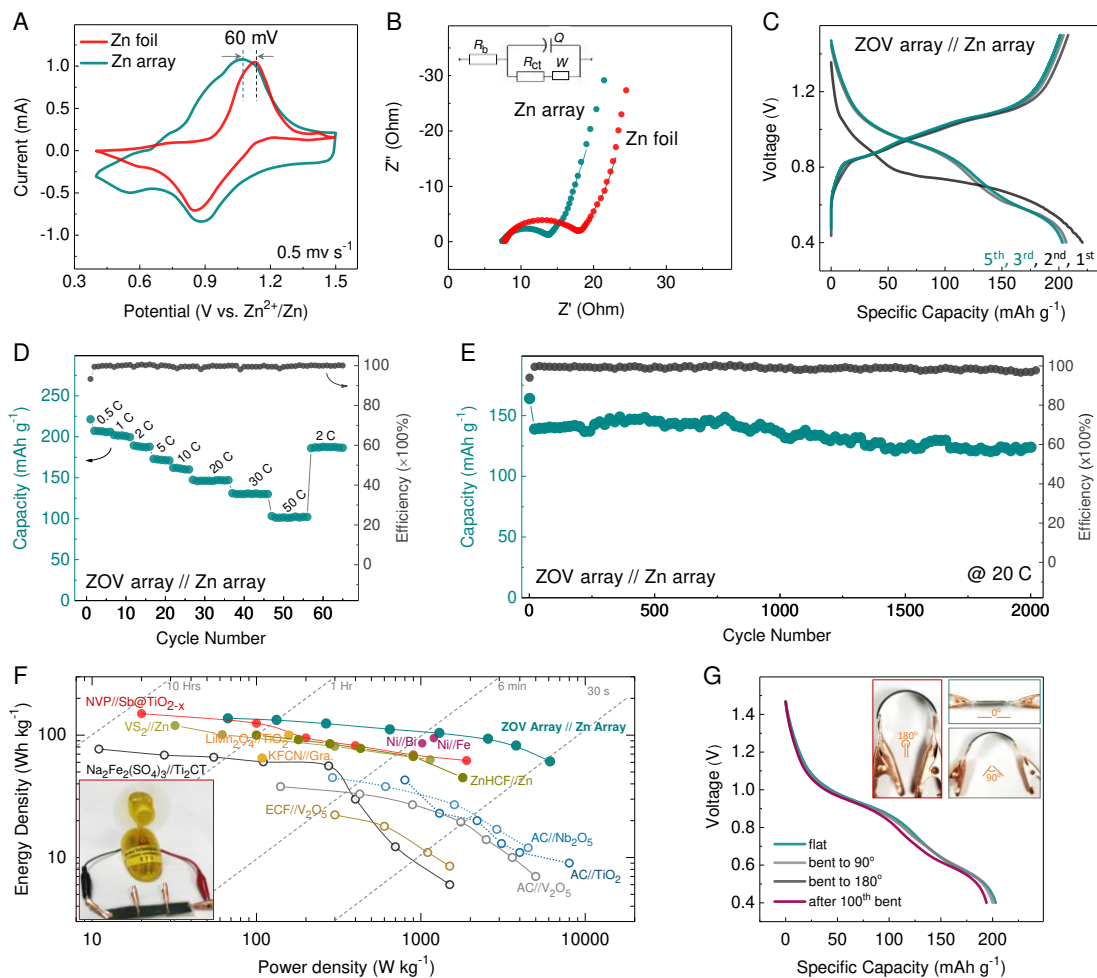


1A. The 3D [Zn(OH)VO<sub>4</sub>] framework is formed with building blocks of tetrahedra [VO<sub>4</sub>] interconnected with octahedral [ZnO<sub>6</sub>] chain and Zn cations that fill the voids with trigonal octahedral and bipyramidal coordination, which further enhances the structural stability of the open framework and expands the interlayer spacing (0.73 nm *versus* 0.57 nm for V<sub>2</sub>O<sub>5</sub> and VS<sub>2</sub>, and 0.58 nm for VO<sub>2</sub>)<sup>[14, 20, 21]</sup> for 2D fast ion transport along the *b*–*c* plane.

The overall morphologies and crystal phases of the as-prepared ZOV array are characterized using scanning electron microscope (SEM), energy-dispersive X-ray (EDX) elemental mapping, and high-resolution transmission electron microscope (HRTEM) images (see data in Figure 1B–D and Figure S1, Supporting Information). In the nanoarchitecture, each lamellar structure is interconnected with each other and thus can facilitate the electrochemical reactions. Noticeably, the ZOV electrode shows a robust mechanical stability and good flexibility (inset in Figure S2A, Supporting Information); It can be bent without any protection, and the film with a high mass loading  $\sim 4.1 \text{ mg cm}^{-2}$  does not peel off during repeated bending. The nanoflakes have typical thickness less than 10 nm (inset in Figure 1B–C and Figure S1, Supporting Information), average lateral width of ca. 400 nm, height ca. 5  $\mu\text{m}$ , and a highly mesoporous structure (5–10 nm, Figure 1C, and Figure S2, Supporting Information). The lateral view of the array in Figure 2D also discovers the single crystalline feature of the array and interplanar spacings of 3.6, 1.8, and 2.1  $\text{\AA}$  for the (400), (800), and (204) planes, respectively, in correlation with the fast Fourier transform pattern along the [010] zone axis. The formation of nanosheets by (010) facets stacking can also be confirmed with extensively exposed channels in *b*–*c* planes. The specific surface area is measured  $\sim 169 \text{ m}^2 \text{ g}^{-1}$  with pores around 8, 10, 22, and 50 nm, indicating a highly mesoporous feature of the arrays. In addition, the metallic zinc array (ca. 20 nm in thickness and ca. 400 nm in width) on GF substrate as the anode is achieved by a facile electrodeposition method (XRD data is shown in Figure 1F).

## Electrochemistry and battery performance





**Figure 2 | Quasi-solid-state ZIB performance with ZOV array as cathode and Zn array as anode.** (A) CV curves comparison after 5 cycles charge/discharge activation at 0.5C of the QSS-ZIBs made of ZOV cathode and Zn array or foil anode (voltage range 0.4 ~ 1.5 V, scan speed  $0.5 \text{ mV s}^{-1}$ ). (B) EIS of the foregoing Zn array and Zn foil electrodes at the fully charged state. An equivalent circuit of  $R_b(Q(R_{ct}W))$  in the inset is used to simulate the resistances, where  $R_b$ ,  $R_{ct}$ ,  $Q$ , and  $W$  are the ohmic resistance of solution and electrodes, the charge transfer resistance, the double layer capacitance, and the Warburg impedance, respectively. (C) Charge-discharge curves of the ZOV array//Zn array device at 0.5C, and (D) rate capability of the cell at varied current densities from 0.5C to 50C. (E) Long-term cycling performance at 20C for 2000 cycles. (F) Ragone plot comparing with other state-of-the-art reported energy storage systems. The calculation includes the mass of active material in both cathode and anode. Inset: Photograph of a small rotation motor (3 V, 0.4 W) connected with fan powered by 3 QSS-ZIBs in series after charging for only 30 seconds. Solid yellow circles are aqueous Li-ion battery of  $\text{LiMn}_2\text{O}_4//\text{TiO}_2$ <sup>[28]</sup>, K-ion battery of  $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}//\text{Graphite}$ <sup>[29]</sup>; Solid dark yellow circles attribute to aqueous Zn-ion battery of  $\text{VS}_2//\text{Zn}$ <sup>[14]</sup>,  $\text{ZnHCF}//\text{Zn}$ <sup>[8]</sup>; Solid red circles represent Na-ion battery of  $\text{NVP}//\text{Sb}@\text{TiO}_{2-x}$ <sup>[30]</sup>; Solid purple circles are  $\text{Ni}/\text{Fe}$ <sup>[31]</sup>,  $\text{Ni}/\text{Bi}$ <sup>[32]</sup> cells; Yellow empty circles are supercapacitor:  $\text{ECF}//\text{V}_2\text{O}_5$ <sup>[33]</sup>; Black empty circles denote to Na-ion hybrid capacitors:  $\text{AC}//\text{V}_2\text{O}_5$ <sup>[34]</sup>,  $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3//\text{Ti}_2\text{CT}$ <sup>[35]</sup>; Blue empty circles are Li-ion hybrid capacitors:  $\text{AC}//\text{TiO}_2$ <sup>[36]</sup>,  $\text{AC}//\text{Nb}_2\text{O}_5$ <sup>[37]</sup>; (G) The discharge curves of the QSS-ZIB under flat, severe bent status (photographs shown as inset), and after repeated bending for 100 times.

1  
2 To demonstrate its application in Zn ion battery, we assembled flexible quasi-solid-state  
3 full cells using the as-obtained ZOV array as the cathode and Zn array (or Zn foil for  
4 comparison) as the anode. Fumed silica/ZnSO<sub>4</sub> with an ionic conductivity ~8.1 mS cm<sup>-1</sup> at  
5 room temperature (Figure S3, Supporting Information) was used as the electrolyte. It should  
6 be mentioned that all the QSS-ZIBs herein have excessive mass loading of the anode part and  
7 the specific capacity was calculated based on the mass of the ZOV array. And the zinc mass in  
8 QSS-ZIBs with Zn foil is much higher than that assembled with Zn array. As can be seen clearly  
9 from the Cyclic voltammetry (CV) curves in Figure 2A, the QSS-ZIB with Zn array anode  
10 displays larger curve area (higher capacity) and smaller polarization. Electrochemical  
11 impedance spectroscopy (EIS) in Figure 2B shows lower charge-transfer resistance ( $R_{ct}$ ) of the  
12 Zn nanoflake array than the Zn foil ( $R_{ct}$  6.3  $\Omega$  for Zn array *versus* 13.5  $\Omega$  for Zn foil) after  
13 cycles. This also implies a higher surface electron mobility and improved electrochemical  
14 activity when the former is used as anode. Herein we utilize 3D conductive GF substrate  
15 supported Zn array as the anode because of two main advantages over conventional Zn foils:  
16 *First*, the 3D porous GF acts as both a light-weight backbone for the growth of Zn array, and a  
17 continuous current flow channels as well as macroporous agent to alleviate dendrite growth.  
18 Using Zn foil will have the issue of severe growth of a thick inactive surface oxide or hydroxide  
19 layer with low conductivity and reversibility,<sup>[6, 22, 23]</sup> leading to device deterioration especially  
20 in long-term cycles due to the electron blocking (see Figure S4–6, Supporting Information).  
21 *Second*, the short ion diffusion length, high surface area, and more reactive sites features of the  
22 zinc nanoarray structure is favorable for the fast and reversible Zn/Zn<sup>2+</sup> redox kinetics, leading  
23 to high-rate capability. Also, the array structure also diminishes the formation of dendrites and  
24 thus favorable to the enhanced long-term cycling stability.<sup>[19, 23, 24]</sup>

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50 From the galvanostatic charge–discharge curves in Figure 2C, one can see that the first Zn<sup>2+</sup>  
51 uptake process initially undergoes a sharp potential drop and then becomes steady. This implies  
52 a relatively large electrochemical polarization that might be due to deactivated surfaces of both  
53 electrodes. The subsequent curves almost overlap, suggesting a stable structure reversibility  
54 and surface state after the activation. A rather high initial coulombic efficiency ~95% is  
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1 achieved with maintained reversible capacity  $\sim 204 \text{ mAh g}^{-1}$  at 0.5C ( $200 \text{ mA g}^{-1}$  is equivalent  
2 to 1 C), corresponding to an  $\approx 2$  electron redox process. The continuous discharge profiles show  
3 two plateau-like regions located at 1.0–0.7 V and 0.6–0.4 V, which presumably correspond to  
4 the insertion/extraction of  $\text{Zn}^{2+}$  ions from ZOV crystal structure. The result is in  
5 correspondence with the rectangular shape and broaden peaks in the foregoing CV curve, which  
6 are typical features of capacitive charge storage behavior of battery materials (to be discussed  
7 below).

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14 The high-rate ability has been regarded as a pivotal indicator for largescale application of  
15 batteries, such as fast recharging of cellphones and electric vehicles, and regenerative braking.  
16 In this regard, the porous thin ZOV nanoarray structure with exposed 2D ion channels is vital  
17 to facilitate ion access and accelerate charge transfer at the electrode/electrolyte interface with  
18 short  $\text{Zn}^{2+}$  and electronic transport path. The high rate performance is evidenced in Figure 2D.  
19 The discharge capacities retain more than  $160 \text{ mAh g}^{-1}$  at 10C and  $101 \text{ mAh g}^{-1}$  at 50C. Finally,  
20 our QSS-ZIB exhibits excellent cycling sustainability even at high rates. The capacity keeps  
21 nearly flat in the first 800 cycles, and a specific capacity of  $125 \text{ mA h g}^{-1}$  can still be maintained  
22 at 20C after 2,000 cycles (ca. 89% of the initial value). In contrast, when aqueous electrolyte  
23 is used, the device shows obvious particle aggregation and the capacity retention is 72% after  
24 only 500 cycles (Figure S6–8, Supporting Information). To the best of our knowledge, this is  
25 the first demonstration of a rechargeable solid-state Zn ion battery with such a long high-rate  
26 lifespan.<sup>[6, 15, 25, 26]</sup> This stability is not accidental, but can be ascribed to the suppressed  
27 chemical dissolution of amphoteric V<sup>[20, 27]</sup> and well preserved structural stability of ZOV by  
28 solid-state electrolyte.

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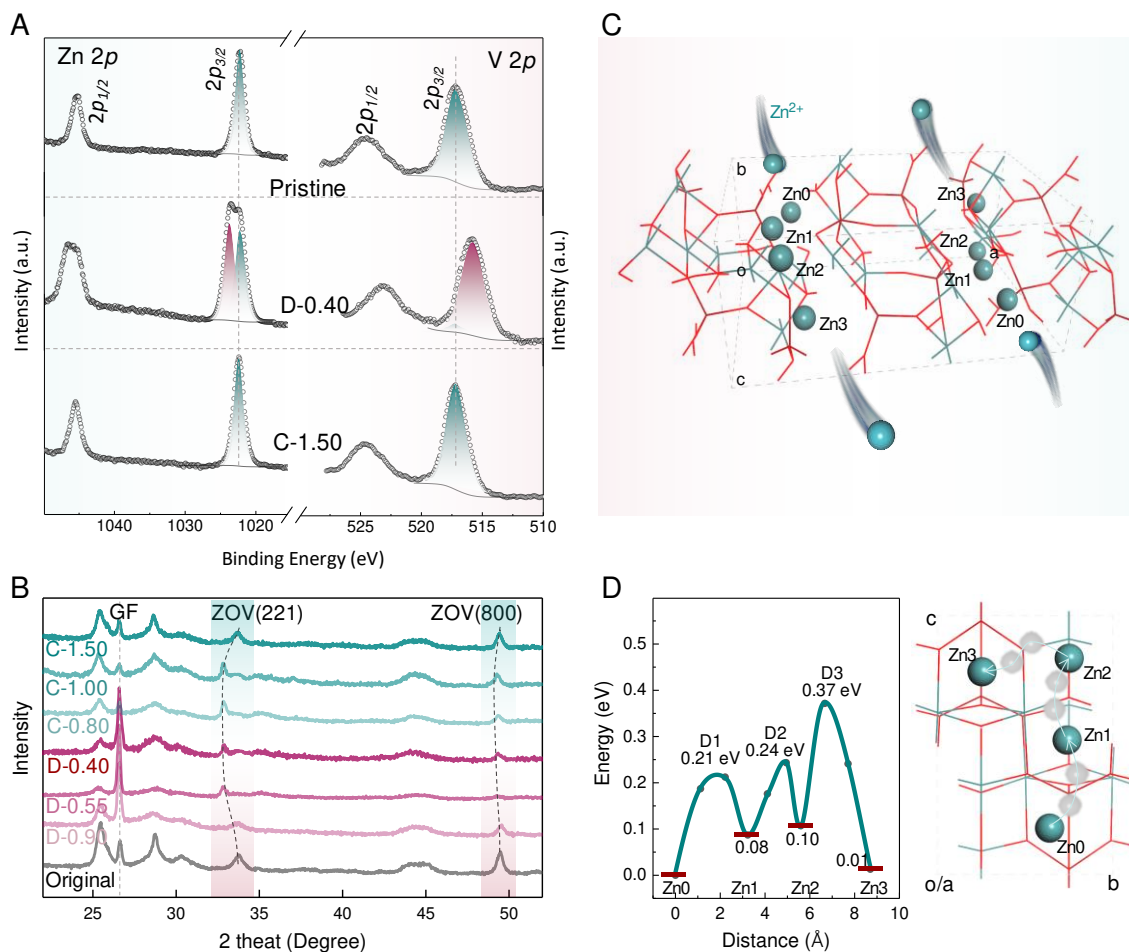
The Ragone plot in Figure 2F compares the array-based ZOV//Zn QSS-ZIB with other reported energy storage devices, such as aqueous supercapacitors, Ni//Fe, Ni//Bi, Li-ion batteries, K-ion batteries, Zn-ion batteries, and organic Li- or Na-ion hybrid capacitors. Our device exhibits a maximum energy density of ca.  $140 \text{ Wh kg}^{-1}$  (with power density  $70 \text{ W kg}^{-1}$ ) and a maximum power density of  $6200 \text{ W kg}^{-1}$  (with energy density  $65 \text{ Wh kg}^{-1}$ ) based on the total active material mass of cathode and anode. More strikingly, the maximum energy density based on the mass of the whole electrode (including current collector) maintains at ca.  $115 \text{ Wh kg}^{-1}$ .

1 kg<sup>-1</sup> thanks to the light-weight GF current collector and freestanding feature (0.6 mg cm<sup>-2</sup>  
2 *versus* ~10 mg cm<sup>-2</sup> for Ti/Zn/stainless steel foils, and ~15 mg cm<sup>-2</sup> for carbon **cloth**). This  
3 value corresponds to at least 200% increase in the energy density compared with traditional  
4 ZIBs with metal foils or carbon cloth supported cathodes and zinc foil incorporated anodes.  
5 Our QSS-ZIB shows a respective depth of discharge of ca. 100% for the ZOV array cathode  
6 and 66% for the zinc array anode, which is superior than the reported ZIBs (49% for quinone  
7 and much lower for other Zn foil based ZIBs)<sup>[1, 2, 5, 11]</sup>. On the basis of a comprehensive  
8 summary, this is so far the best energy/power densities (including cathode, anode, and current  
9 collectors) among reported ZIBs. As summarized in Figure 2F, these characteristics are at least  
10 comparable to and probably slightly better than the best Li<sup>+</sup>/Na<sup>+</sup> ion hybrid capacitors, and  
11 solid-state Li<sup>+</sup>/Na<sup>+</sup> ion batteries reported to date.  
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23 Additionally, our device can be bent without deteriorating their discharge profiles and  
24 capacities (Figure 2G), and there is no obvious capacity sacrifice (>96% retention) after  
25 repeated 100 times bending. To demonstrate the applications, we show that three QSS-ZIB  
26 cells in series connection, after charging for only 30 sec, can power a rotation motor (3 V, 0.4  
27 W) and fan (inset in Figure 2F). In a nutshell, our all-array QSS-ZIB based on ZOV cathode//Zn  
28 anode exhibits an excellent Zn<sup>2+</sup> storage property with superior high-rate cycling stability, as  
29 well as high energy/power density, and can meet the rapid power change from the grid.  
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### 40 **Zinc migration mechanism**

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**Figure 3 | Zn<sup>2+</sup> migration in 2D ZOV array cathode.** (A) *Ex-situ* high-resolution XPS spectra of the Zn 2p and V 2p in pristine, fully discharge (D-0.40), and charge (C-1.50) stage. (B) *Ex-situ* XRD patterns as a function of different voltage stages collected during the second galvanostatic discharge–charge profile at 0.5C. (C) Molecular structure evolution from Zn<sub>2</sub>(OH)VO<sub>4</sub> (stick mode) to Zn<sub>3</sub>(OH)VO<sub>4</sub> upon Zn<sup>2+</sup> insertion (green balls) with four different zinc occupation sites denoted with Zn0, Zn1, Zn2, and Zn3. The schematic illustration of zinc shuttles showing the Zn<sup>2+</sup> extraction/insertion 2D paths along exposed b–c planes. (D) First-principle calculation of the in-plane b–c diffusion energy barriers and the corresponding pathways for Zn-ion migration. The arrows indicate optimum diffusion paths.

We use *ex-situ* XPS and XRD to provide more insight about the structural evolution of the 2D ZOV array electrode during charge/discharge cycles. In the Zn 2p region, only one peak of Zn 2p<sub>2/3</sub> component (1022.2 eV) from the original Zn sites in ZOV is observed for the pristine and fully charged (C-1.50) stages. Both this Zn 2p<sub>2/3</sub> peak and the V 2p<sub>2/3</sub> (V<sup>5+</sup> signal at 517.2 eV) recover to their original position after a full charge/discharge cycle, indicating excellent composition reversibility of the ZOV array. After full discharge (D-0.40), one new peak of Zn

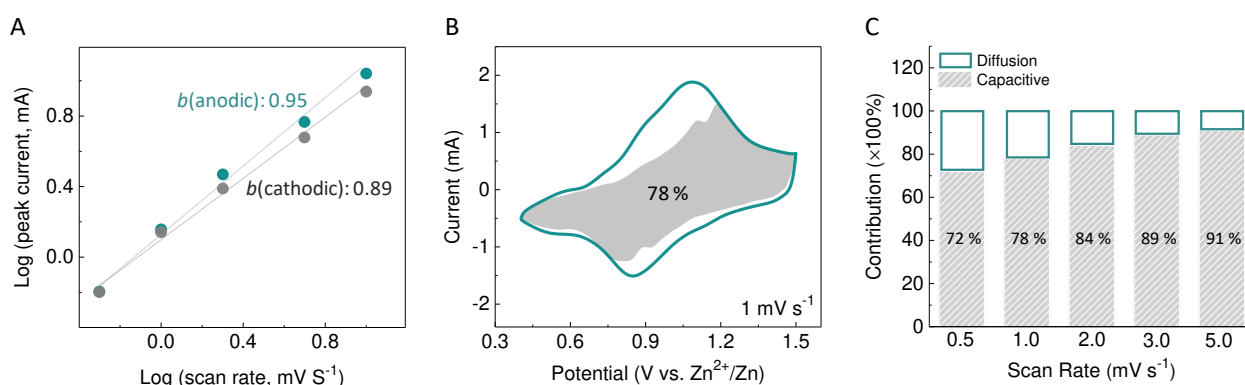
1  $2p_{2/3}$  component arises at the higher binding energy of 1023.6 eV, which is due to the ingoing  
2 Zn ions<sup>[5, 26]</sup>. Correspondingly, a red-shift of the V  $2p_{2/3}$  peak to V<sup>3+</sup> component is also  
3 evidently seen<sup>[5, 38]</sup>, which is in accordance with the 2-electron redox reaction shown in the  
4 previous galvanostatic discharge–charge result. Further insight is disclosed by XRD and  
5 Raman investigation (see details in Figure S9, Supporting Information). It can be seen from  
6 Figure 3B that the characteristics (221) and (800) peaks shift to smaller 2 theta angles during  
7 Zn<sup>2+</sup> intercalation and return to their original positions in the subsequent deintercalation. No  
8 new peaks appear. Hence the XPS and XRD data suggest that the intercalation and  
9 deintercalation cycle involves a solid solution reaction without any structure transition.

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19 On the basis of the above results, the electrochemical reaction during the Zn<sup>+</sup> ion storage  
20 process of the ZOV array can be described using the equation:  $Zn_2(OH)VO_4 + Zn^{2+} + 2e^- \leftrightarrow$   
21  $Zn_3(OH)VO_4$ . Its local structure evolution after Zn-ion intercalation was estimated based on  
22 density functional theory calculation with GGA–PBE (see details in Method part). Four  
23 different zinc occupation sites denoted with Zn0, Zn1, Zn2, and Zn3 can be found in the  $b$ – $c$   
24 planes in Figure 3C. The fast kinetics of the ZOV array are consistent with the low Zn<sup>2+</sup>  
25 migration energy barriers. Figure 3D shows the calculated in-plane ( $b$ – $c$ ) Zn-ions migration  
26 pathways D1, D2, and D3, where D1 (from the Zn0 site to a neighboring Zn1 site) exhibits the  
27 smallest energy barrier of 0.21 eV. As a comparison, other traditional cathode framework  
28 structures such as LiFePO<sub>4</sub> (0.55 eV for Li<sup>+</sup>), NaFePO<sub>4</sub> (0.32–3.03 eV for Na<sup>+</sup>), Na<sub>2</sub>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  
29 (0.55–1.0 eV for Na<sup>+</sup>) with 1D migration channels, Na<sub>2</sub>FePO<sub>4</sub>F (0.31–0.59 eV for Na<sup>+</sup>), V<sub>2</sub>O<sub>5</sub>  
30 (0.39–1.66 eV for K<sup>+</sup>), TiS<sub>2</sub> (1.16 eV for Mg<sup>2+</sup>), VO<sub>2</sub> (0.5 eV for Al<sup>3+</sup>) with 2D migration  
31 channels, show much higher energy barriers<sup>[39]</sup>. These calculations suggest that the largely  
32 exposed  $b$ – $c$  plane with small thickness, which is parallel to the 2D diffusion paths, is favorable  
33 for fast Zn<sup>2+</sup> migration and high rate energy storage.

### 51 52 **Intercalation pseudocapacitance**

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54 After we have confirmed the solid solution reaction mechanism without phase  
55 transformation on (de)intercalation, facile 2D ion diffusion pathways, and the superior fast  
56 charge/discharge, it is reasonable to deduce that an intercalation pseudocapacitive behavior  
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exist in our QSS-ZIB.<sup>[40]</sup> Here, electrochemical kinetic analysis was carried out to gain further insight into the pseudocapacitive charge storage and diffusion-controlled processes of the all-array based ZOV//Zn QSS-ZIB<sup>[17, 41]</sup>. The degree of capacitive effect can be qualitatively analyzed by the power law relationship between scan rate  $v$  and current  $i$  ( $i = av^b$ , where  $a$  and  $b$  are constants,<sup>[17, 41]</sup>  $b = 0.5$  for a diffusion-controlled process and 1.0 for a capacitor-like process<sup>[42]</sup>). The  $b$  values at anodic and cathodic peaks are 0.95 and 0.89, respectively, indicating a capacity contribution from surface-induced pseudocapacitive behavior (Figure 4A). The CV curves at various scan rates with similar shapes are shown in Figure S10, Supporting Information. The ratio of Zn-ion pseudocapacitive contribution from the total capacity can be quantified by separating the diffusion-controlled and pseudocapacitive current response<sup>[42]</sup> (Figure 4B). Around 78% of the total capacity is found capacitive, even at a relatively slow rate of  $1.0 \text{ mV s}^{-1}$ , which increases with accelerating the scan rate reaching 91% at  $5.0 \text{ mV s}^{-1}$  (Figure 4C). The specific capacity is found much larger than the typical EDLC<sup>[43]</sup>, suggesting that the capacitive current is dominated by an intercalation pseudocapacitive behavior except for the convex peak region. It is likely that the high fraction of capacitive current observed in this QSS-ZIB system stem from the mesoporous and thin-sheet array features of the both electrodes<sup>[44]</sup>. Hence, it is not surprising that our all-array based ZOV//Zn QSS-ZIB leads to a high-rate and stable Zn-ion storage.



**Figure 4 | Intercalation pseudocapacitive behavior analysis.** (A) Dependence of the peak anodic ( $\sim 1.17 \text{ V}$ ) and cathodic ( $\sim 0.80 \text{ V}$ ) peak currents on the scan rate from  $0.5$  to  $10 \text{ mV s}^{-1}$ . (B) Capacitive contribution (gray part) and diffusion contribution (void part) at  $1.0 \text{ mV s}^{-1}$ . (C) Normalized contribution ratios of capacitive (gray part) capacity at different scan rate.



1 In summary, we report the synthesis of a new 2D layered zinc orthovanadate (ZOV) and  
2 demonstrated its outstanding property as the cathode material in rechargeable zinc-ion battery  
3 (ZIB). The superior  $\text{Zn}^+$  storage performance is a result of the ultrathin mesoporous array  
4 feature with high surface areas and single-crystalline layered structural property with short 2D  
5 fast ion migration pathways in exposed  $b$ - $c$  planes. A solid-solution reaction mechanism with  
6 small  $\text{Zn}^{2+}$  migration barrier and its derived intercalation pseudocapacitive behavior are also  
7 responsible for the fast electrochemical kinetics and rate capability. Full quasi-solid-state ZIBs  
8 assembled from such a ZOV array cathode and metallic Zn nanoflake array show high rate  
9 performance and long-cycle stability. No obvious aggregation, pulverization or dendrite growth  
10 has been observed on the Zn nanoflake array. Our encouraging results may boost further  
11 development of ZIBs by smart engineering of the array-type nanostructured electrode materials.  
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### 25 Supporting Information

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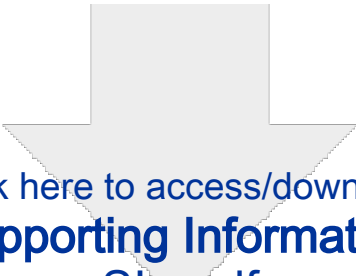
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