

Supporting information

VO₂ Phase Change Electrodes in Li-ion Batteries

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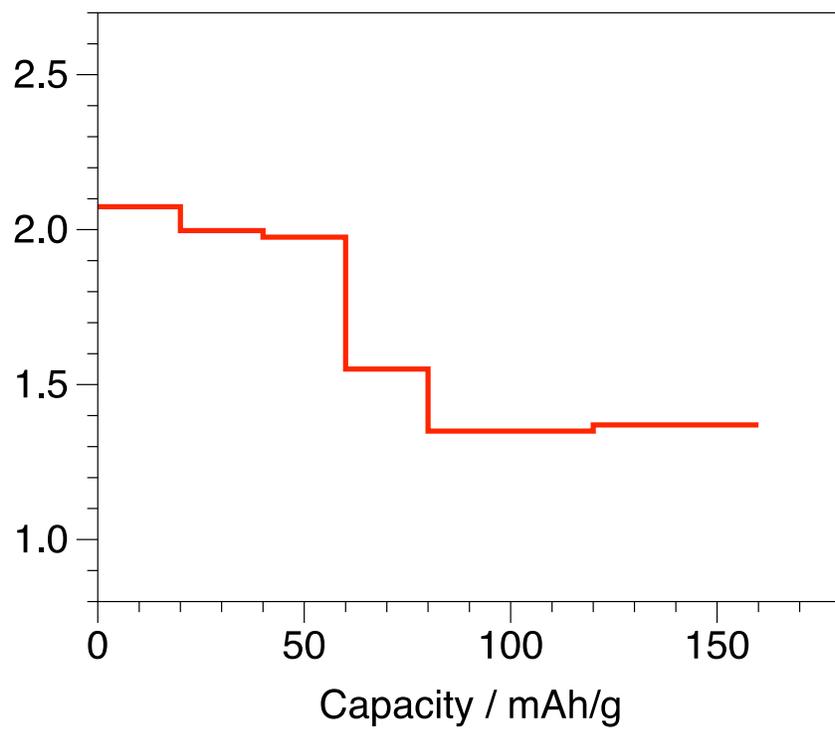


Figure S1. The simulated voltage discharge profile of Rutile VO₂

Electrolyte-electrode optimization

$\text{VO}_2(\text{M})$ half cells were initially assembled using 1M LiTFSI in EC-DMC (1:1 v/v) as electrolyte. The initial discharge capacity obtained at a current rate of C/10 (Theoretical capacity = 323 mA/g) was 44.8 mAh/g, corresponding to an insertion of Li equivalent to 0.14 per VO_2 unit. **Figure S2** shows the variation of discharge specific capacity of the $\text{VO}_2(\text{M})$ system in a conventional electrolyte at increasing scan rates. The Coulombic efficiency and the low capacity indicated a poor electrochemical behavior of this electrode-electrolyte pair. Further post-mortem analysis showed re-oxidation problem to V_2O_5 and further dissolution of the material into the electrolyte. Similarly, the $\text{VO}_2(\text{R})$ system at 70 °C had a more severe degradation mechanism that involved the re-oxidation of VO_2 to V_2O_5 and its further dissolution (or simultaneously) into the electrolyte causing the separator and anode to turn yellow upon cycling. Higher coloration was detected in the R phase due to an accelerated re-oxidation/dissolution at higher temperatures. (**Figure S3**)

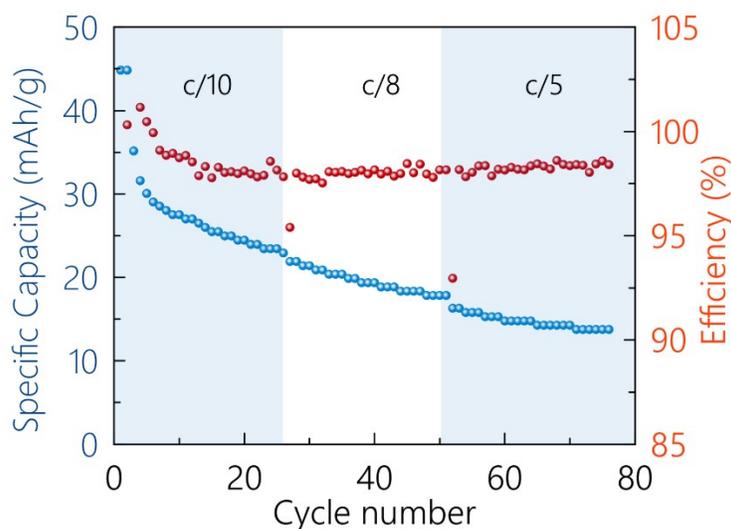


Figure S2. Cycling performance of $\text{VO}_2(\text{M})$ at 25 °C in increasing scan rates using a conventional organic electrolyte.



Figure S3. Left panel shows the dissolution of $\text{VO}_2(\text{M})$ into the EC: DMC organic electrolyte system (blue coloration) compared to no coloration in the ionic liquid electrolyte. Right panel shows the re-oxidation of VO_2 to V_2O_5 (characterized by its yellow coloration) and dissolution into the electrolyte at room and elevated temperatures.

Upon optimization of the electrode-electrolyte, a free-standing film electrolyte (based on polymer) was also used since it possesses the advantage of no liquid electrolyte being used, hence reduce the chance of dissolution

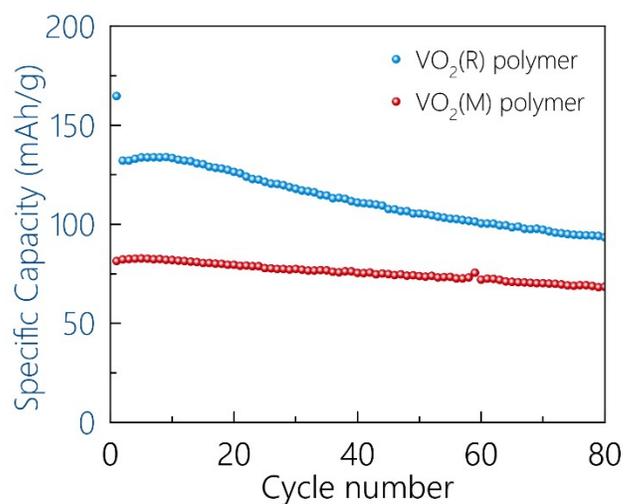


Figure S4 shows the cycling performance at a scan rate of C/10 for both R and M phase. Compared to the organic electrolyte, the M phase in this electrolyte showed a higher initial capacity of 82 mAh/g and a capacity retention of 81.4% at 80 cycles. The capacity increased in the R phase to 164.6 mAh/g and 126.8 mAh/g in the first and second discharge cycle, but, compared to the M phase, it reached a capacity retention (based on the second cycle) of 80% at the 50th cycle and a capacity retention of 66% at 80 cycles.

Table S1. Diffusion coefficient at 0.1 mV/s for VO₂(M) and VO₂(R)

Phase	peak	I _{peak} (A)	E _{peak} (V)	D (m ² /s)
M	cathodic	1.22x10 ⁻⁰⁴	2.37	1.4x10 ⁻¹³
	anodic	1.80x10 ⁻⁰⁴	2.73	3.0x10 ⁻¹³
R	cathodic	2.50x10 ⁻⁰⁴	2.44	6.7x10 ⁻¹³
	anodic	3.45x10 ⁻⁰⁴	2.63	1.3x10 ⁻¹²

Differential Scanning Colorimetry studies of VO₂(M) phase at different SOC's

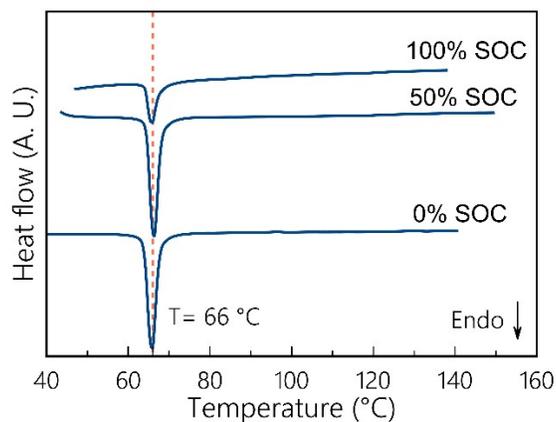


Figure S5 Displaying the DSC curves for the VO₂(M) phase at different SOC conditions (lithiated): 0%, 50%, and 100%. Hardly any peak shift is observed for VO₂(M) samples at 50% and 100% SOC, suggesting that lithiation hardly affects the MTI transition temperature in VO₂.