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# Supplementary Information

for

# Advancing High Capacity 3D $VO_2(B)$ Cathodes for Improved Zinc-ion Battery Performance

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## Experimental Section

*Chemicals:* The raw materials used to synthesis $VO_2$ (B) via the hydrothermal approach were Vanadium (V) oxide ($V_2O_5$ – Sigma-Aldrich) and oxalic acid dihydrate ($H_2C_2O_4.2H_2O$ – Scientific Laboratory Supplies). For the multiwave synthesis method, ammonium metavanadate ($NH_4VO_3$ – Thermo Scientific) and formic acid ($CH_2O_2$ - VWR Chemicals).

The raw materials utilised for slurry formation were the Super-P conductive carbon black (MTI Corporation), polyvinylidene fluoride (PVDF – Alfar Aesar) and N-Methylpyrrolidone (NMP - Sigma-Aldrich). Please note that no chemicals required additional treatment or purification before utilisation.

*Material Synthesis*: The initial synthesis of $VO_2$(B) material was phase one; the two main methods were hydrothermal synthesis[1] using Teflon-lined autoclaves and microwave digestion[2] using Teflon liners in a multiwave reactor.

The hydrothermal synthesis used $V_2O_5$ as the vanadium material, which was stirred magnetically with oxalic acid dihydrate and deionised water (1.2g:1.8g:40ml, respectively) at 75°C for 1 hour. The solution was then transferred to a 50ml Teflon-lined autoclave, which was heated in a hydrothermal oven at 180°C [1] for 72 hours.

Ammonium metavanadate was the vanadium material used in the microwave reactor for multiwave synthesis, which was stirred with formic acid and deionised water (0.7g:4.8ml:60ml, respectively) magnetically for 1 hour. The mixture was transferred into Teflon liners and reacted at 180°C for 520 minutes (8 hours 40 minutes).[2] The multiwave reactor (Anton Paar, Multiwave 500) available in the lab was restricted to 3 hours and 15 minutes, thus the process was conducted in 3 batches of near equal timing.

Both resulting solutions were washed three times with deionised water and ethanol each, and then dried in a vacuum oven at 70°C over night.

*Cathode Fabrication:* The conventional cathodes were assembled using carbon paper as the current collector and casting a slurry on it with a doctor blade. The slurry consisted of $VO_2$ active material, Super P and polyvinylidene fluoride (PVDF) at a ratio of 7:2:1. The PVDF was dissolved in (N-Methylpyrrolidone) NMP to ensure a more uniform dispersion of PVDF binder in the slurry and extra NMP was added to get the desired consistency. The slurry was mixed in a Thinky[5] mixer 3 times for 2 minutes with $VO_2$ and Super P, once for each addition of NMP and 3 times more with the PVDF in NMP solution. The resulting slurry was casted on the carbon paper and dried for 30-60 minutes on a hot plate at 50°C, then vacuum oven dried at 70°C or freeze dried overnight.

The 3D cathodes were assembled in an identical method, bar one difference; the current collector was carbon paper combined with vitreous carbon foam (Sigma-Aldrich 3000c, 2.5 mm thick, 0.05 g/cm$^3$). The two were held together, and dunked into the slurry, and dried accordingly.

*Coin Cell Assembly:* The coin cells were assembled using CR2032 cell cases for testing of the cathode in a zinc ion battery. The synthesised cathodes were punched into 14mm diameter circles and placed in the centre of the case, on to which the separator (19mm diameter) was placed. 150µl of electrolyte was added drop wise using a pipette; the electrolyte used was 3M $Zn(CF_3SO_3)_2$ (in $H_2O$). Lastly, the Zn anode (zinc foil punched into a 14mm diameter circle) was placed in the centre, followed by the spacer and the spring. A manual hydraulic crimping machine was used to close the cell, which was pumped up to approx. 750 psi. All cells were left to rest for 10 hours before electrochemical testing. The 3D cathode cell was assembled in the same method, but in a LIR2450 cell case, with two acrylic rings around the cathode for mechanical stability.

The conventional cathode cell uses a round spring with a single 1 mm thick spacer, while the cell with the 3D electrode contains two spacers (0.5 mm and 1 mm) and uses a wavy spring instead. This adjustment accommodates the larger cell case required for the 3D cathode, which has increased thickness compared to the conventional cathode and needs more space than the CR2032 case can provide. The CR2032 case would compress the 3D cathode, compromising its structural integrity. The additional 0.5 mm spacer is used in the 3D cathode cell within a CR2450 case to ensure the electrodes remain in place. The wavy spring was chosen for the 3D cathode cell because its evenly distributed pressure points prevent crushing of the 3D cathode, and the larger open space at the center reduces the risk of compression at the core. The 3D cathode cell was assembled in a CR2450 case, with two acrylic rings around the cathode for added mechanical stability.

*Mass Loading and Drying Processes:* The next phase focused on the mass loading of the active material in the cathode, comparing high mass loading and low mass loading cathodes electrochemical capacity, as well as structural and physical properties. This was competed by using a measured doctor blade, with thickness of 50, 100, 150 and 200 µm, which allowed for uniform slurry casting, resulting in a more accurate comparison of mass loading. The mass loadings referred to in this report are low and high, which are approx. 2.4 mg cm$^{-2}$ and 5.6 mg cm$^{-2}$, respectively, and are the mass loadings of the active material (70% of total mass loading). This is based off the cathode diameter being 14 mm (1.4 cm), which was used to calculate the area. The active mass of $VO_2$(B) in the cathode was divide by the area to give the active mass loading of $VO_2$(B) material in mg per cm$^2$.

*Material Characterisation:* The morphology of the VO2 (B) material synthesized was analysed by SEM (Zeiss EVO LS15) and TEM. XRD (PANalytical AERIS benchtop XRD system) was conducted to analyse the crystal structure of the material, and a Raman spectrum (Renishaw inVia Raman Microscope) was obtained to analyse the chemical structure, phase and polymorphism.

*Electrochemical Tests:* Initially, CV curves were tested over a working voltage range of 0.2 to 1.6 V at different scan rates, ranging from 0.1 to 1 mV s$^{-1}$, using a Biologic MPG-2 battery testing system. The voltage range was decreased to 1.4V for the 3D cathode cells due to a smaller potential window indicated in the CVs obtained. Furthermore, galvanostatic charge-discharge measurements were taken at different specific currents, ranging from 100 to 10,000 mA g$^{-1}$, decreasing to 50 to 2000 mA g$^{-1}$ for the 3D cathode, due to the high mass resulting in high specific currents. Long-term cycling of the cells was measured, at specific currents of 1000 and 2000 mA g$^{-1}$, using a Neware battery tester. Electrochemical impedance evaluation was conducted in the frequency range of 10 mHz to 100 kHz at a voltage amplitude of 10 mV.

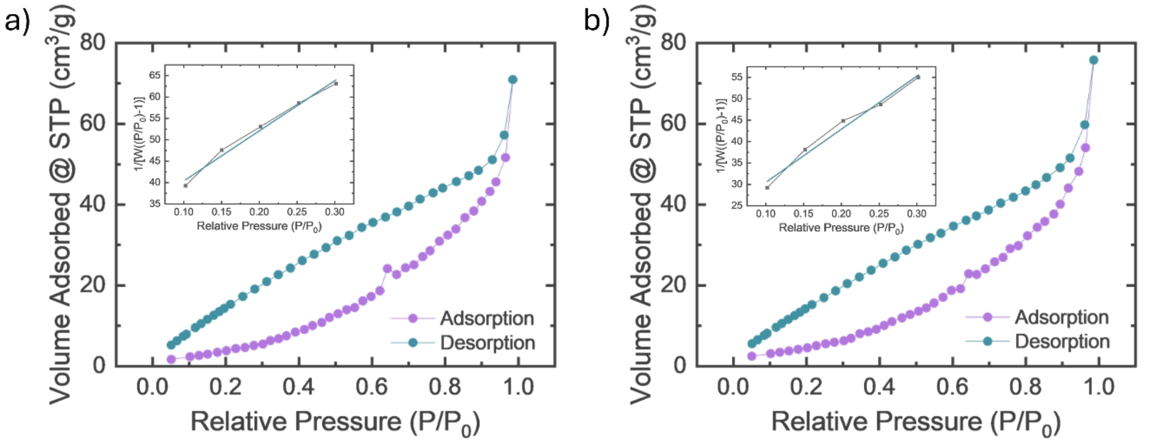

***Figure S1***. *BET and isotherm plot a) multiwave reacted and b) hydrothermally synthesised* $VO_2(B)$.

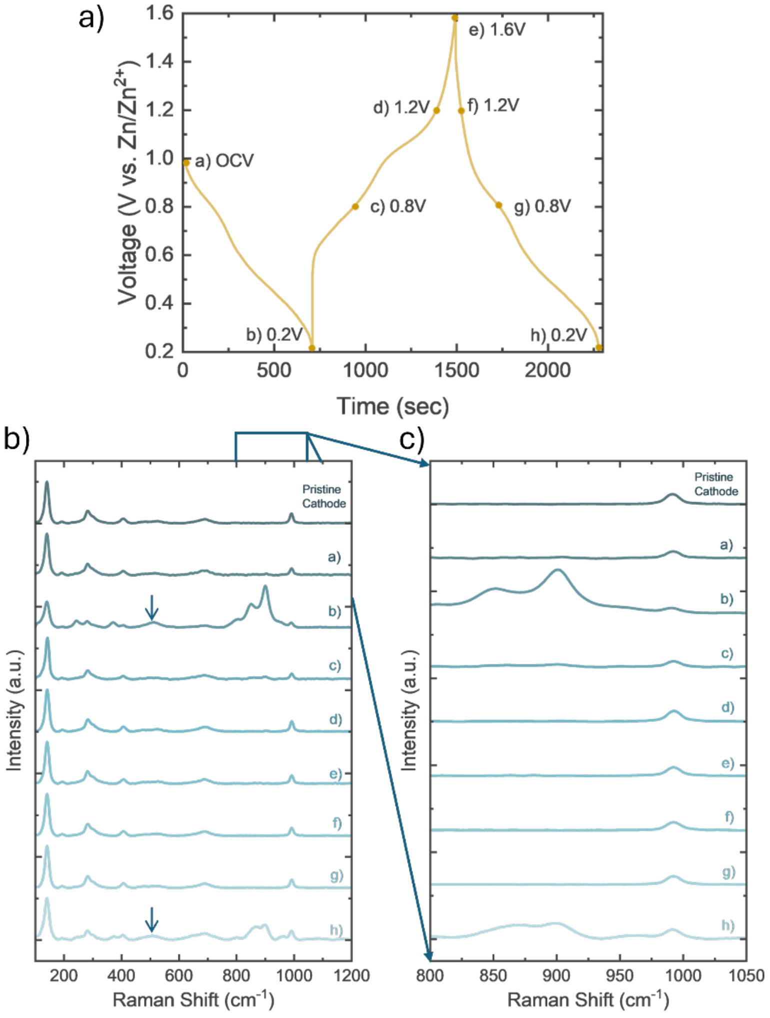

***Figure S2.*** *a) Plot of discharge and charge steps of AZIBs. b) Raman spectra of cathode of cell after (dis)charge processes, with c) zoomed in section of shift 800 – 1050* $cm^{-1}$.

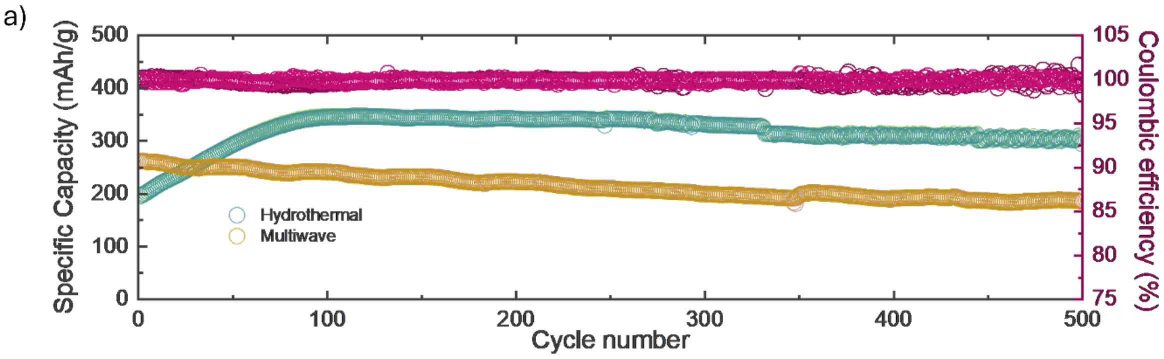

***Figure S3.*** *Long-term cycling comparison of hydrothermally synthesised and microwave reacted* $VO_2$*(B) at 1000 mA* $g^{-1}$.

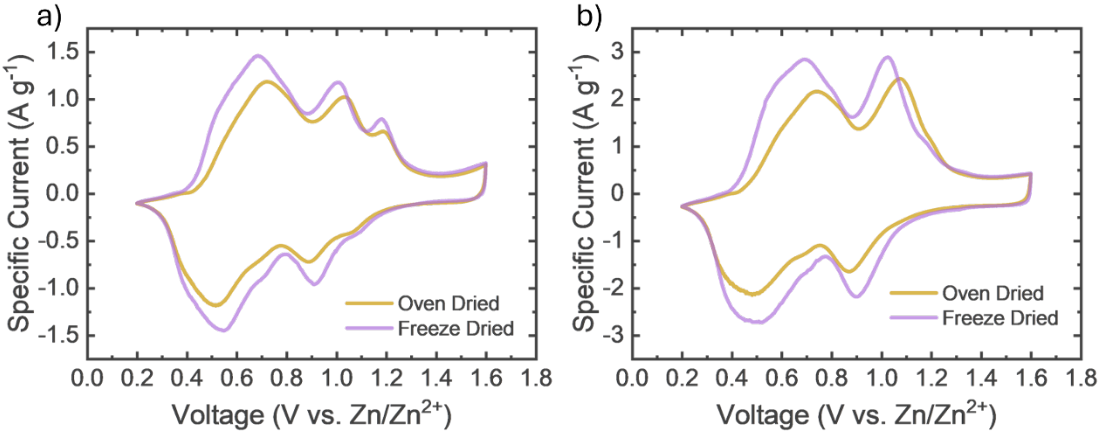

***Figure S4.*** *Comparative CV curves of low mass cathodes, comparing drying methods at a scan rate of a) 0.5 mV* $s^{-1}$ *and b) 1.0 mV* $s^{-1}$.

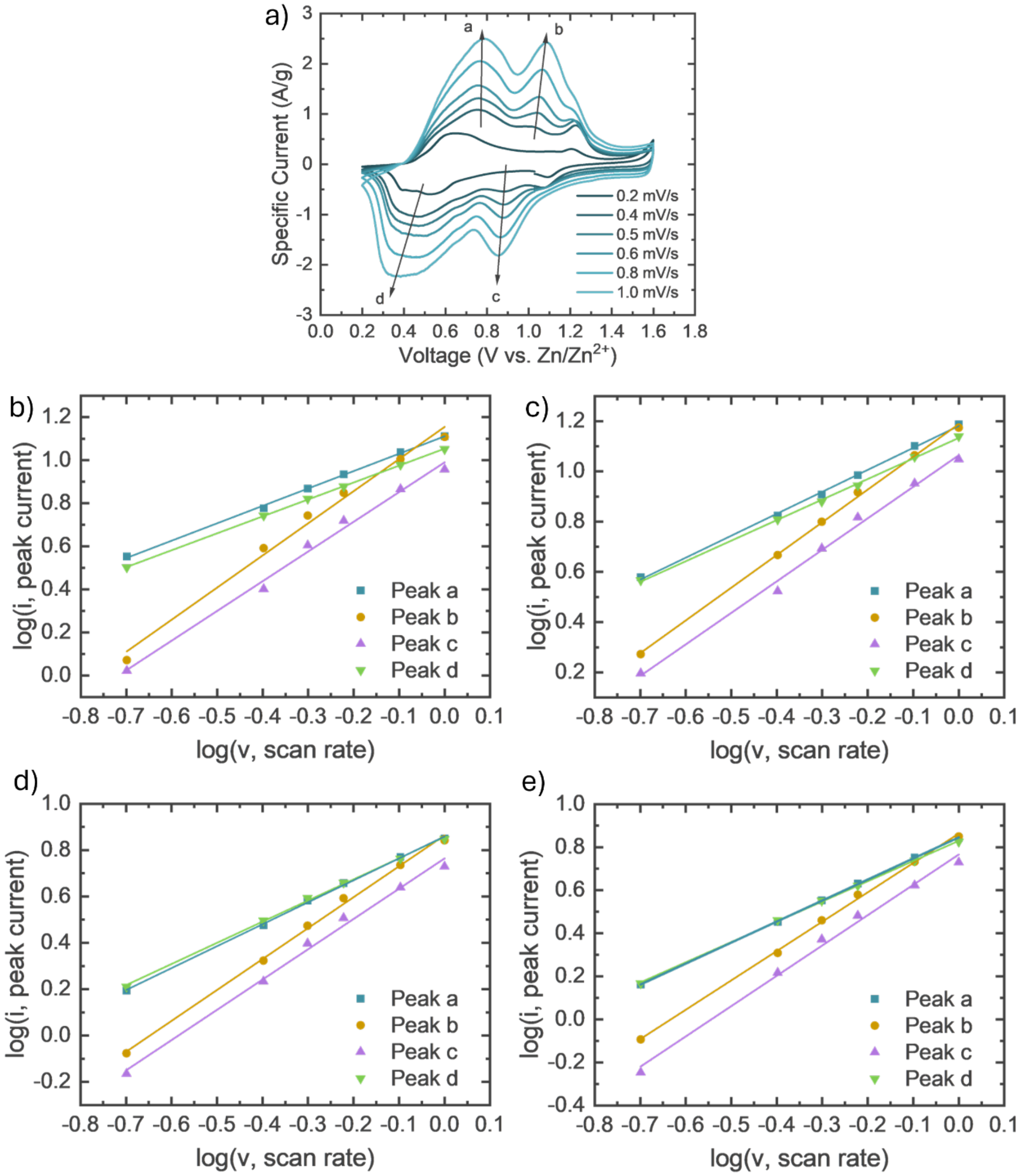

***Figure S5.*** *a) CV curve of high mas loading, freeze dried cathode with corresponding peaks for the calculated b values. b values of CV peaks of cells with b,c) high mass loading cathodes, oven and freeze dried, respectively, and d,e) low mass loading of oven and freeze dried cathodes, respectively.*

| Peak | Oven | | Freeze | |
|---|---|---|---|---|
| | Low | High | Low | High |
| a | 0.94 | 0.81 | 0.98 | 0.92 |
| b | 1.29 | 1.29 | 1.35 | 1.30 |
| c | 1.22 | 1.17 | 1.27 | 1.26 |
| d | 0.91 | 0.77 | 0.94 | 0.84 |

***Table S1*** *– Calculated b values of the two anodic and two cathodic peaks on the CV curves.*

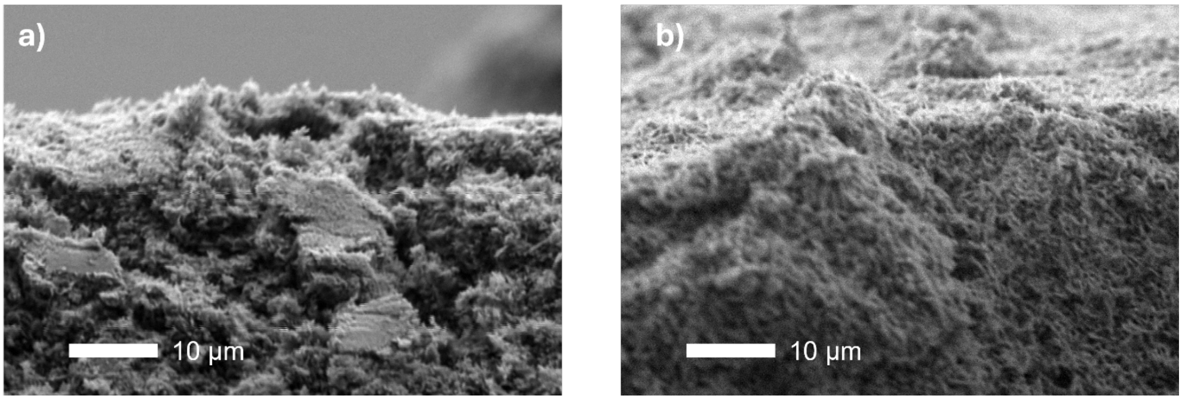

***Figure S6*** *– High magnification cross sectional SEM images of* $VO_2$ *(B) cathodes dried via a) vacuum oven and b) freeze dryer.*

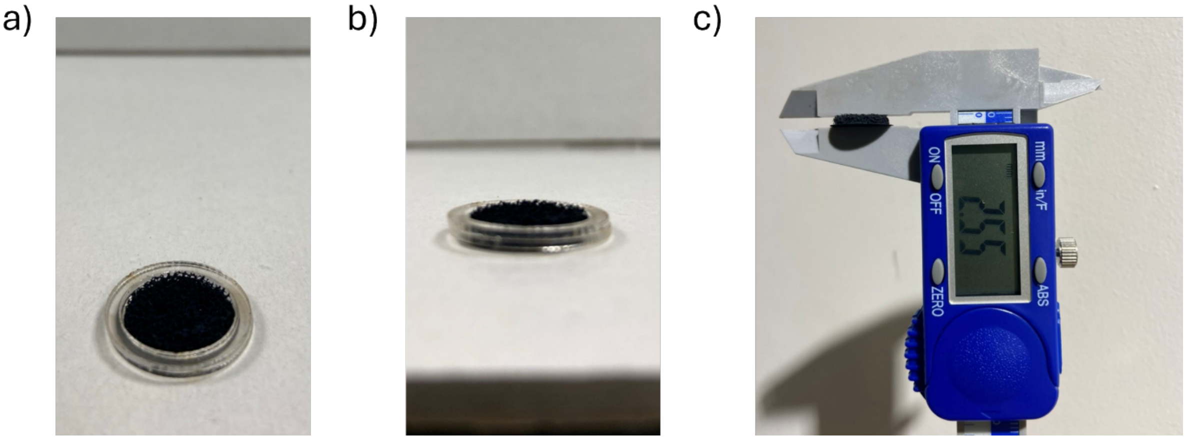

***Figure S7.*** *A picture of the 3D electrodes with an acrylic ring structure around it for structural integrity from an a) above and b) side angle, and c) thickness of the 3D electrode.*

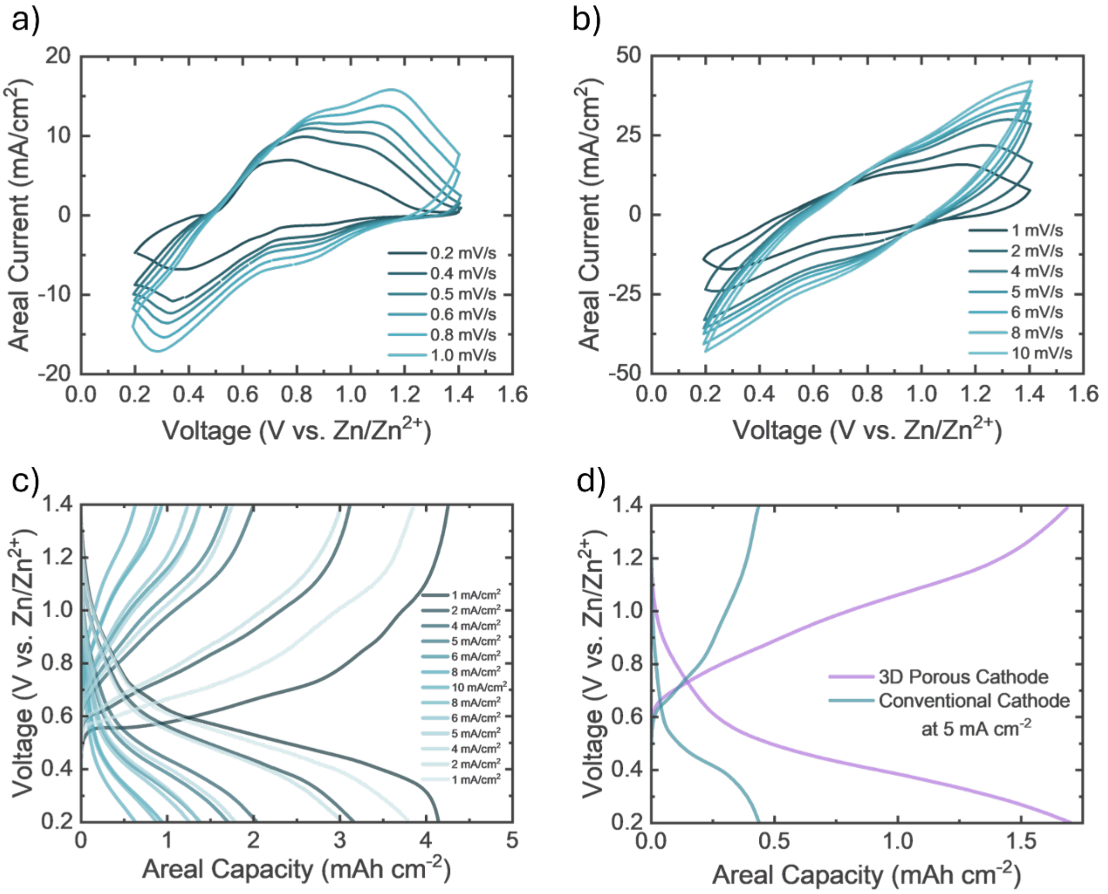

***Figure S8.*** *a) CV curves of AZIB with 3D cathode with scan rate ranges of a) 0.2 – 1.0 mV* $s^{-1}$ *and b) 1 – 10 mV/*$s^{-1}$*. c) Full GCD curves of 3D cathode cell, and e) comparative GCD curves at an applied current of 5 mA/*$cm^2$*.*

## References

1. Ding, J. *et al.* Ultrafast Zn2+ Intercalation and Deintercalation in Vanadium Dioxide. *Advanced Materials* **30**, 1800762 (2018).
2. Deka Boruah, B. *et al.* Vanadium Dioxide Cathodes for High-Rate Photo-Rechargeable Zinc-Ion Batteries. *Adv Energy Mater* **11**, 2100115 (2021).