

Electronic Supplementary Information (ESI)

Electrochemical Exploration of Calcination Temperature Effects of Mesoporous Zinc Vanadate Anode Material for Na-Ion Battery

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Experimental

Materials and Methods

ZnV₂O₄ was prepared by solvothermal technique with different calcination treatments. Initially, 2.5 mmole of Zn(NO₃)₂·6H₂O and 5 mmole of NH₄VO₃, were dissolved in 40mL methanol under vigorous stirring and subsequently 7.5 mmole of C₂H₂O₄ was added into the mixture solution of Zn and V. Afterwards, the equal volume percentage of HNO₃ and H₂O₂ were slowly poured into the solution to promote exothermic reaction. Then, the homogeneous mixed solution was transferred into 100 ml of Teflon-lined stainless autoclave and reacted at 200°C for 24 h using oven. The reacted sample was collected after cooling to room temperature and washed with ethanol and acetone for several times. Finally, the sample was dried in vacuum oven and calcined at 500, 600 and 700 °C for 4 h under H₂/N₂ flow in the heating rate of 2°C/min. The obtained ZnV₂O₄ samples were labelled as calcined at 500, 600 and 700 °C for ZVO-500, ZVO-600 and ZVO-700, respectively.

Physico-chemical characterizations

The products were characterized by powder X-ray diffraction (XRD, Bruker D8 Advance Eco) with Cu K α radiation ($\lambda= 1.5418\text{\AA}$). The morphology and structure of the products were analysed by scanning electron microscopy (SEM, Hitachi S-4100) and transmission electron microscopy (TEM, HF3300), then

element mapping by energy-dispersive X-ray spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS, JEOL Photoelectron Spectrometer (ESCA), JPS-9200, monochromatic Al-K α). The valences of metal elements (V, Zn) in sample powders were identified by X-ray absorption near-edge structure (XANES) and its derivative spectra that were collected at the beam line TPS 44A of National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The XANES spectra were collected in a transmission model by a Lytle detector in the energy ranges of V, Zn *K*-edges at room temperature. In addition, the collected XANES spectra were calibrated with a corresponding metal foil standard, and then normalized using Athena (version of 0.9.26) software. N₂ adsorption-desorption analyses were measured on ASAP 2020, Micrometrics and Barrett-Joyner Halenda (BJH) method was used to calculate pore size distribution.

Electrochemical measurements

For the electrochemical tests, CR2032 coin cell batteries were assembled. Anode electrode were prepared by making a slurry of 70 wt. % ZnV₂O₄, 15 wt. % Super-P (Carbon black, 40 nm), and 9 wt. % of Carboxymethyl cellulose and 6 wt. % of styrene butadiene rubber (CMC and SBR) in H₂O. After mixing the slurry thoroughly, it was coated onto a Cu foil with a thickness of 10 μ m and

dried. Then, the electrode was punched with a diameter of 14 mm and dried at 120 °C for 8 h in vacuum oven to remove the residual water. Na-ion storage Coin cells were assembled in an Ar-gas filled glove box with H₂O and O₂ contents at < 0.5 ppm. Half-cell configuration was assembled using Na metal as a counter electrode, 1M of NaClO₄ in Ethylene carbonate (EC) and Diethyl carbonate (DEC) (3:7 in volume ratio) with 5 wt. % of Fluoroethylene carbonate (FEC) as electrolyte system, and glass fiber filter disks as the separators. Na-ion storage performance of the capacity, cycle life and C-rates were analyzed using constant voltage and current AcuTech battery test System in the voltage range of 0.01 to 3.0 V at 25 °C. The prepared electrode (anode) mass was loaded in the range of 2.30 ± 0.30 mg/cm². Cyclic voltammograms (CV) were measured using CH Instruments Analyzer CHI 6273E at a scan rate of 0.1 mV·s⁻¹ in the potential window of 0.01 V to 3.0 V. Electrochemical Impedance spectroscopy was used to investigate the kinetics behaviour of the samples and tested in the frequency range of 0.01-100KHz.

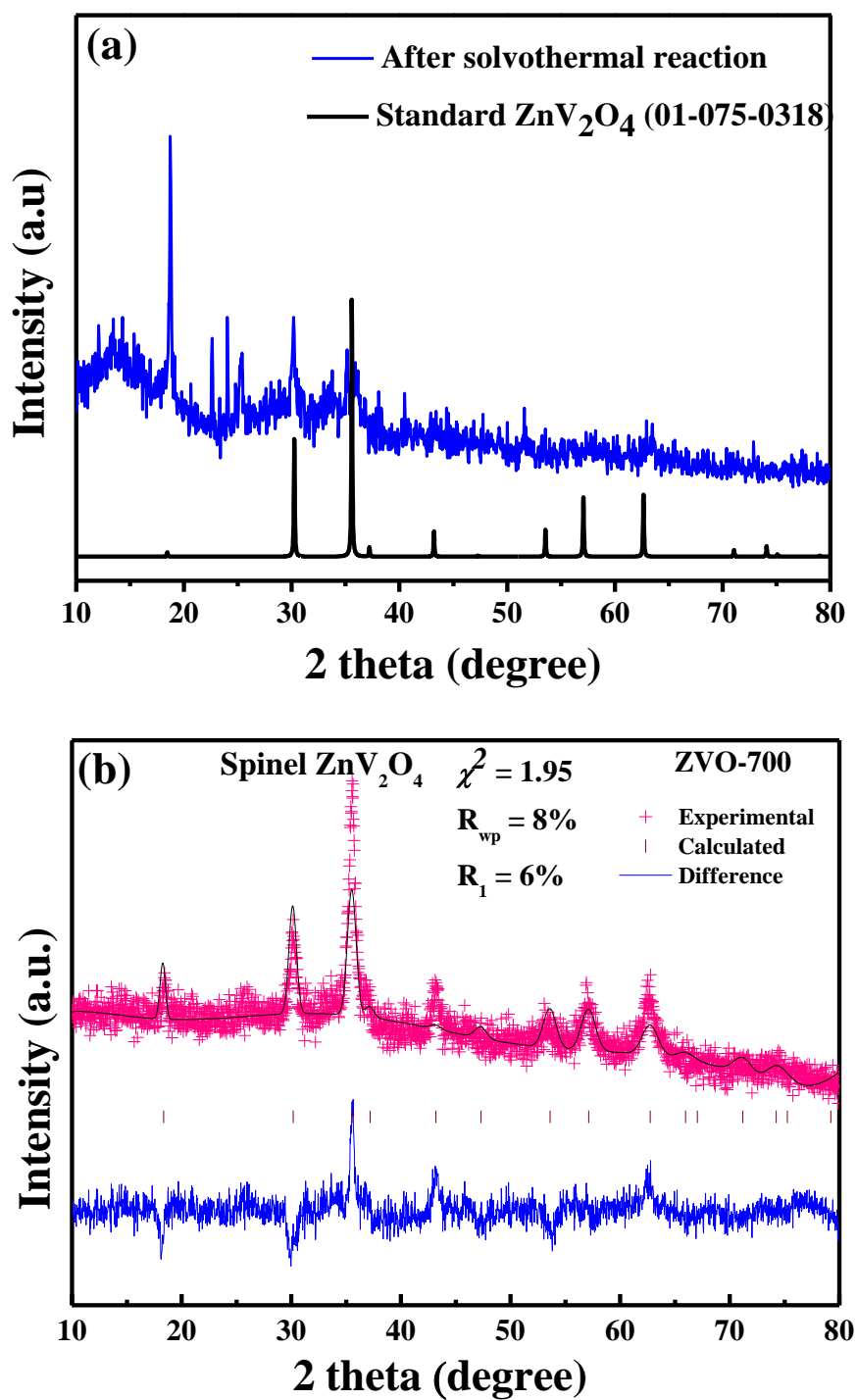


Fig. S1 (a) XRD pattern of after solvothermal reaction and (b) Rietveld refinement of ZVO-700 sample.

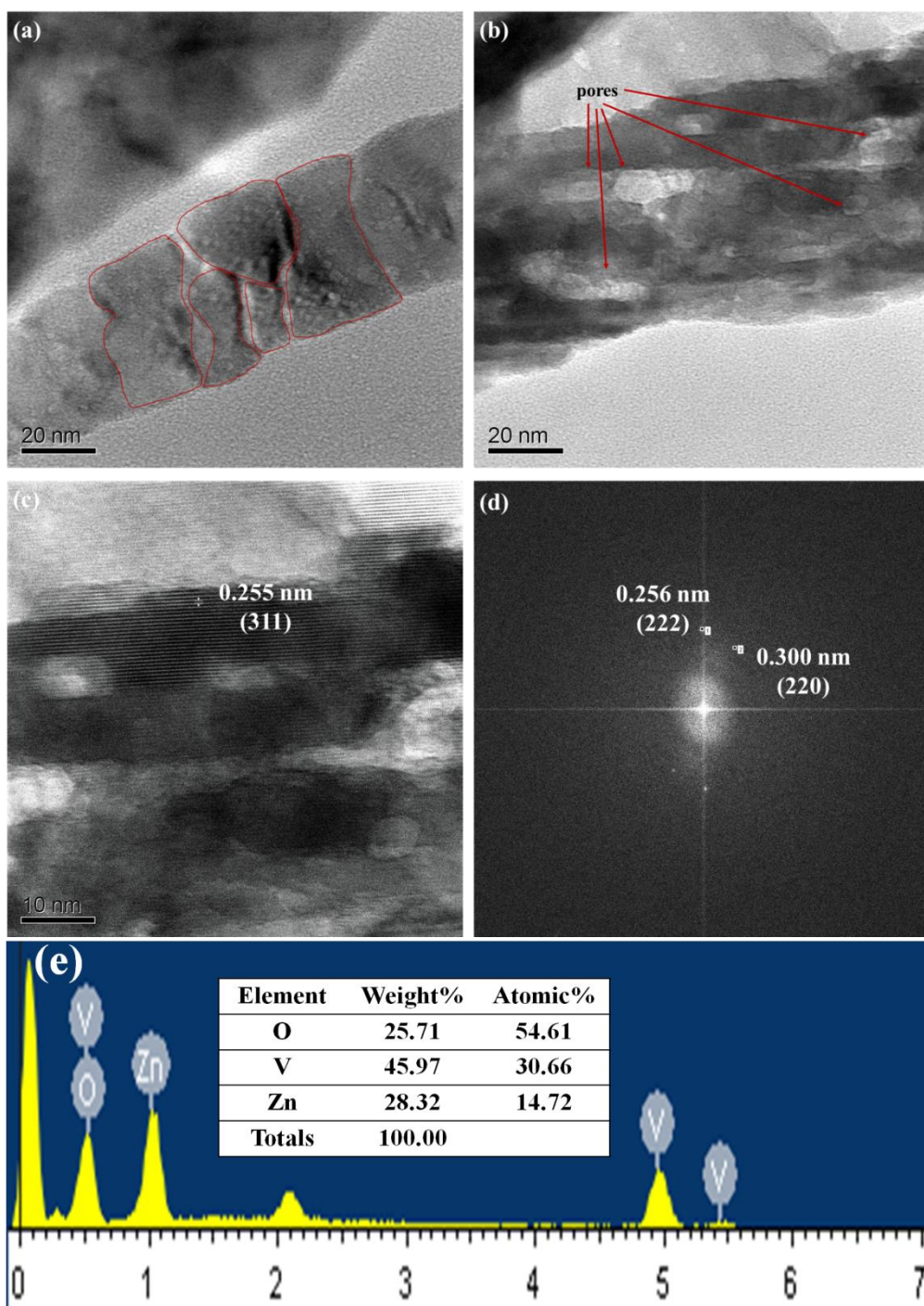


Fig. S2 (a and b) HR-TEM images, (c) HR-TEM lattice fringes view image, (d) the electron diffraction image and (e) EDX spectrum (inset the corresponding atomic %) of ZVO-700 sample.

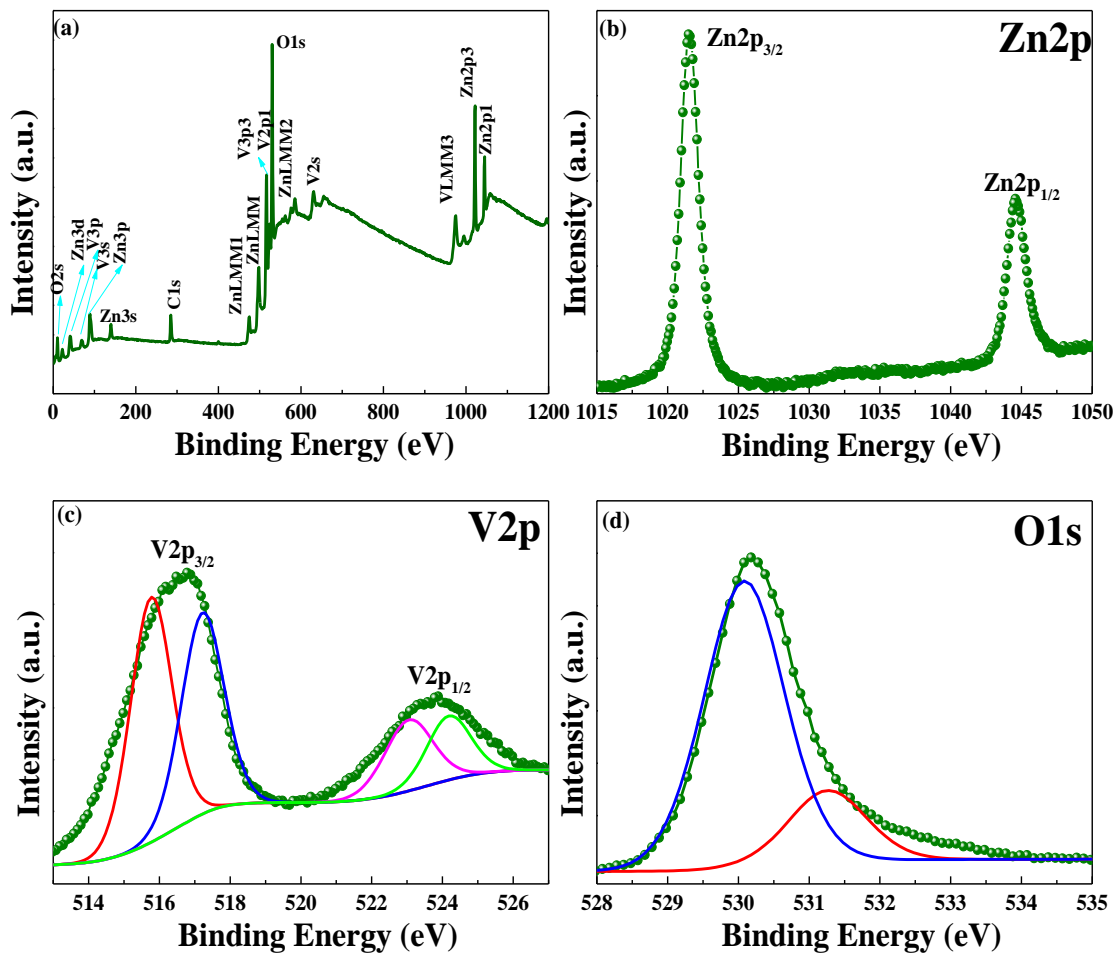


Fig. S3 (a) XPS wide range spectra of ZVO-700 (b) Zn2p, (c) V2p, and (d) O1s, respectively.

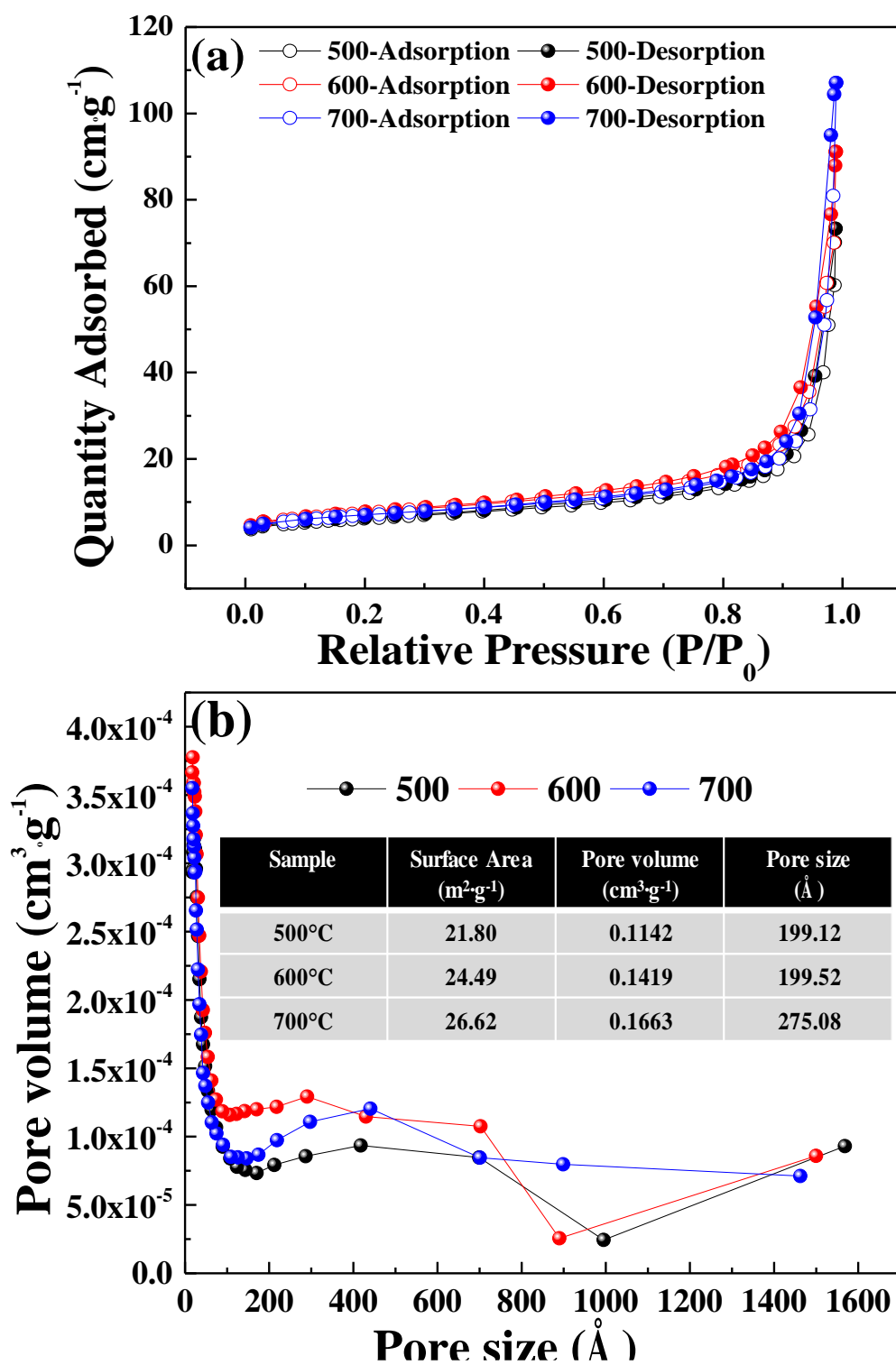


Fig. S4 (a) N_2 adsorption-desorption isotherms curves of ZVO-500, ZVO-600 and ZVO-700 samples and (b) Pore volume measurements of ZVO-500, ZVO-600 and ZVO-700 (Inset of table estimated parameters from N_2 adsorption-desorption isotherms measurement).

Table. S1 Comparison of the discharge/charge capacities and coulombic efficiencies of ZVO-500, ZVO-600 and ZVO-700 electrode cells during the formation cycle tests.

Cycle Number (ZVO-500)	Discharge Capacity (mAh·g ⁻¹)	Charge Capacity (mAh·g ⁻¹)	Coulombic Efficiency (%)
1 st	178.37	88.16	49.42
2 nd	100.61	83.26	82.75
3 rd	93.06	81.84	87.94
Cycle Number (ZVO-600)			
1 st	251.75	141.90	56.37
2 nd	158.10	136.19	86.14
3 rd	147.62	133.01	90.11
Cycle Number (ZVO-700)			
1 st	296.89	153.41	51.67
2 nd	176.40	144.72	82.04
3 rd	164.60	142.86	86.79

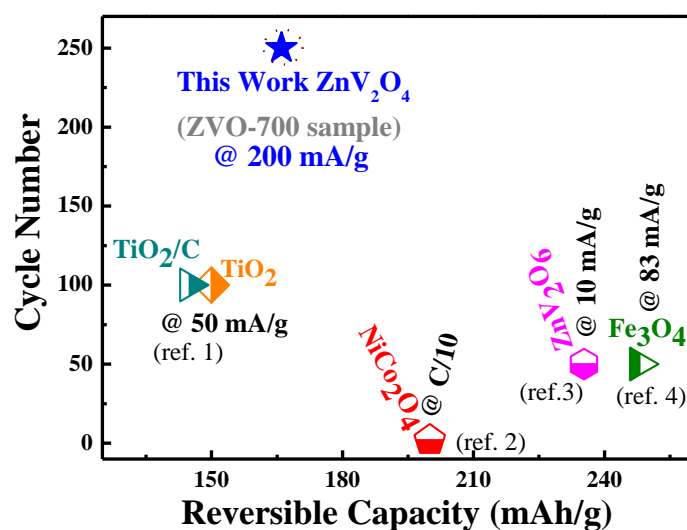


Fig. S5 Comparison of reversible cyclic capacity with the corresponding current density of reported metal oxide based anode materials for SIBs.

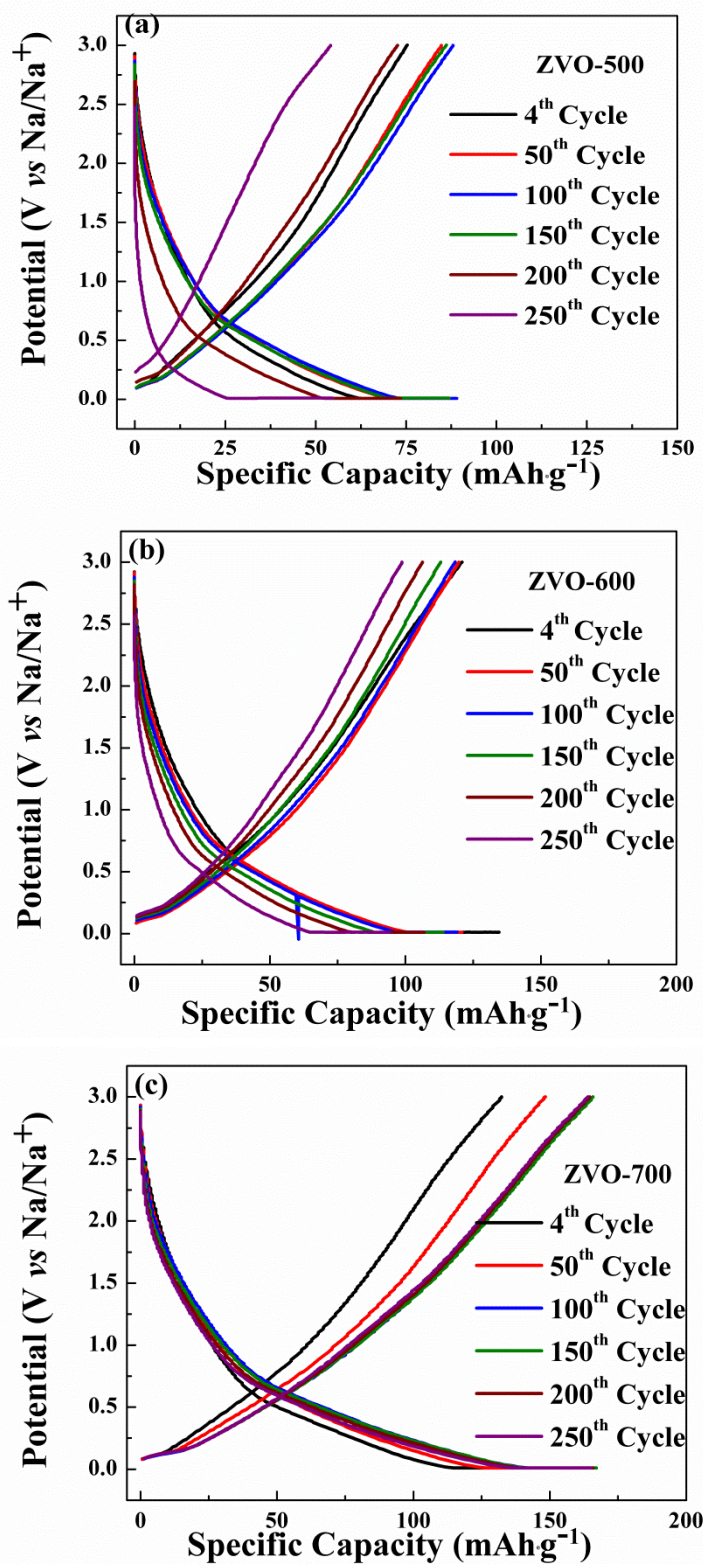


Fig. S6 Galvanostatic charge/discharge of (a) ZVO-500, (b) ZVO-600 and (c) ZVO-700 at 200 mA g⁻¹.

Table. S2 Average discharge capacities of ZVO-500, ZVO-600 and ZVO-700 at different current densities.

Current density (mA·g⁻¹)	ZVO-500 Average discharge capacities (mAh·g⁻¹)	ZVO-600 Average discharge capacities (mAh·g⁻¹)	ZVO-700 Average discharge capacities (mAh·g⁻¹)
200	89.70	106.40	125.78
400	84.19	99.21	110.87
800	77.61	92.89	98.26
1600	67.54	78.38	83.36
3200	52.29	57.84	67.46
200	91.53	108.21	125.02

In order to understand the Warburg impedance, equation was used to quantify the sloping line in the AC impedance spectra [5-7]:

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_{Li} D_{Li}^{0.5}} \right)$$

where R is the ideal gas constant, T is temperature in Kelvin, F is the Faraday's constant, A is the electrode surface, C_{Na} is the concentration of Na in the electrolyte, and D_{Na} is the diffusion coefficient. It can be clearly seen from the results that ZVO-500 has the slowest diffusion kinetics of Na^+ ions, which could be attributed to its highly agglomerated morphology. On the other hand, ZVO-600 and ZVO-700 have a very close diffusion coefficient, which agrees with their respective AC impedance spectra. After 100 cycles, their diffusion coefficients decreased faintly, indicating increased internal impedance in the cell which could be attributed to some side reactions inside the cell that have evolved during the cycle test and mechanical stresses due to volume expansion that resulted from the (de)sodiation process.

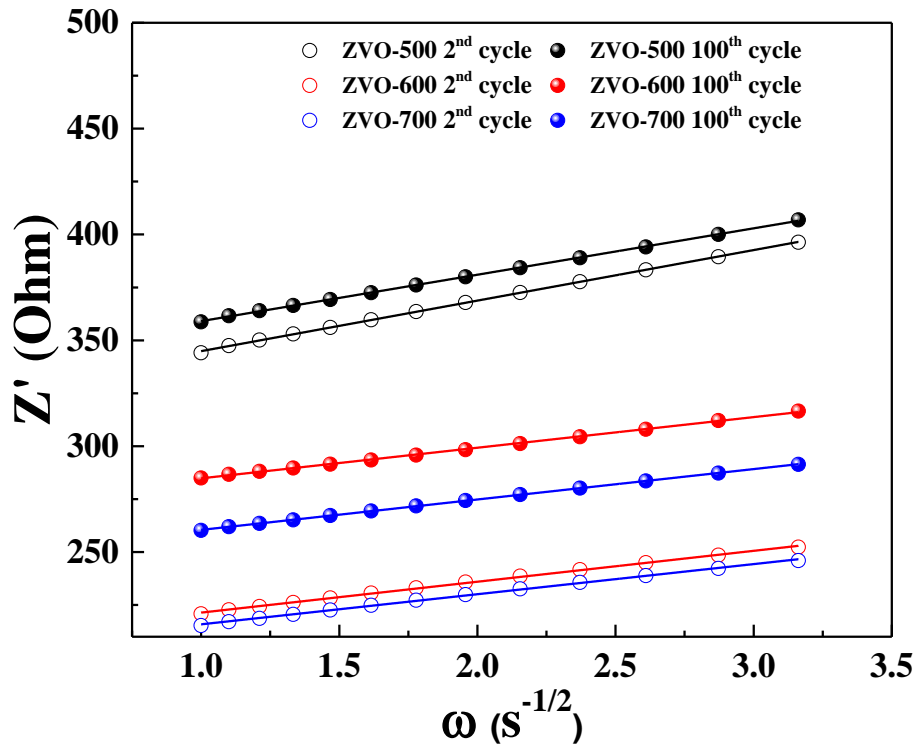


Fig. S7 Linear fitting of Warburg impedance of the ZVO-500, ZVO-600 and ZVO-700 electrode cells after 2nd and 100th cycles.

Table. S3 Impedance parameter values of ZVO three electrodes at after 2nd and 100th cycles.

Sample	From Fig. 4(f):EIS					
	R_S (Ω)		R_{SEI} (Ω)		R_{CT} (Ω)	
	2 nd Cycle	100 th Cycle	2 nd Cycle	100 th Cycle	2 nd Cycle	100 th Cycle
ZVO-500	14.41	16.40	285.65	364.01	25.82	33.23
ZVO-600	12.69	15.23	247.31	269.77	13.28	24.56
ZVO-700	9.21	13.42	218.87	231.63	12.61	17.23
Sample	From Fig. S5:Linear fit of EIS					
	Slope		Diffusivity coefficient ($\text{cm}^2\cdot\text{s}^{-1}$)			
	2 nd Cycle	100 th Cycle	2 nd Cycle	100 th Cycle		
ZVO-500	23.87	21.92	6.41×10^{-15}	7.60×10^{-15}		
ZVO-600	14.59	14.46	1.72×10^{-14}	1.75×10^{-14}		
ZVO-700	14.22	14.36	1.80×10^{-14}	1.77×10^{-14}		

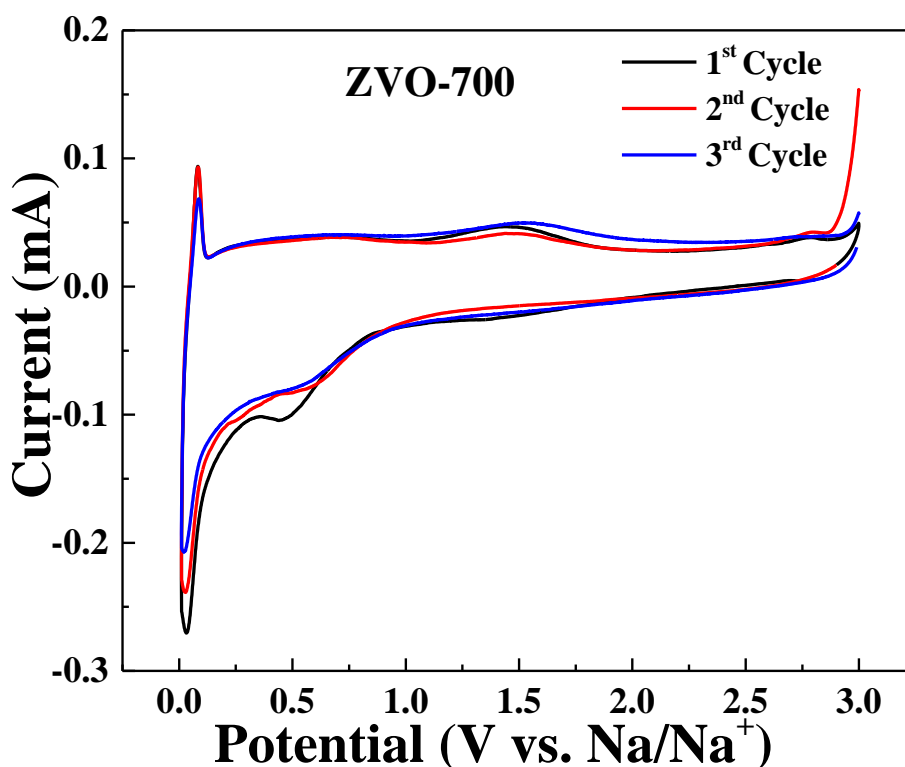


Fig. S8 CV profiles of ZVO-700 samples at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$ from 0.01–3.0V.

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