# Insights into the enhanced electrochemical performance and energy storage mechanism of manganese vanadate cathode for rechargeable aqueous zinc ion batteries

**Hong Liu [a], Litao Han [a], Chen Lu [a, *], Shi Tao [a], Fanjun Kong [a, b *], Bin Qian [a, b]**

*[a] School of Electronic and Information Engineering, Changshu Institute of Technology, Changshu 215500, China*

*[b] School of Physical Science and Technology, Soochow University, Suzhou 215006, China*

**Synthesis of MVO/NG composite**

The MVO/NG composite was synthesized by a simple co-precipitation method and following calcination treatment. Typically, 0.753 g of $Mn(NO_3)_2 \cdot 4H_2O$ was dissolved in 10 ml of distilled (DI) water (solution A). The 0.2 g of graphene oxide (GO) and 0.351 g of $NH_4VO_3$ were dispersed in 37 ml of DI water (solution B) under sonication. The solution A was added to solution B with continuously stirring. After 1 h, the black precursor was obtained by washing several times with DI water, and then drying in vacuum at 80℃ for 12 h. Finally, the N-doped reduced GO wrapped $MnV_2O_6$ nanrods (MVO/NG) composite was formed by calcined at 350 ℃ for 8 h in $N_2$ with a heating rate 2 ℃/min. For comparison, MVO rods were synthesized with the same method without GO.

**Characterization**

The crystal phases of MVO rods and MVO/NG composite were characterized by X-ray diffractometer (XRD, RUGAKU SmartLab SE) using Cu $K_\alpha$ radiation ($\lambda$=1.5418Å). Thermo gravimetric analysis (TGA, Micro for TriStar II Plus 2.02) of MVO/NG composite were carried out from room temperature to 1000 °C with a temperature ramp of 10 °C $min^{-1}$ in air atmosphere. Elemental analysis test of MVO/NG composite was performed on the FlashSmart (Thermo Scientific). X-ray photoelectron spectroscopy (XPS) spectra of MVO/NG composite were recorded to analyze the elemental bonding state with an Escalab250Xi spectrometer. Field-emission scanning electron microscopy (FE-SEM, Hitachi Regulus8100) and transmission electron microscopy (TEM, Talos F200X) performed were conducted to investigate morphology and microscopic structure of MVO rods and MVO/NG composite.

**Electrochemical Measurements**

The working electrodes on carbon paper consisted of 70 wt% MVO rods or MVO/NG composite, 20 wt% acetylene black and 10 wt% polyvinylidene. The CR2032-type coin cells were assembled using Zinc foil as the counter electrode, glass fiber filter paper as the separator and 2 M $ZnSO_4$ as the electrolyte. Galvanostatic charge and discharge tests were performed on a LAND CT2001A in the voltage range

0.3-1.9 V at a current rate of 0.2 A $g^{-1}$. Cyclic voltammetry (CV) between 0.3 and 1.9 V at a scan rate of 0.1 mV $s^{-1}$ and in-situ electrochemical impedance spectroscopy (EIS) in the frequency range from 0.1 Hz and 10 KHz were performed on the VSP electrochemical workstation (Bio-logic, FRA). For the Galvanostatic Intermittent Titration Technique (GITT) experiments, batteries after 100 cycles at 0.2 A $g^{-1}$ are galvanostatically cycled under a current flux density of 50 mA $g^{-1}$ for a transient time of 10 min with a relaxed time of 30 min.

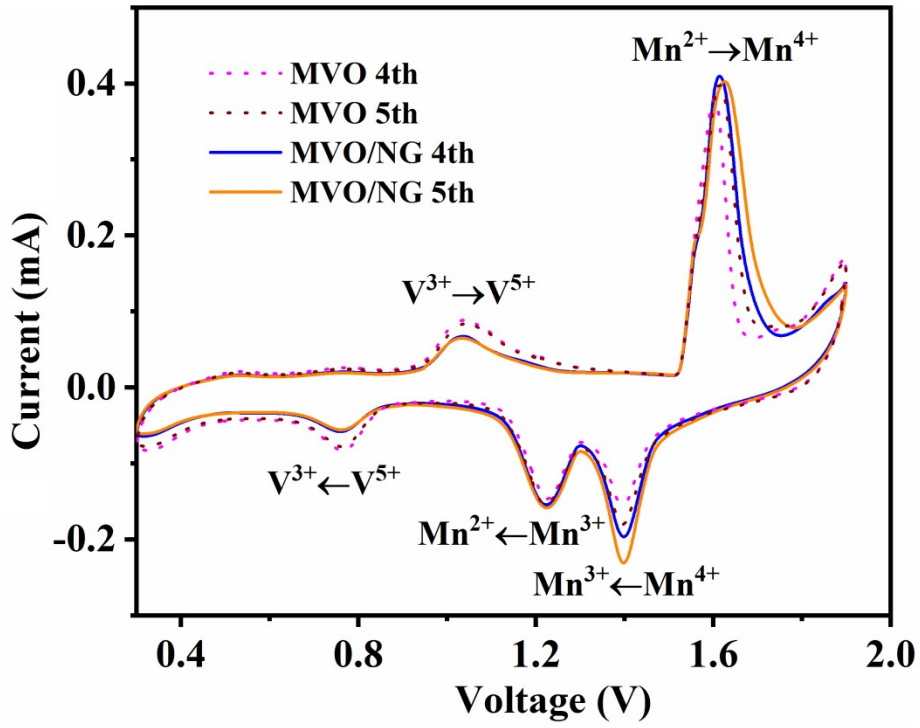


**Fig. S1. CVs of MVO rods MVO rods and MVO/NG composite in the 4th and 5th scanning cycle.**

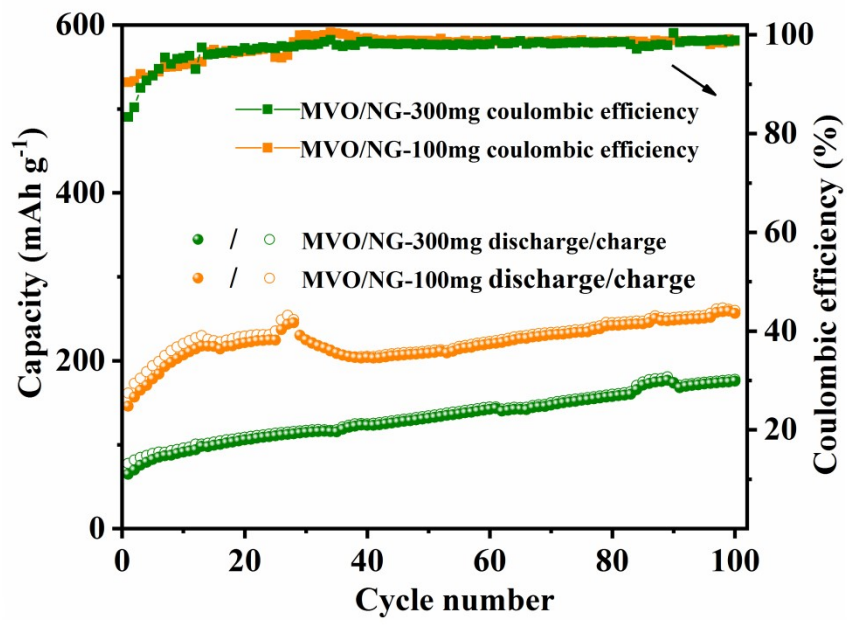


**Fig. S2. Cycling performance of MVO/NG composite with different NG content.**

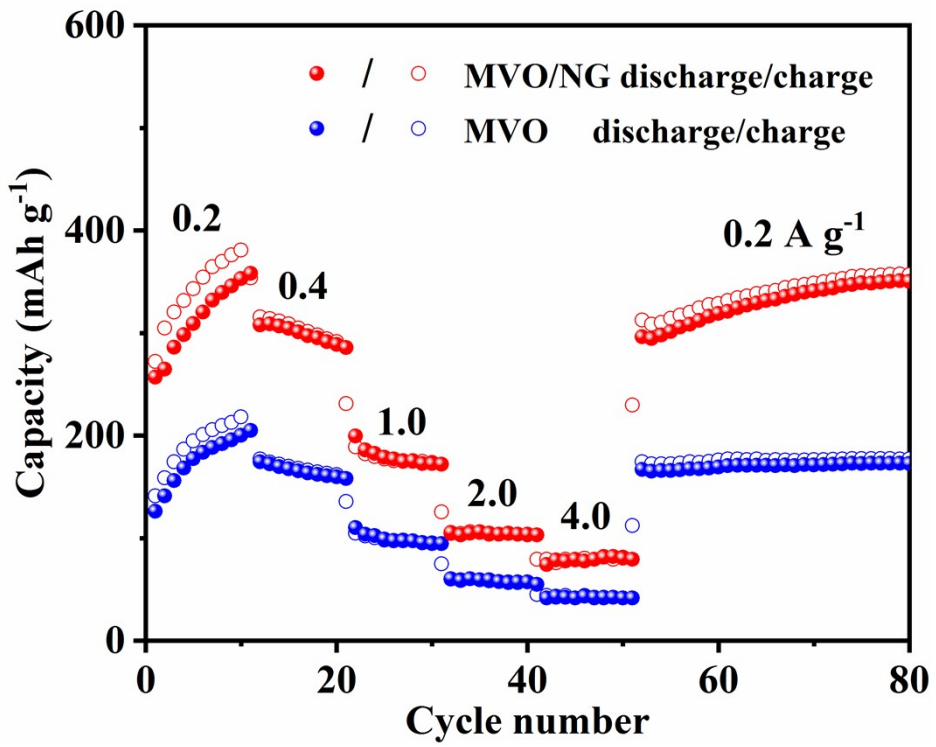


**Fig. S3. Rate performance of MVO rods and MVO/NG composite.**

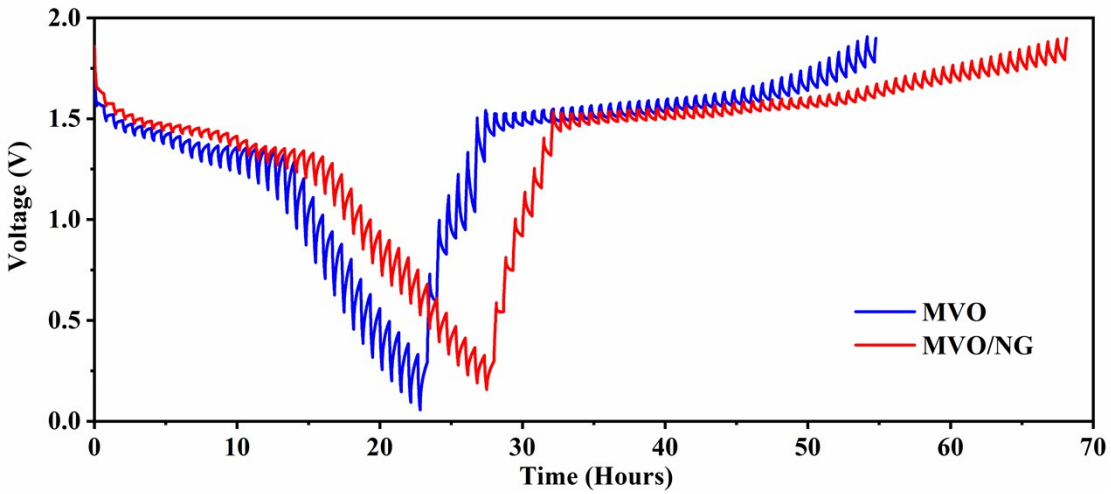


**Fig. S4. The GITT curves of MVO rods and MVO/NG composite.**

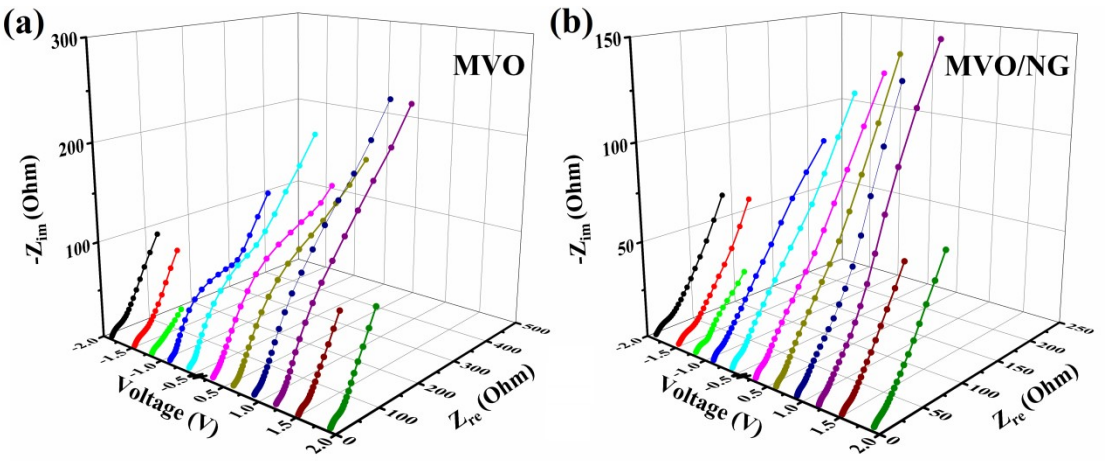


**Fig. S5. In-situ EIS Nyquist plots of MVO rods and MVO/NG composite.**

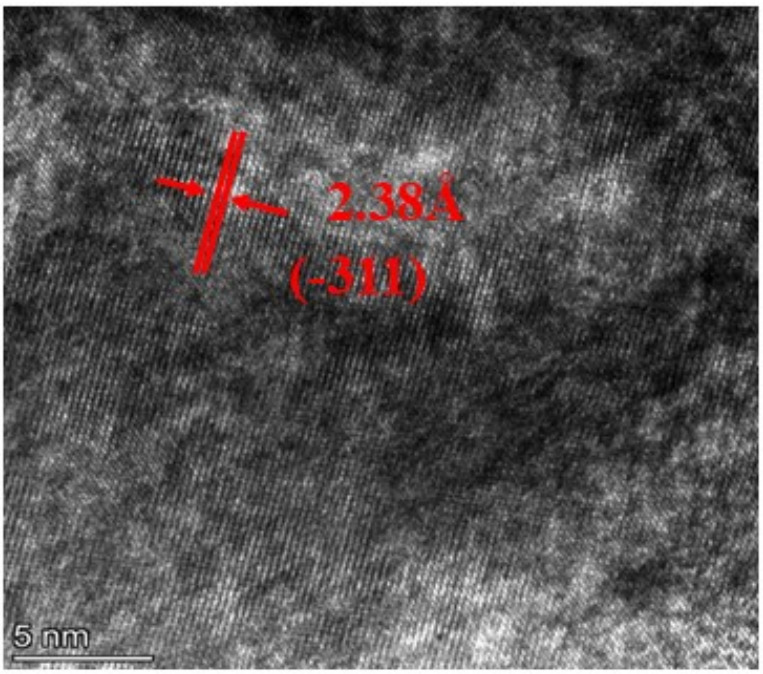


**Fig. S6. HRTEM image in the discharged state of 0.3 V of MVO/NG composite**

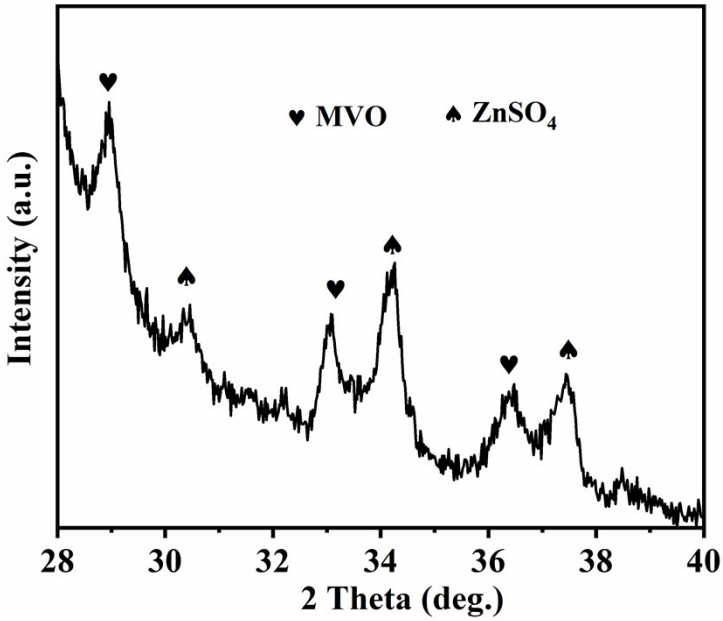


**Fig. S7. XRD pattern of MVO/NG composite after 100 cycles.**

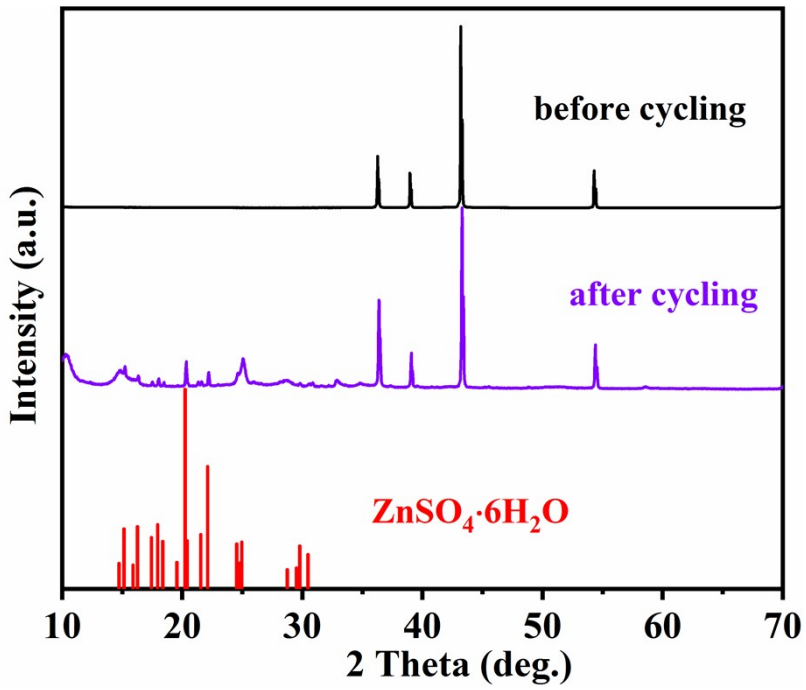


**Fig. S8. XRD patterns of Zn anode before cycling and after 100 cycles.**

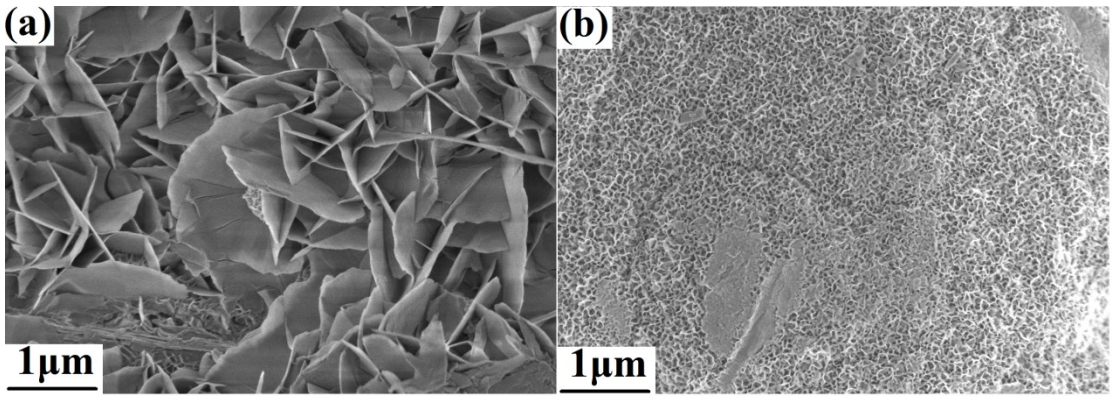


**Fig. S9. Ex situ SEM images of (a) MVO rods and (b) MVO/NG composite after 100 cycles.**

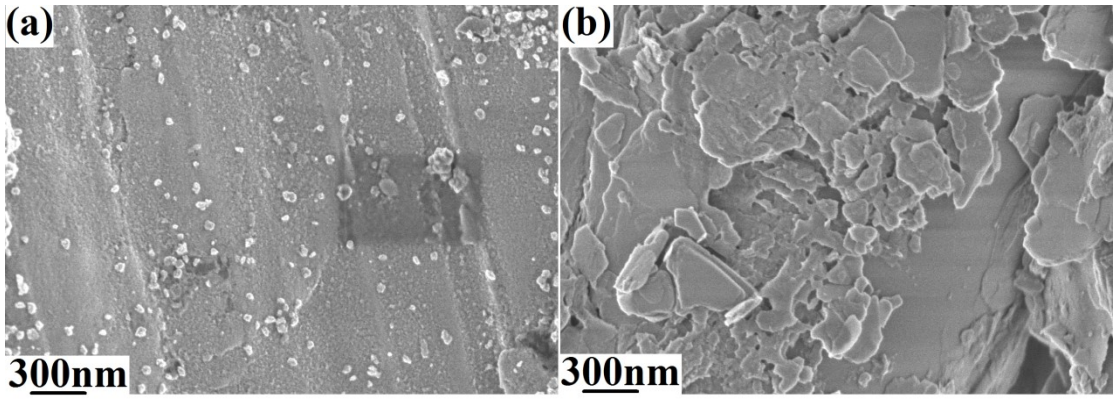


**Fig. S10. Ex situ SEM images of Zn anode (a) before cycling and (b) after 100 cycles.**

**Table S1. $Zn^{2+}$ storage performance of other V-based electrodes reported for AZIBs.**

| Materials | Constructing methods | Cycling stability ($mAh\ g^{-1}/A\ g^{-1}$/cycles) | Ref. |
|---|---|---|---|
| $MnV_2O_4$ | Hydrothermal-Calcination | 272/0.2/50 | 1 |
| $MoV_2O_8$ | Hydrothermal-Calcination | 282.4/0.1/100 | 2 |
| $MnV_2O_6$/PANI | Hydrothermal | 258.8/0.1/100 | 3 |
| $Na_{1.1}V_3O_{7.9}$@rGO | Hydrothermal-Calcination | 220/0.3/100 | 4 |
| $MgV_6O_{16}\cdot 6H_2O$ | Sol-Gel | 289/0.02/300 | 5 |
| $V_2O_5$@rGO | Solvothermal-Calcination | 270/0.1/100 | 6 |
| $Ag_2V_4O_{11}$@rGO | Hydrothermal | 328/0.1/100 | 7 |
| $VSe_2/V_2O_5\cdot nH_2O$/rGO | Hydrothermal | 327.4/0.2/100 | 8 |
| $Cu_{0.26}V_2O_5$@C | Hydrothermal-Calcination | 328.8/0.2/100 | 9 |
| $Co_3V_2O_8$@$MnO_2$ | Hydrothermal | 245.4/0.1/10 | 10 |
| $MnV_2O_6$/NG | Co-precipitation-Calcination | 331.1/0.2/100 | **This work** |


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