Electronic Supplementary Information (ESI)

MgV_3O_8 Anode Exhibiting Enhanced Rate Capability and Stability for Lithium Storage Applications

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1. Experimental Section

1.1 *Synthesis of MgV_3O_8.*

In a typical route, 0.03 mol ammonium vanadate (NH_4VO_3) and 0.01 mol magnesium nitrate hexahydrate ($6H_2O{\cdot}Mg(NO_3)_2$) were dissolved in 40 mL deionized water using the stoichiometric ratio of Mg/V=1:3. Then, critic acid monohydrate (CAS) was added into this solution, with CAS : Mg : V=4:1:3 in mole ratio. The above solution vigorously stirred at 60 °C for 30 min. Stop stirring when the solution changed from orange-yellow to dark blue, the polybasic chelate solution was directly transferred to a resistance furnace in an air atmosphere at 450 °C. It took about 5 min to form gelatinous mass. Upon further heating, the resultant mass swelled suddenly accompanied by the release of a lot of gases, which resulted in large volume expansion of the precursor and formation of bubble-like bulks. The black product after cooling with the furnace was MgV_3O_8.

1.2 *Materials characterizations.*

The crystal structures of sample were detected by X-ray diffractometer (XRD, Bruker D Advance) and XRD patterns were obtained at a scan rate of 1 ° min^{-1} with Cu-Kα radiation. The morphological characterizations of all samples were carried out by field emission scanning electron microscope (FESEM, ZEISS Sigma 300), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) with the selected area electron diffraction pattern (SAED) function as well as an energy dispersive spectroscopy detector. The surface valence states and elemental compositions were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The Raman signals of samples were identified on a Raman Spectrometer (Renishaw inVia) with an excitation laser wavelength of 514.5 nm. The Mg/V mole ratios in the entire MgV_3O_8 were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5110). N_2 adsorption-desorption isotherms were obtained by using a Micromeritics 3Flex analyzer at the testing temperature of 77 K. The Brunauer-Emmett-Teller method was utilized to calculate the surface areas. The pore size distributions were retrieved by using the Barrett-Joyner-Halanda (BJH) method from the adsorption branch of the isotherms. The thermogravimetry analyses (TGA, Rigaku Thermo plus TG 8120) were carried out from RT to 800 °C with a heating rate of 10 °C min^{-1} in air.

1.3 *Electrochemical measurements.*

Half-cell tests were carried out in a 28 °C. The working electrodes were made by mixing the below active materials, poly (vinylidene fluoride) (PVDF) and Super P at a weight ratio of 7:2:1, followed by coating on a piece of Cu foil and drying at 60 °C for 12 h under vacuum condition. The CR2032 coin-type cells were assembled in a glovebox filled with high purity argon ($H_2O < 0.01$ ppm, $O_2 < 0.01$ ppm). The lithium foil was used as the counter electrode, and the polypropylene film (Celgard-2300) served as the separator. 1 mol $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), and ethylene methyl carbonate (EMC) with the volume ratio of 1:1:1 was used as the electrolyte. Cyclic voltammetry (CV) test was conducted using the CT2001A battery instrument at a scan rate of 0.2–1.0 mV s^{-1}. The galvanostatic charge/discharge curves, cycling and rate performances were tested on a NEWARE Automatic Battery Test System in a voltage range of 0.01−3.0 V. The galvanostatic intermittent titration technique (GITT) was used with a current density of 0.1 A g^{-1} for 10 min followed by

30 min of relaxation time to achieve equilibrium potential on an Ivium Vertex.One Electrochemical Workstation.

2. Figures and Tables

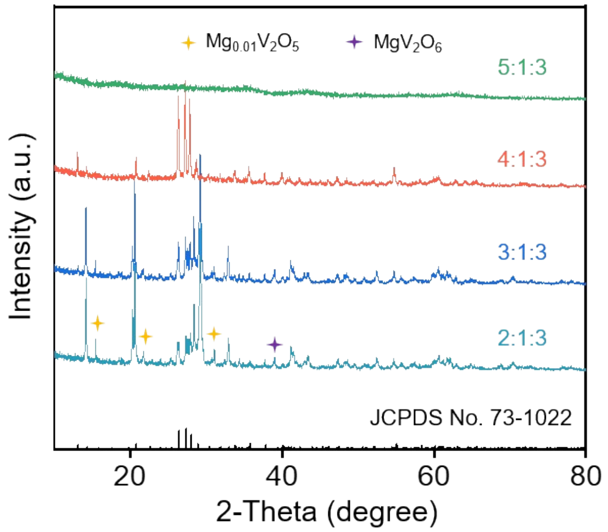

Fig. S1 The XRD patterns of the products obtained by the solution combustion synthesis with different mole ratio of CAS:Mg:V.

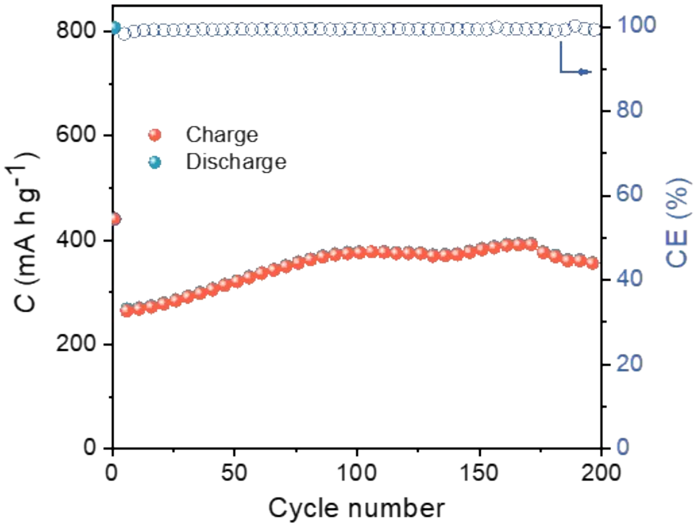

Fig. S2 Cycle stability of MgV_3O_8 electrode at 0.2 A g^{-1} for 200 cycles.

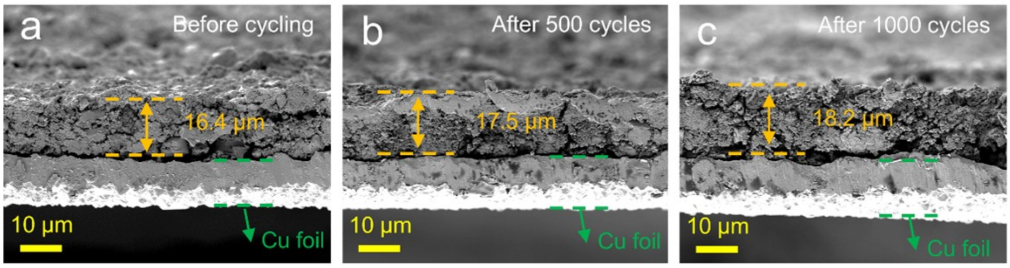

Fig. S3 Cross-sectional SEM images of MgV_3O_8 electrode. (a) Before cycling. (b) After 500 cycles. (c) After 1000 cycles for Li-ion storage.

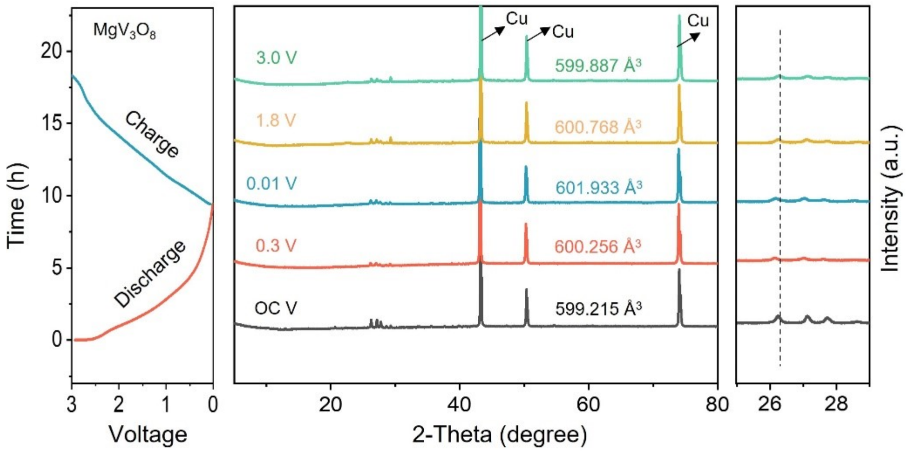

Fig. S4 *Ex situ* XRD patterns of MgV_3O_8 at different lithiation/delithiation potentials.

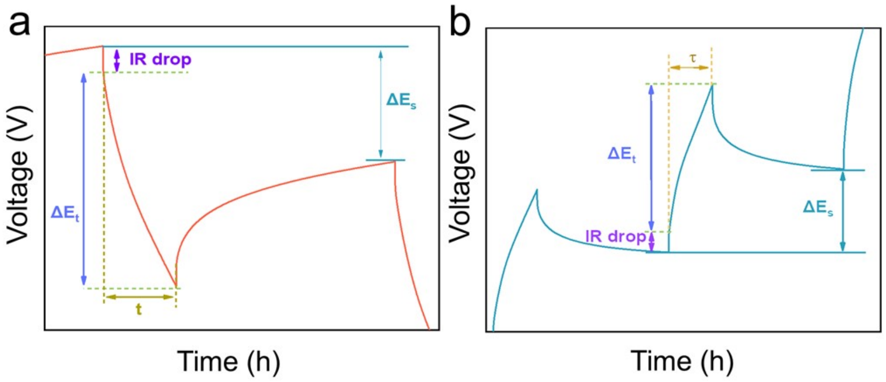

Fig. S5 Schematic representation of the GITT in (a) discharge, and (b) charge process. τ: the relaxation time; ΔEs: voltage change due to the current pulse; $\Delta E\tau$: voltage change during the current pulse (eliminating the voltage changes after relaxation time).

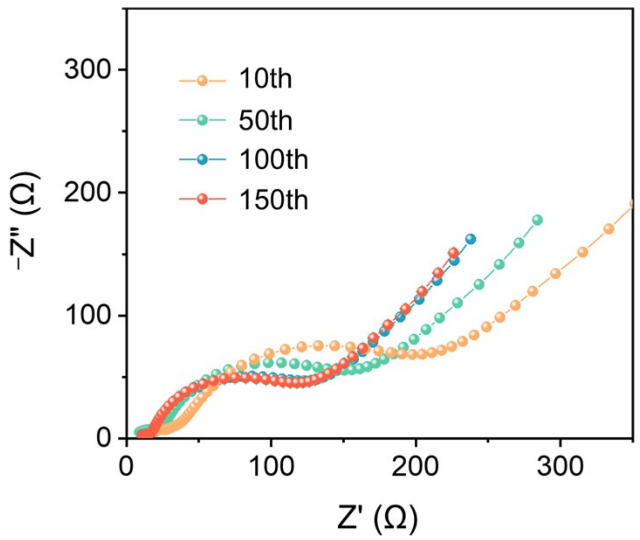

Fig. S6 EIS spectra of full delithiation (to 3.0 V) MgV_3O_8 electrode at different cycles.

Table S1 XRD Rietveld diffraction refined parameters of MgV_3O_8.

a = 10.3796(0) Å, b = 8.5470(0) Å, c = 7.7692(3) Å, Volume (V) = 600.001 Å^3, α = γ = 90°, β = 119.481°; Density (ρ) = 4.72 g/cm^3; R_{wp} = 5.63, R_p = 4.3, χ^2 = 1.68.

Atom type	Wyckoff site	*x*	*y*	*z*	Occupancy	U_{iso} (Å^2)
Mg1	8j	0.1285(3)	0.1923(7)	0.3013(2)	0.5	0.027
V1	8j	0.1285(3)	0.1923(7)	0.3013(2)	0.5	0.027
V2	4i	0.3789(7)	0	0.2232(2)	1	0.015
V3	4i	0.3149(8)	0.5	0.2882(3)	1	0.016
O1	4g	0	0.1944(7)	0	1	0.044
O2	8j	0.4726(1)	0.1636(1)	0.2881(8)	1	0.013
O3	8j	0.2759(0)	0.3366(9)	0.376(2)	1	0.003
O4	4i	0.1943(6)	0.5	0.0374(6)	1	0.025
O5	4i	0.4990(0)	0.5	0.3051(6)	1	0.032
O6	4i	0.2427(7)	0	0.3007(1)	1	0.022

Table S2 The ratio of Mg/V in MgV_3O_8 powders was tested by ICP-OES.

Samples	Mg/V mole percentage (a.u.)
MgV_3O_8	0.338

Table S3 Performance comparison of MgV_3O_8 with the reported M (alkaline earth metals)-V-O materials for LIBs.

Anode	Current density (mA g^{-1})	Capacity (mA h g^{-1})	Cycles	Fade rate	Volume expansion rate	Ref.
MgV_3O_8	200	356.8	200	~0%	0.34%	Our work
$SrVO_3$	200	~238	200	~5%	2.30%	[1]
CaV_4O_9	1000	475.8	500	~4%	＞1.34%	[2]

References

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[2] P. Wu, X. Xu, Y. Wu, F. Xu, X. Wang, J. Meng, C. Han, X. Liu, Z. Zhu, L. Mai, *Adv. Energy Mater.*, 2021, **11**, 2003612.