Supporting Information

Cubic MnV_2O_4 fabricated through a facile sol-gel process as anode material for lithium-ion batteries: morphology and performance evolution

Ni Wen,[a] Siyuan Chen,[a] Qiuchen Lu,[a] Qinghua Fan,[a] Quan Kuang,[a] Youzhong Dong[a] and Yanming Zhao*[a,b]

[a]School of Physics, South China University of Technology, Guangzhou, 510640, P. R. China

[b]South China Institute of Collaborative Innovation, Dongguan, 523808, P. R. China

*Corresponding authors.

E-mail addresses: zhaoym@scut.edu.cn (Y. M. Zhao).

We investigate the structural variations of MnV_2O_4 electrode in the initial two cycles over the potential range from 0.01 V to 3 V by employing in-situ XRD tests (Fig. S1). As shown in Fig. S1a, it is clearly seen that all diffraction peaks of MnV_2O_4 gradually weakens with the first discharge process being in progress, implying the decomposition of the electrode material. Interestingly, these peaks do not seem to disappear completely, which may be because, on the one hand, the MnV_2O_4 is not fully reacted, and on the other hand, the peaks of the newly formed material coincide with some of the peak positions before the decomposition of the MnV_2O_4. In order to further identify Li^+ ion storage mechanism of the MnV_2O_4 electrode in the subsequent cycle, the zoom in the part regions of the in-situ XRD patterns of the MnV_2O_4 electrode during the initial two cycles are displayed in Fig. S1b−f. During the first discharge, all newly generated peaks shift subtly toward a lower position. Amazingly, these diffraction peaks recuperate the initial position when fully charging. What's more, these diffraction peaks exhibit the same variation even during the second cycle, proving the occurrence of solid solution behavior, and these peaks should be lithium vanadium oxide solid solution. The periodic evolution phenomenon discloses that subsequent cyclic reactions are reversible after MnV_2O_4 is decomposed during the first discharge. Based on the CV and in-situ XRD analysis, the lithium storage mechanism of MnV_2O_4 is supposed to be the coexistence of conversion reaction and solid solution behavior. However, contrary to our expectation, no peaks of manganese and its oxides peak can be detected, which may be accredited to the amorphous phase.

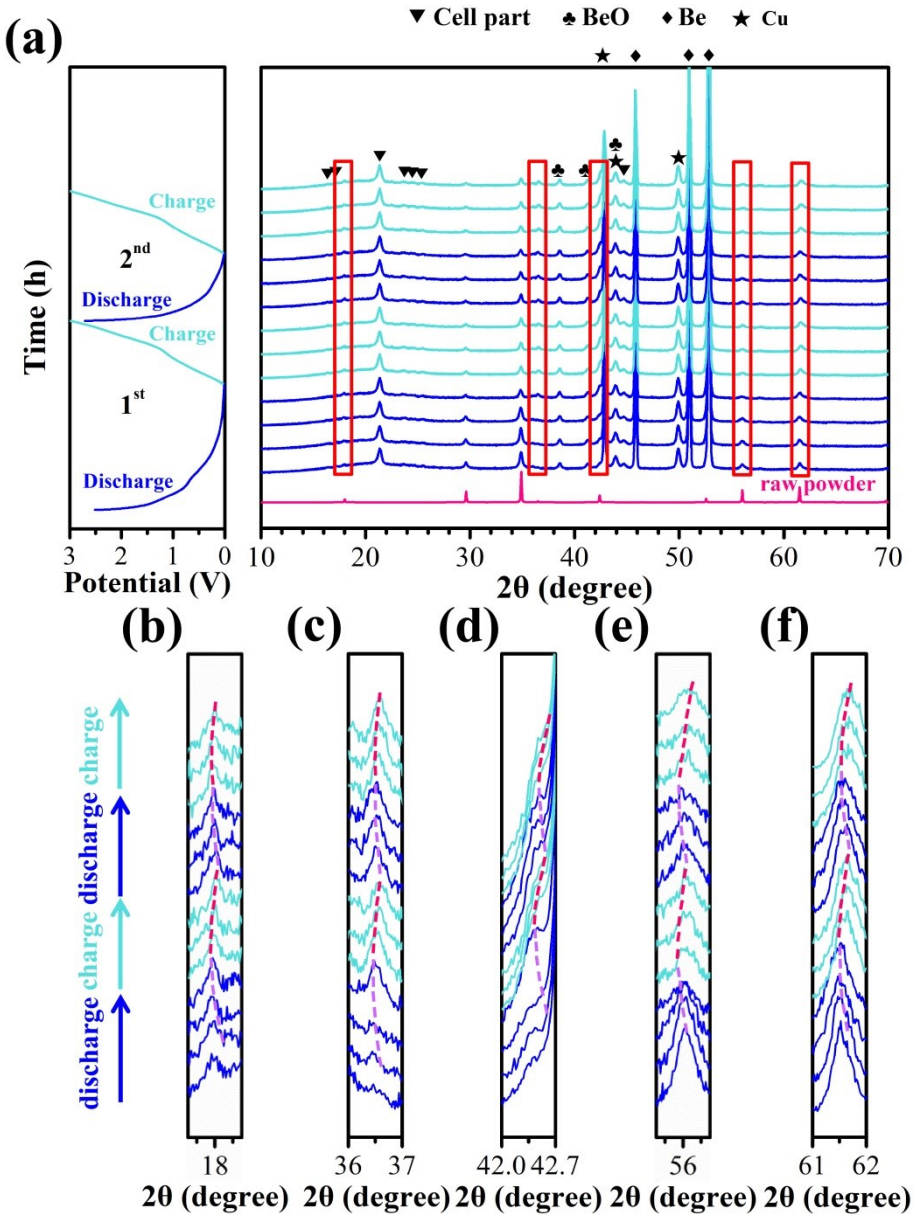

Fig. S1 (a) Selected in-situ XRD patterns of the MnV_2O_4 electrode in the initial two cycles and corresponding discharge/charge curves (left). (b−f) The zoom in the part regions of the in-situ XRD patterns.

Table S1. A comparison of electrochemical performances of various spinel-type binary vanadium oxides anode materials.

Anode Materials	Capacity ($mAh \cdot g^{-1}$)	Current Density ($mA \cdot g^{-1}$)	Cycles (n)
Nanophase MnV_2O_4 particles[1]	550	200	50
MnV_2O_4/NC double-layer hollow sandwich nanosheets[2]	717	500	300
Clewlike ZnV_2O_4 hollow spheres[3]	524	50	50
Hierarchical ZnV_2O_4 microspheres[4]	638	100	280
Hierarchical mesoporous nanoflowers of Zn_2VO_4[5]	528	300	300
Nanoporous CoV_2O_4 compounds[6]	771	200	100
Spinel Fe_2VO_4[7]	225	3 $mA \cdot cm^{-2}$	30
MnV_2O_4 (This work)	**1325**	**200**	**500**

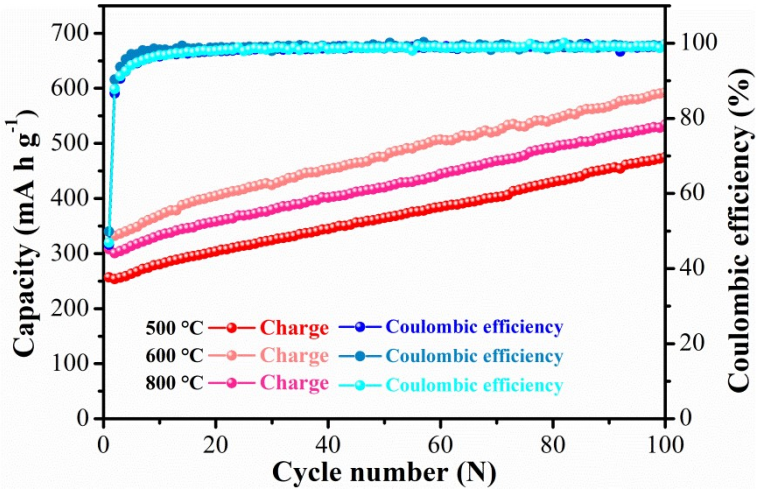

Fig. S2 Cycling performances and the corresponding Coulombic efficiencies of MnV_2O_4 prepared at different temperatures at a current density of 200 mA g^{-1} within a voltage range of 0.01–3 V versus Li^+/Li.

The GITT profiles of the MnV_2O_4 electrodes after 100 cycles, 300 cycles and 500 cycles at a current density of 200 mA g^{-1}, respectively, are shown in Fig. S3a. In order to obtain such a continuous curve, the cells need to be discharged/charged at a current density of 200 mA g^{-1} with a current pulse duration of 10 min, followed by 100 min interval time. The Li^+ ion diffusion coefficients (D_{Li+}) of MnV_2O_4 electrodes can be calculated according to the following equation:[8]

$$D_{Li^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B A}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad \left(\tau \ll \frac{L^2}{D_{Li^+}}\right)$$

where τ represents the current pulse time, m_B the mass of the active material, M_B the molecular

weight, V_M the molar volume, A the contact area of electrode-electrolyte, ΔE_s the voltage changes caused by the current pulse, ΔE_τ the voltage changes during the constant current pulse, and L the Li^+ ion diffusion length equaling to thickness of electrode.

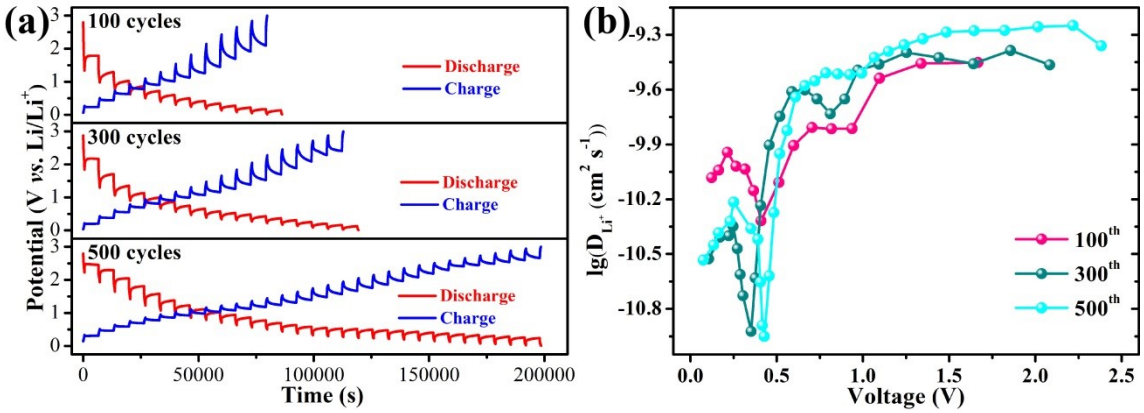

Fig. S3 (a) GITT profiles of the MnV_2O_4 electrodes after 100 cycles, 300 cycles and 500 cycles at a current density of 200 mA g^{-1}, respectively. (b) The calculated Li^+ ion diffusion coefficients.

References

1. X. Wang, Z. Jia, J. Zhang, X. Ou, B. Zhang, J. Feng, F. Hou and J. Liang, *J. Alloys Compd.*, 2021, **852**, 156999.
2. F. Jing, J. Pei, Y. Zhou, Z. Qin, B. Cong, K. Hua and G. Chen, *J. Colloid Interface Sci.*, 2022, **607**, 538−545.
3. L. Xiao, Y. Zhao, J. Yin and L. Zhang, *Chem. - Eur. J.*, 2009, **15**, 9442−9450.
4. C. Zheng, L. Zeng, M. Wang, H. Zheng and M. Wei, *CrystEngComm*, 2014, **16**, 10309−10313.
5. Z. Tariq, S. U. Rehman, J. Zhang, F. K. Butt, X. Zhang, B. Cheng, S. Zahra and C. Li, *Mater. Sci. Semicond. Process.*, 2021, **123**, 105549.
6. J. Lu, I. Maggay and W. Liu, *Chem. Commun.*, 2018, **54**, 3094−3097.
7. T. Yang, D. Xia, Z. Wang and Y. Chen, *Mater. Lett.*, 2009, **63**, 5−7.
8. Y.-S. Lee and K.-S. Ryu, *Sci. Rep.*, 2017, **7**, 1−13.