Supporting Information

VO_2 Nanoflakes as the Cathode Material of Hybrid Magnesium-Lithium-Ion Batteries with High Energy Density

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Experimental section

Synthesis of VO_2 nanoflakes

For a typical synthesis, vanadium dioxide nanoflakes were successfully prepared through a hydrothermal reaction.[1] Briefly, V_2O_5 (2 mmol), $H_2C_2O_4 \cdot 2H_2O$ (4.8 mmol) and PEG4000 (1.7 mmol) were dissolved in 33 mL deionized water, after vigorous stirring at 40 °C in a water bath for 24 h, a homogeneous liquid was obtained. Subsequently, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and stayed at 180 °C for 24 h. After cooled to room temperature, the prepared products were collected and washed with deionized water and pure alcohol several times and finally dried at 70 ° C for 24 h.

Preparation of Electrolytes

The APC electrolytes for MIBs were prepared according to Oren Mizrahi et al.[2] All chemical preparations and experiments were carried out under pure argon atmosphere in Vigor glove boxes (＜1 ppm of oxygen and water) at room temperature. The detailed process is as follows: 0.667 g aluminum chloride (Aldrich, 99.99%) dissolved in 15 mL THF (Aldrich, 99.9% and dried by activated 4 Å molecular sieves) slowly enough to avoid the white fog under vigorous stirring and kept for 12 h. Then the transparent solution was added to phenyl magnesium chloride (Macklin, 2 M solution in THF) dropwise under continuous stirring and the resulting light brown solution (Fig. S1) was stirred for another 12 h to form the APC solution. Finally, the hybrid MLIB electrolyte was obtained with the addition of various amounts of LiCl.

Material characterization

X-ray diffraction (XRD) measurements were performed to investigate the crystallographic properties using a D8 Advance X-ray diffractometer with a non-monochromated Cu Kα X-ray source. Field emission scanning electron microcopy (FESEM) images and energy dispersive X-ray spectra (EDS) were collected with a JEOL-7100F microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded by using a JEM-2100F microscope.

Measurement of electrochemical performance

The electrochemical properties were measured by assembly of 2016 coin-type cells in a glove box filled with pure argon gas, using a Mg foil as the anode, APC-LiCl as the electrolyte, and

cathode electrodes fabricated with 60% VO_2 flakes as the active material, 30% of acetylene black and 10% of PTFE (polytetrafluoroethylene). Galvanostatic discharge/charge cycling of the cells was performed in a potential range of 0.5-2 V vs. Mg^{2+}/Mg with a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy were measured with an electrochemical workstation (Autolab PGSTAT 302 and CHI 760D).

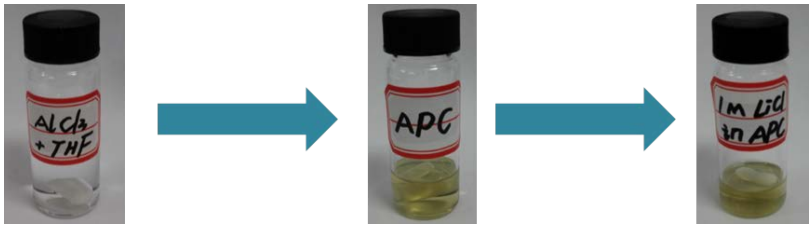

Figure S1. The transparent solution of $AlCl_3$ dissolved in THF, 0.25 M APC and 1 M LiCl in APC

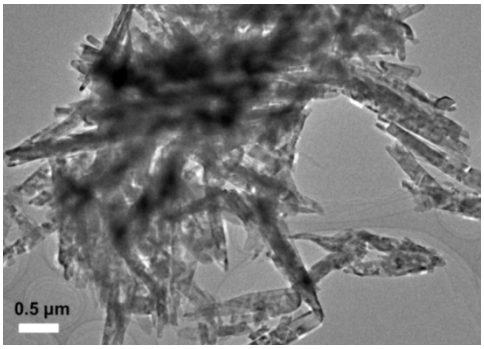

Figure S2. The TEM images of VO_2 nanoflakes with low magnification

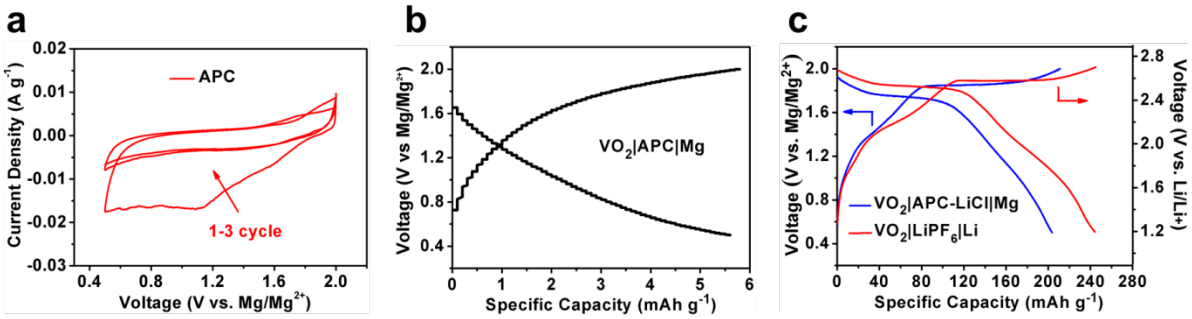

Figure S3. (a) CV curves of VO_2 cathode assembled in MIB in the range of 0.5-2 V at the scan rate of 0.1 mV S^{-1}. (b) Voltage profiles of VO_2|APC|Mg battery and (c) Voltage profiles of VO_2| APC-LiCl |Mg hybrid battery and VO_2| $LiPF_6$|Li LIB battery.

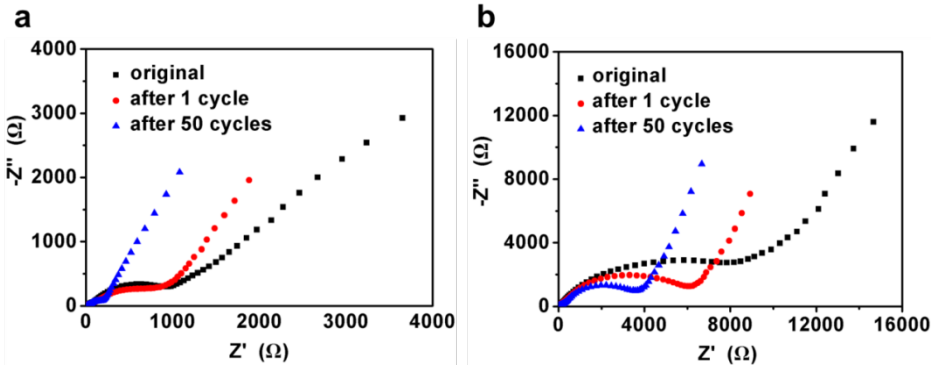

Figure S4. Nyquist plots of (a) VO_2|APC-LiCl|Mg battery and (b) VO_2|APC|Mg battery before cycling, after the first cycle and after 50 cycles.

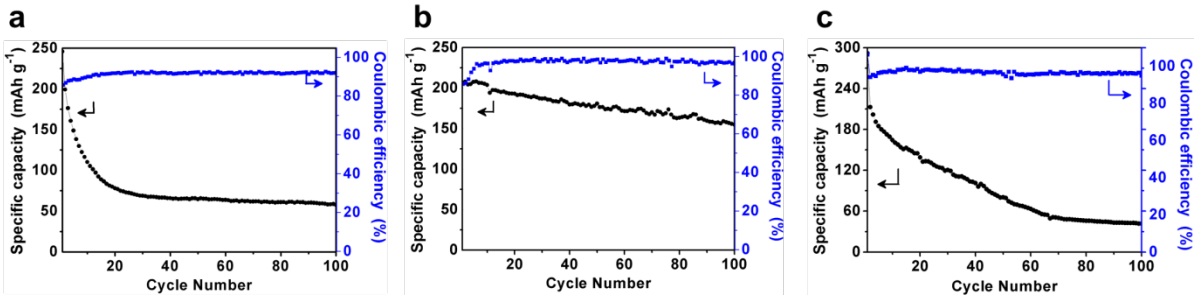

Figure S5. Cycling performance of LIB in THF-LiCl electrolyte and hybrid MLIBs in APC-LiCl electrolyte at the current density of 100 mA g^{-1} with the electrochemical window of (a) 1.2 – 2.7 V, (b) 0.5 – 2 V and (c) 0.01-2 V.

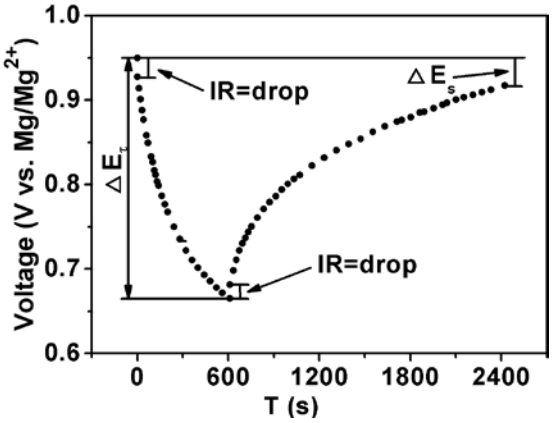

Figure S6. GITT potential response curve with time. The experiment was conducted at constant current pulse of 20 mA g^{-1} for 10 min followed by a relaxation period of 30 min.

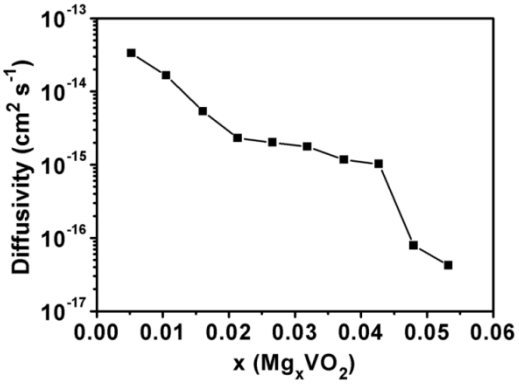

Figure S7. Mg ions diffusivity versus the state of discharge.

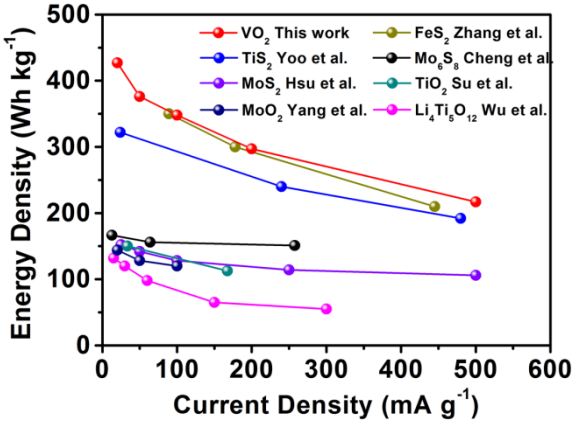

Figure S8. The comparison of the energy density of VO_2 based MLIB with previous MLIBs in coin cells at different current densities.

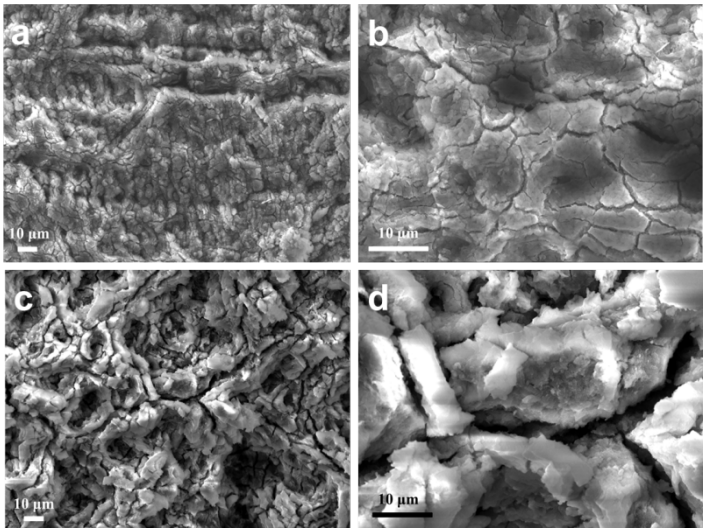

Figure S9. The SEM images of Li metal. (a-b) before cycles and (c-d) after 300 cycles.

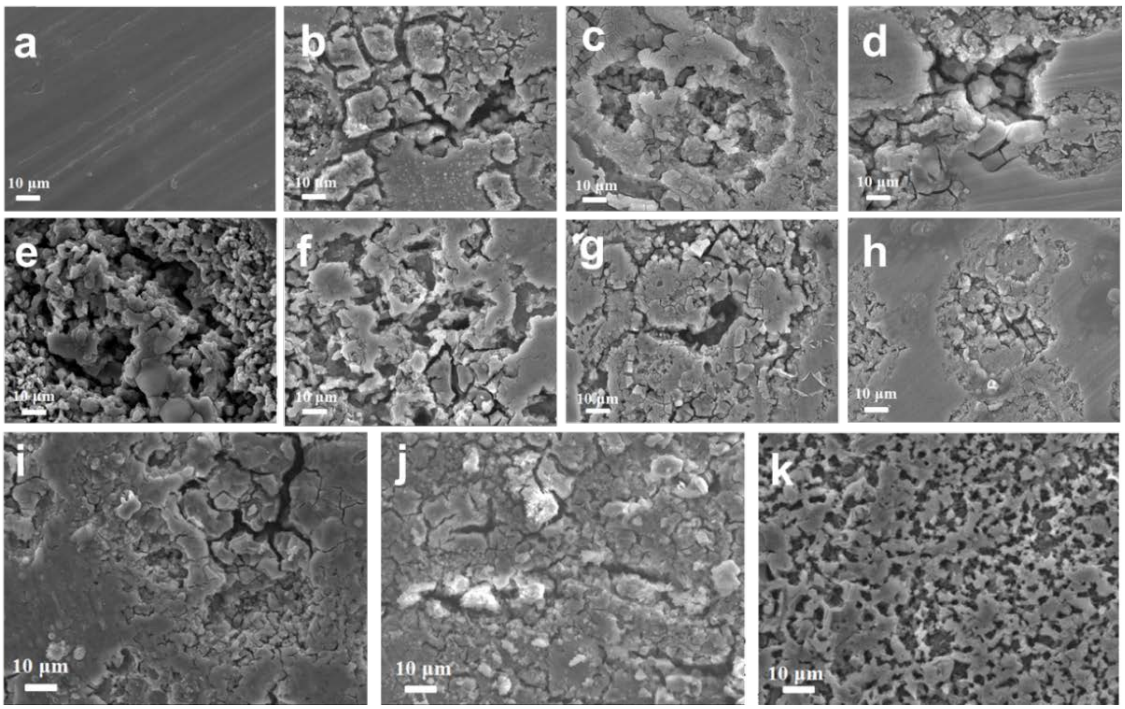

Figure S10. SEM images of Mg anode with the current density of 100 mA g^{-1} (a-e) are the SEM images of Mg anode in the 1st cycle respectively discharged to 2 V, 1.7 V, 1 V, 0.5 V, and 0.01 V. (f-h) recharge back to 1 V, 1.5 V, and 2V, (i-k) Mg anode after 100, 150, and 300 cycles.

$$D^{GITT} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

Scheme 1. Where τ refers to constant current pulse time, m_B, V_M, M_B, and S are the mass, molar volume, molar mass of the cathode material, and electrode-electrolyte interface area, respectively. ΔE_S is voltage difference during a single-step experiment, and ΔE_τ is the total change of cell voltage during a constant current pulse excluding the IR drop.

References

1. Niu, C.; Meng, J.; Han, C.; Zhao, K.; Yan, M.; Mai, L. VO_2 Nanowires Assembled into Hollow Microspheres for High-Rate and Long-Life Lithium Batteries. *Nano Lett.* **2014,** 14, 2873-2878.

2. Mizrahi, O.; Amir, N.; Pollak, E.; Chusid, O.; Marks, V.; Gottlieb, H.; Larush, L.; Zinigrad, E.; Aurbach, D. Electrolyte Solutions with a Wide Electrochemical Window for Rechargeable Magnesium Batteries. *J. Electrochem. Soc.* **2008,** 155, A103-A109.