

Supporting Information

Nanoengineered Vanadium Oxide Composite as High-performance Anode for Aqueous Li-ion Hybrid Battery

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Experimental

Synthesis of V₂O₅-LSG: Graphite oxide (GO) was synthesized via a modified Hummer's method.¹ In a typical synthesis, 40 mg of freeze-fried GO powder was diluted with the addition of 5.8 mL of DI water and dispersed by 2-minute tip sonication. 160 mg of VCl₃ (Fisher Scientific) was dissolved in 4.2 mL of DI water and bath sonicated for 2 hrs. Next, the VCl₃ solution was uniformly added to the GO suspension within 1 h via a syringe pump while stirring. The resulting mixture was then drop-cast onto graphite paper (Panasonic) at a density of 200 μL cm⁻² and left to dry under ambient conditions. Next, the dried film was laser-scribed using a 40 W Full Spectrum Laser Muse 2D Vision Desktop CO₂ Laser Cutter with a 12% power setting, and electrodes were cut out of the film using a 10 mm hole punch. Finally, the electrodes were placed in a furnace which was set to 60 °C for 1 h, ramped up to 300 °C at 2 °C/min and then left at 300 °C for 0.5, 1 or 2 h. The as-made V₂O₅-LSG electrodes were weighed using a micro-balance and the electrode mass was determined to be 1.4 – 1.6 mg.

Materials characterization: Scanning electron microscopy (SEM) images of the V₂O₅-LSG composite were collected using a JEOL JSM-67 Field Emission Scanning Electron Microscope. Transmission electron microscopy (TEM) was performed on a Tecnai G2 T20 iCorr TEM (FEI Inc.). X-ray powder diffraction (XRD) was performed using a Panalytical X'Pert Pro X-ray powder diffractometer using Cu Kα radiation with a wavelength of 0.154 nm on a SiO₂ crystal zero-background plate. In order to eliminate the coinciding signals from graphite paper, glass slides were used as the substrate instead and the active materials were scratched off to maximize the signals. The unassigned small peaks in the spectra are from SiO₂ impurities. The X-ray photoelectron spectroscopy (XPS) spectra were acquired using a Kratos Axis Ultra DLD

spectrometer equipped with a monochromatic Al K α X-ray source. The mass of the electrode was measured by a Mettler Toledo MX5 microbalance with 0.001 mg sensitivity. Raman spectroscopy was carried out using a Reinshaw inVia confocal Raman microscope with a 633 nm laser.

Fabrication of LiMn₂O₄ and rGO/V₂O₅: The active material, LiMn₂O₄ (MTI) or V₂O₅ (Sigma-Aldrich) was mixed with conductive carbon black or rGO, and PVDF binder, in the ratio 85:10:5. The slurry was cast on a graphite paper substrate using a doctor-blade and then punched into 10 mm discs. The resulting electrode mass was determined to be 1.4 – 1.6 mg.

Electrochemical testing: Three-electrode measurements including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were carried out using a Biologic VMP3 electrochemical workstation (VMP3b-10, USA Science Instrument). For three-electrode experiments, graphite paper and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The electrolyte is 21 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) unless stated otherwise. Coin cell tests were carried with an approximately equal mass of cathode and anode using an MTI battery cycler.

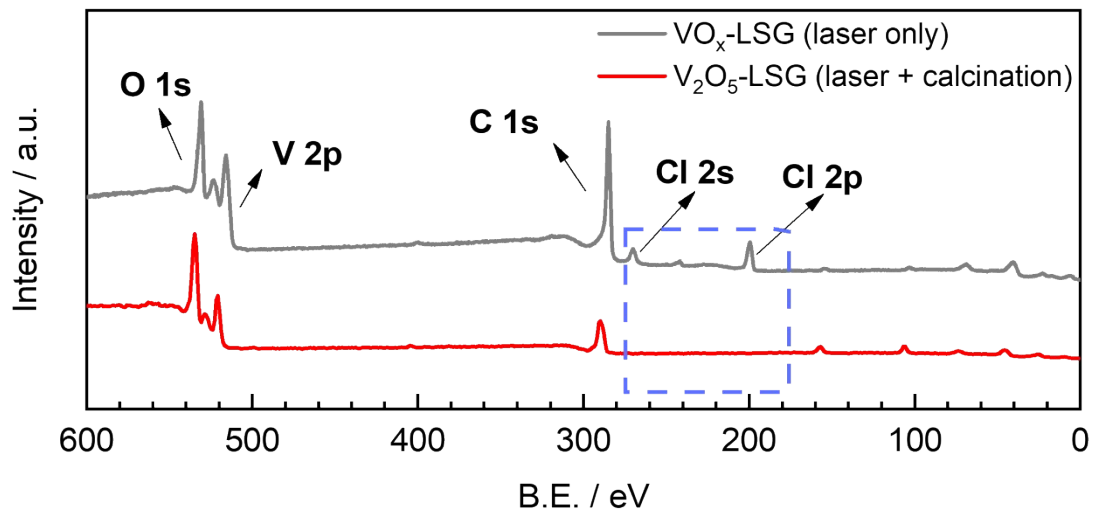


Figure S1. XPS survey spectra of V₂O₅-LSG and VO_x-LSG.

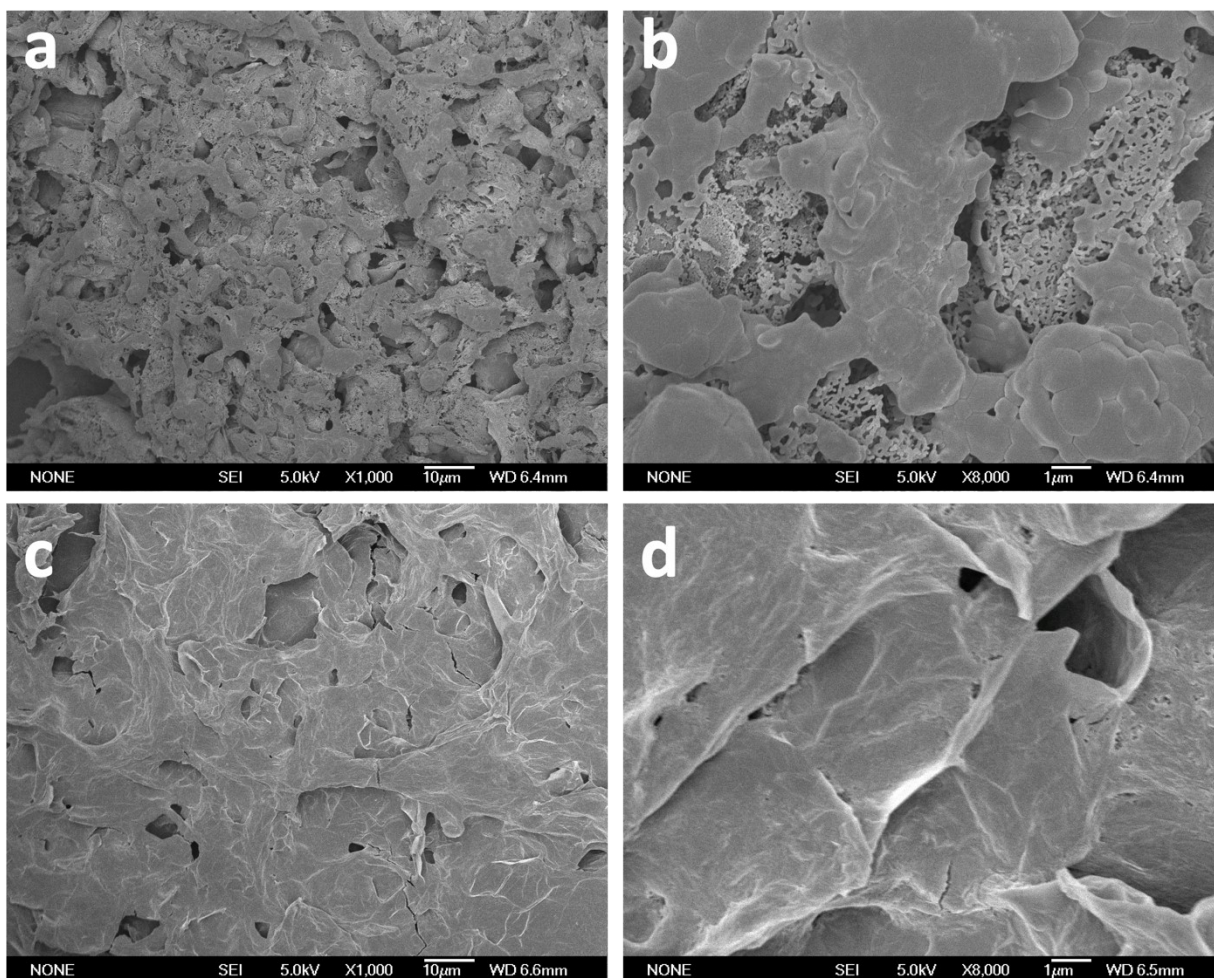


Figure S2. (a-b) Low- and high-magnification SEM images of the VO_x-LSG composite. (c-d) Low- and high-magnification SEM images of the VCl₃-GO composite.

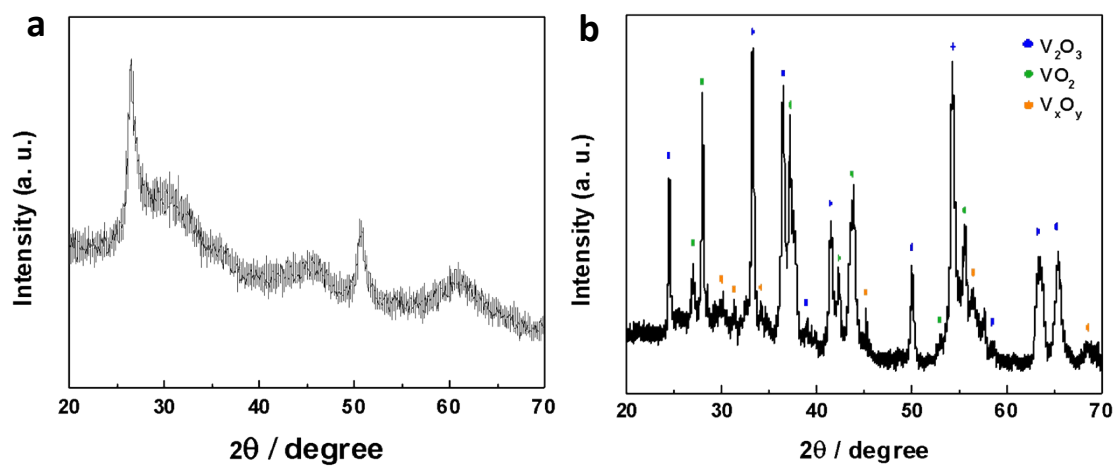


Figure S3. (a) XRD pattern of VCl₃-GO composite. (b) XRD pattern of the VO_x-LSG composite matching V₂O₃ (JCPDS no. 34-0187) and VO₂ (JCPDS no. 09-0142).

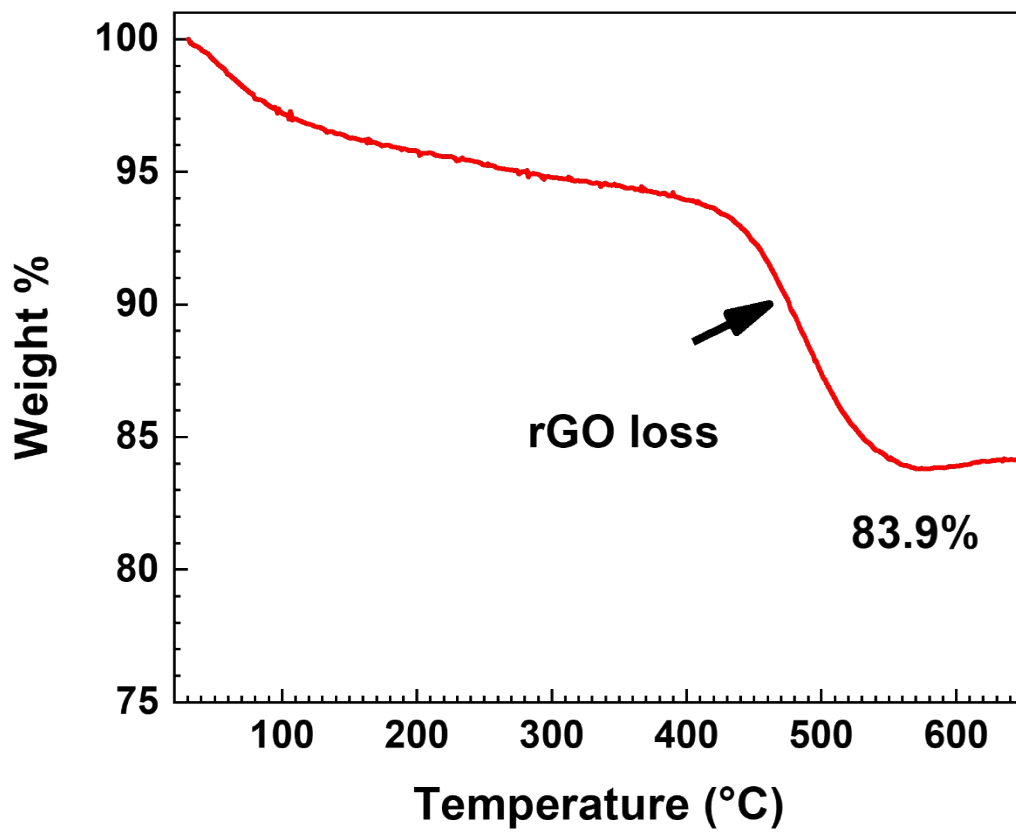


Figure S4. Thermogravimetric analysis of V₂O₅-LSG.

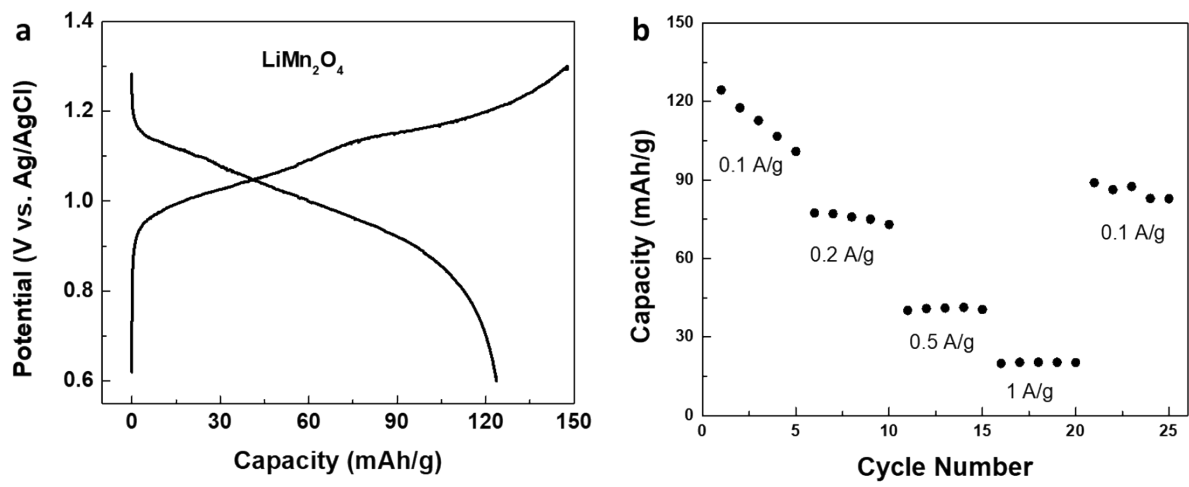


Figure S5. (a) Voltage profile and (b) rate performance of a LiMn_2O_4 cathode.

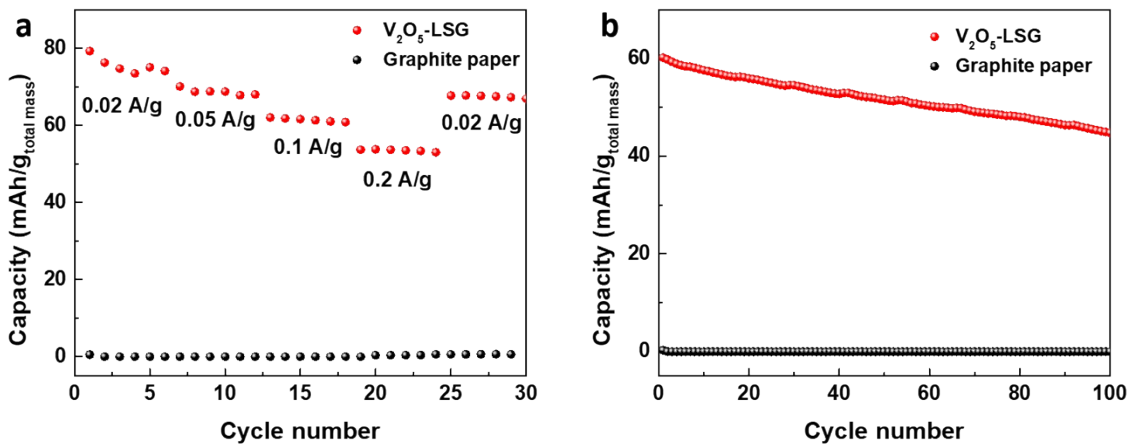


Figure S6. (a) Rate performance and (b) Capacity and Coulombic efficiency of a graphite paper||LiMn₂O₄ cell over cycling at 0.1 A g⁻¹.

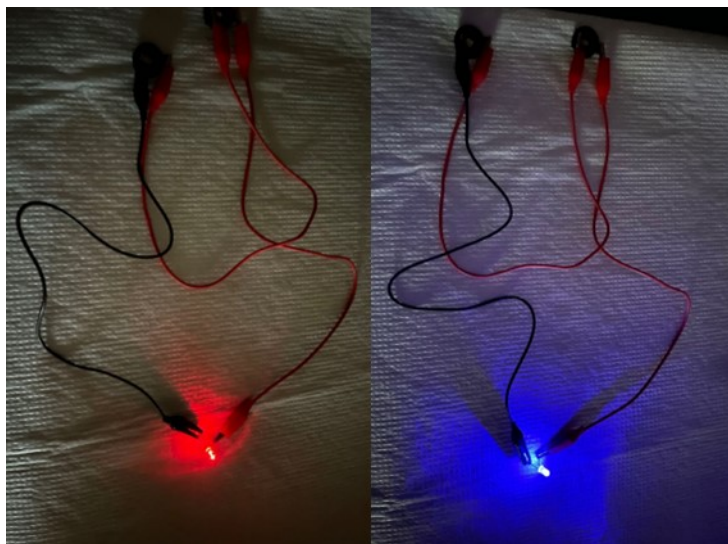


Figure S7. Optical images of LED bulbs powered by 2 V_2O_5 -LSG||LiMn₂O₄ coin cells connected in series.

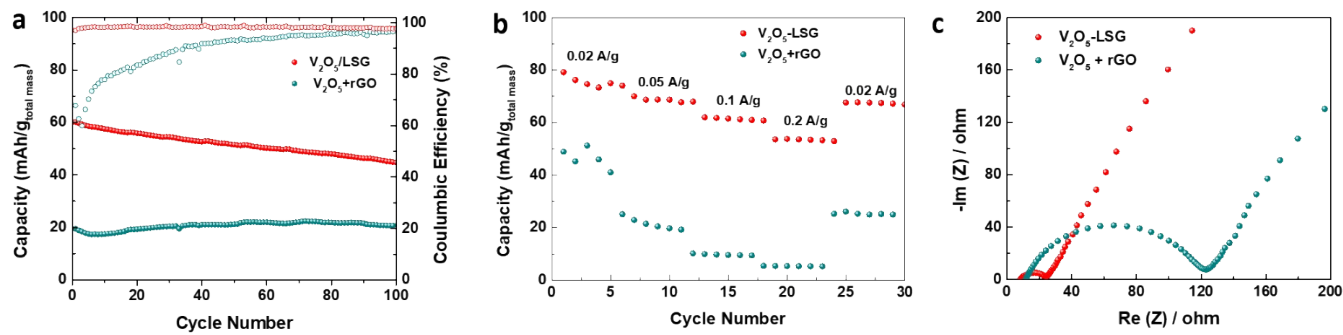


Figure S8. (a) Capacity and Coulombic efficiency and (b) rate performance of a $V_2O_5+rGO||LiMn_2O_4$ cell over cycling at 0.1 A g^{-1} . (c) A Nyquist impedance plot of V_2O_5 -LSG and V_2O_5+rGO composite.

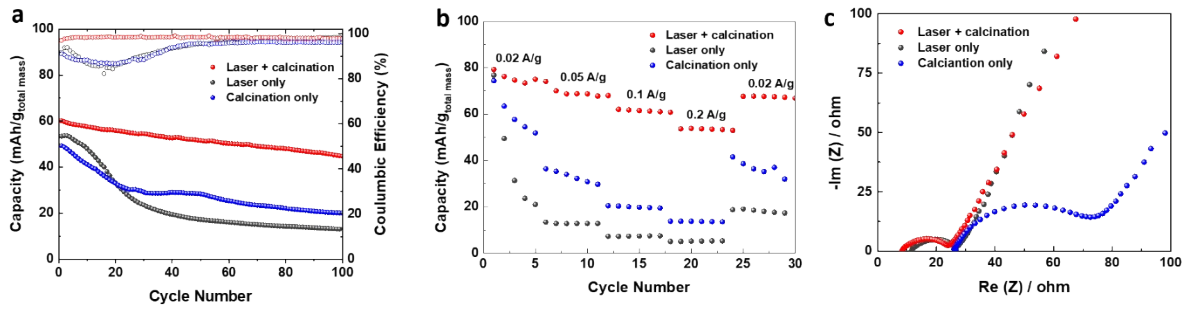


Figure S9. (a) Capacity and Coulombic efficiency and (b) rate performance of calcination only and laser only anodes paired with an LiMn_2O_4 cathode. (c) A Nyquist impedance plot of calcination only and laser only anodes.

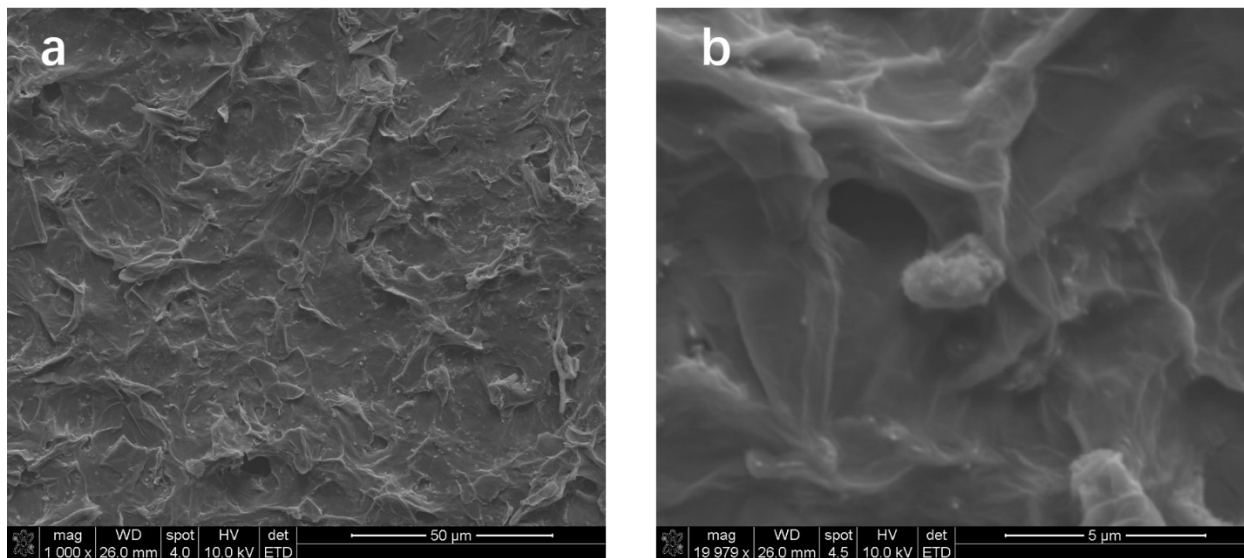


Figure S10. (a) low- (b) high-resolution SEM images of calcination only V_2O_5/rGO samples.

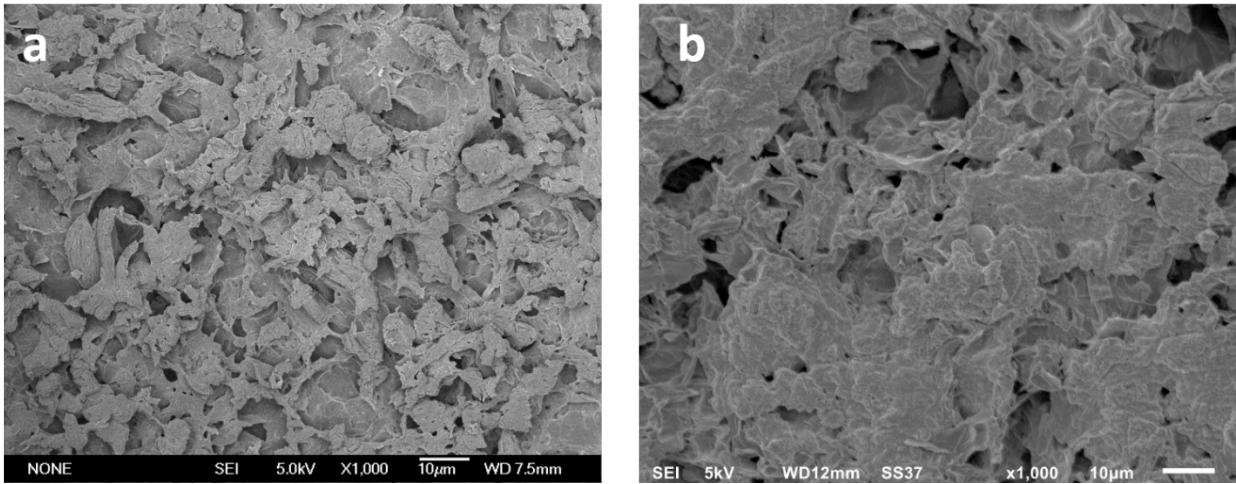


Figure S11. SEM images of V₂O₅-LSG a) before cycling b) after 100 cycles at 1C.

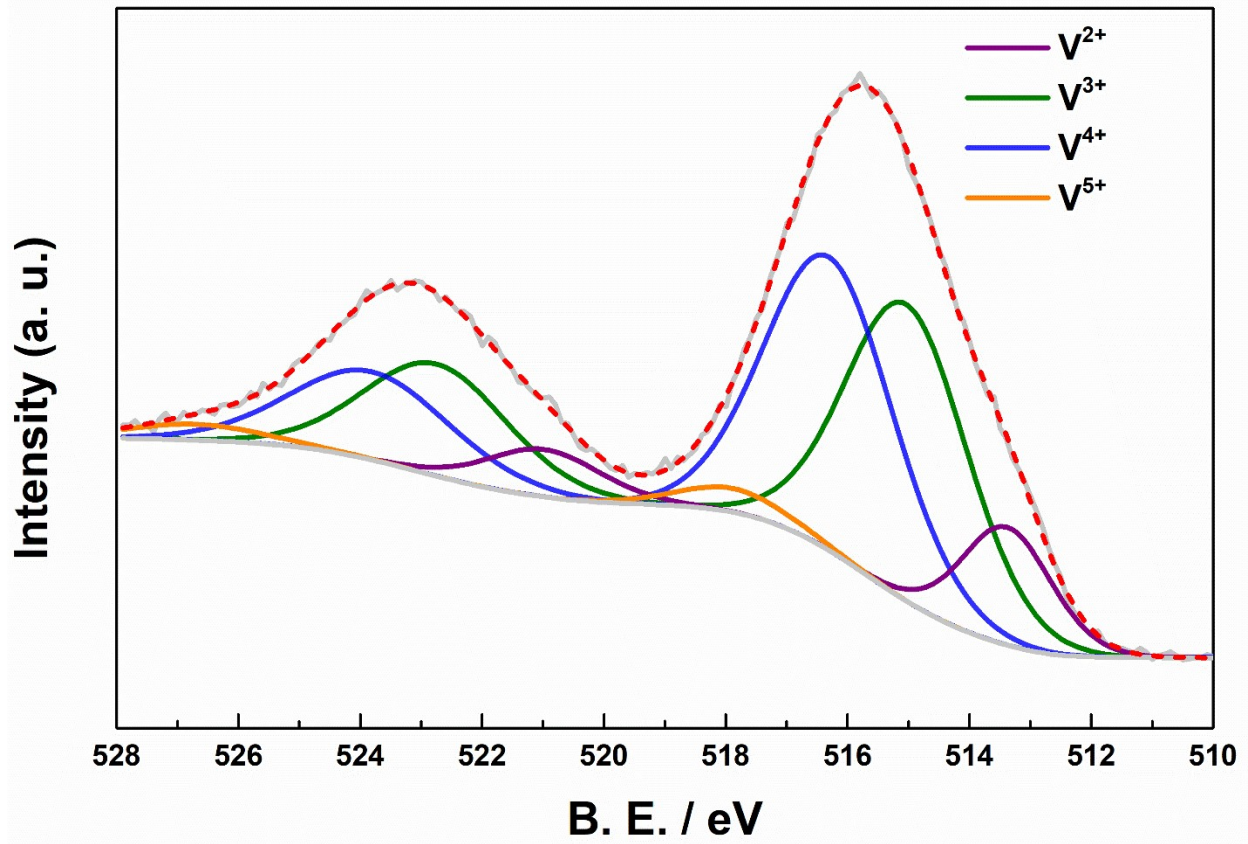


Figure S12. XPS of V2p spectra of VO_x-LSG composite.

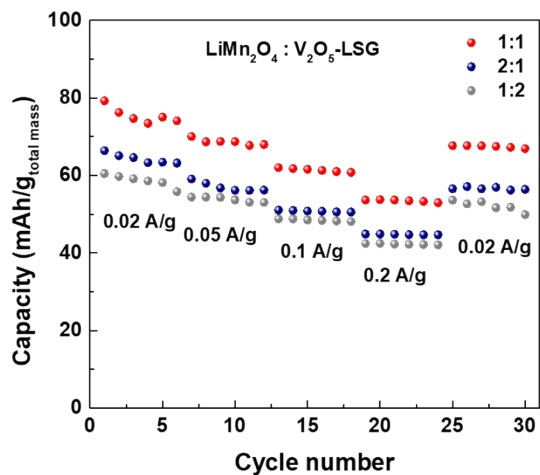


Figure S13. Rate performance of V₂O₅-LSG||LiMn₂O₄ cells at 0.02 A/g, 0.05 A/g, 0.1A/g, 0.2A/g and 0.02 A/g with LiMn₂O₄: V₂O₅-LSG mass ratio 1: 1, 2: 1 and 1: 2.

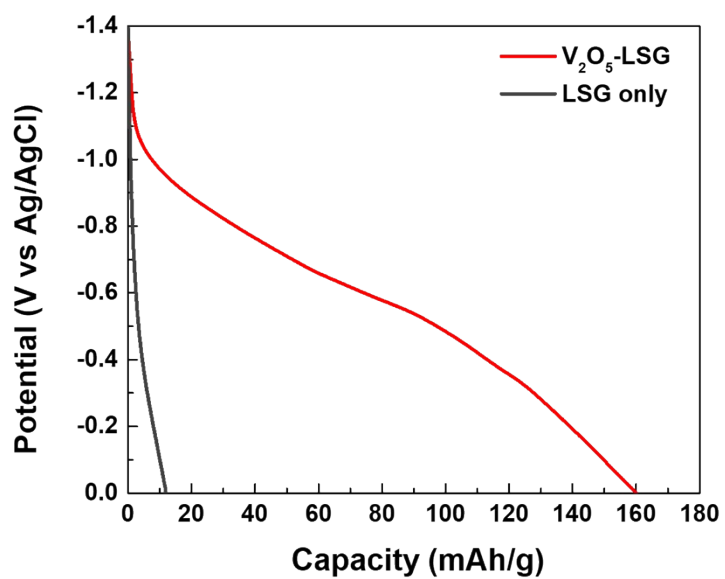


Figure S14. Capacity-voltage profiles of V₂O₅-LSG electrode and LSG only electrode at 0.1 A/g.

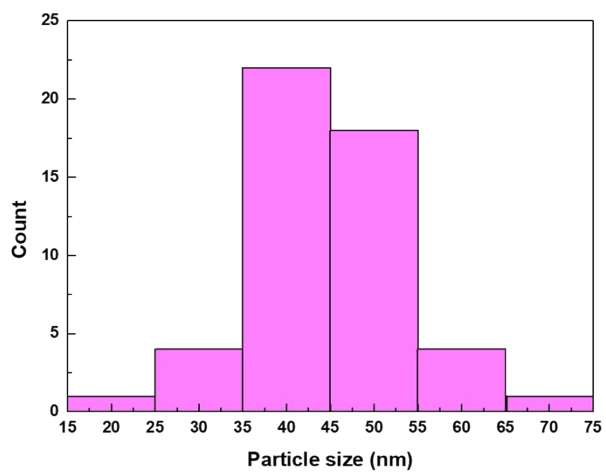


Figure S15. A plot showing the size distribution of VO_x particles based on **Figure 2c**.

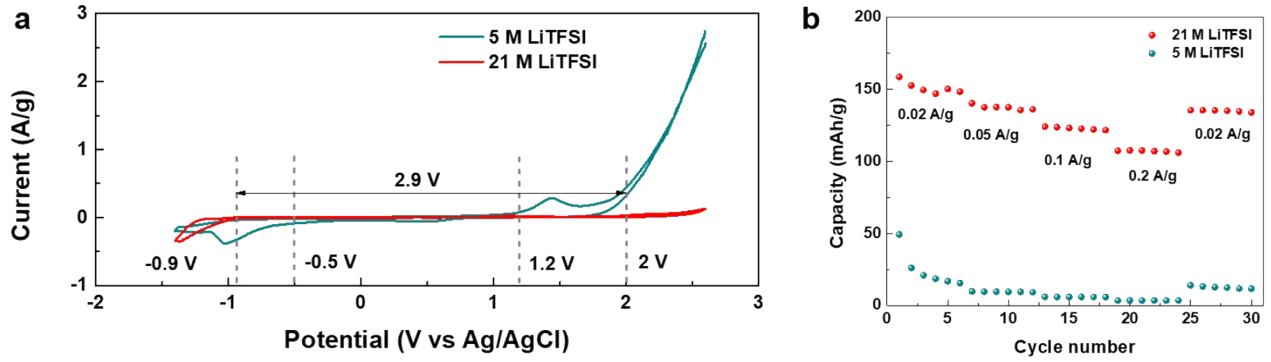


Figure S16. (a) Electrochemical potential window measured by cyclic voltammetry for 5 M and 21 M LiTFSI. (b) Rate performance of a V_2O_5 -LSG|| $LiMn_2O_4$ cell cycled at 0.02 A/g, 0.05 A/g, 0.1A/g, 0.2A/g and 0.02 A/g with 5 M and 21 M LiTFSI electrolyte.

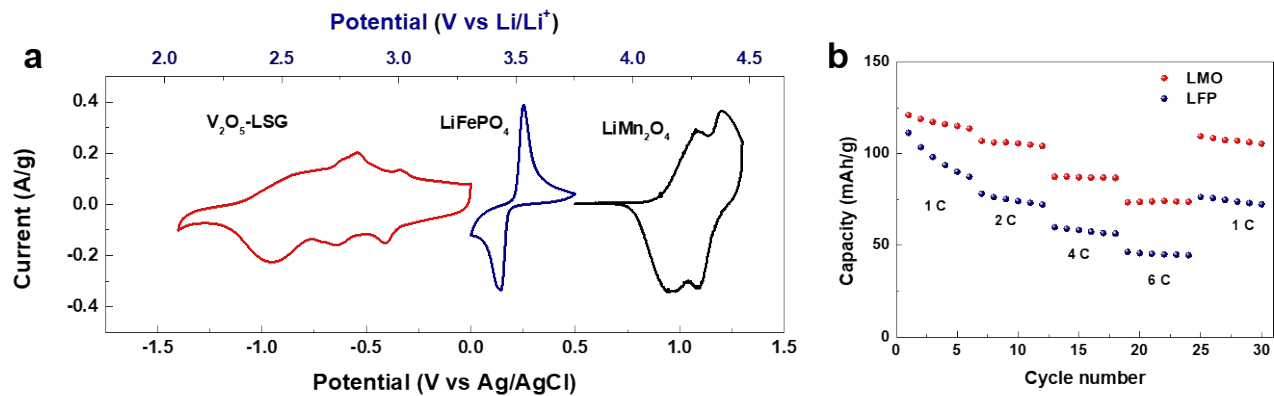


Figure S17. (a) Potential windows of V_2O_5 -LSG, $LiFePO_4$ and $LiMn_2O_4$ in 21 M LiTFSI electrolyte. (b) Rate performance of a V_2O_5 -LSG|| $LiMn_2O_4$ cell and a V_2O_5 -LSG|| $LiFePO_4$ cycled at 1 C, 2 C, 4 C, 6 C and 1 C.

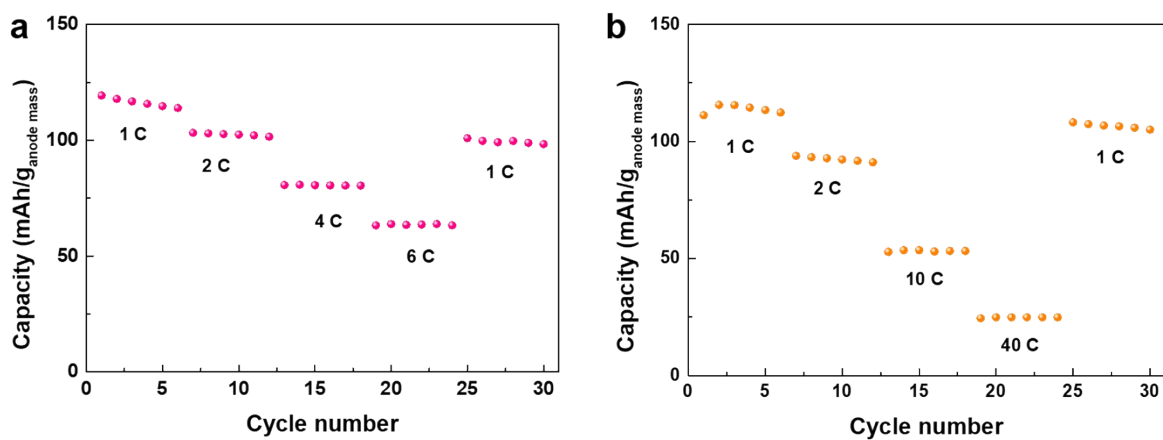


Figure S18. Rate performance of a V₂O₅-LSG||LiMn₂O₄ cell at (a) 1 C, 2 C, 4 C, 6 C and 1 C. (b) 1 C, 2 C, 10 C, 40 C and 1 C.

Table S1. Electrochemical Performance of a V₂O₅-LSG||LiMn₂O₄ Cell

Capacity (mAh/g)	Average voltage	Energy density (Wh/kg)	Current density (A/g)	time per discharge (h)	Power density (W/kg)	Figure showing data
75.00	1.087	81.53	0.01	6.0	13.6	Figure 5a
69.00	1.036	71.48	0.025	2.2	32.5	Figure 5a
61.00	1.066	65.03	0.05	1.0	65.0	Figure 5a
53.00	0.883	46.80	0.1	0.36	130.0	Figure 5a
26.00	1.300	33.80	0.25	0.104	325.0	Figure S18
12.00	1.300	15.60	0.5	0.024	650.0	Figure S18

References

- (1) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J Am Chem Soc* **1958**, *80* (6), 1339–1339. <https://doi.org/10.1021/ja01539a017>.