

Electronic Supporting Information

Stabilization of Decavanadates for the Application as Cathode Materials in Lithium-ion Batteries

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1. Instrumentation

Single-crystal X-ray diffraction (scXRD) revealed the crystal structure of **DMA{V₁₀}** using a Bruker D8 Quest single-crystal diffractometer with a Photon II detector using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on a Spectro Arcos FHS12.

Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209F1 analyzer at a heating rate of 10.0 K min^{-1} in a range between 30 and 700 °C under air in an Al₂O₃ crucible.

Attenuated total reflection-fourier transform-infrared (ATR-FT-IR) spectroscopy was recorded using a PerkinElmer Spectrum Two ATR-FT-IR spectrometer in a range between 4000 and 450 cm⁻¹.

Raman spectroscopy was performed on a Renishaw inVia microscope, using a 633 nm laser excitation with a laser power of 5 mW.

Powder X-ray diffraction (pXRD) patterns were collected using a STOE Stadi P diffractometer with Cu K α ($\lambda=1.5406 \text{ \AA}$) radiation in the range between 3 ° to 94 °.

Scanning electron microscopy (SEM) and **Energy-dispersive X-ray spectroscopy (EDX)** were performed on a Zeiss Gemini LEO 1550 VP equipped with a Silicon Drift Detector (OXFORD Instruments) using a 10 kV electron beam.

Electrochemical characterization

Galvanostatic Testing was conducted using Swagelok-type cells, which were assembled in an Ar-filled glovebox (H₂O < 1 ppm; Oxygen < 1 ppm). Electrode slurries were prepared inside the glovebox by manual mixing 70 wt.-% **DMA{V₁₀}** with 20 wt.-% carbon black and 10 wt.-% poly (vinylidene difluoride) (PVDF) binder with *N*-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry electrode fabrication. The mixed slurry was coated on an aluminum foil by the doctor blade technique (250 μm). The coating was pre-dried at 40 °C under vacuum for several hours and subsequently dried at 120 °C under vacuum for 12 h. Electrodes were cut (12 mm diameter) and contained approximately 1-2 mg of active material. As-prepared electrodes were used as positive electrodes versus metallic lithium (thickness: 0.38 mm) as anode. The electrolyte consisted of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and di-methyl carbonate (DCM) in a volume ratio of 1:1. A Whatman™ GF/C™ glass microfiber filter was used as separator. The half-cells were galvanostatically charged and discharged in the corresponding voltage ranges vs. Li⁺/Li using an Arbin BT2000 battery tester in a Binder KB115 climatic chamber at 25 °C. Specific capacities were referenced against the active material.

Cyclic Voltammetry (CV) was carried out at a sweep rate of 0.05 mV s^{-1} within a potential range between 1.0 and 4.2 V vs. Li⁺/Li using a Bio-logic VMP3 potentiostat in a Binder KB115 climatic chamber at 25 °C.

Electrochemical Impedance spectroscopy (EIS) was performed on a bio-logic VMP3 potentiostat in a frequency range between 10 mHz to 200 kHz and an amplitude of 10 mV.

2. Synthesis and Characterization

Synthesis of $(C_2H_8N)_5Li[V_{10}O_{28}] \cdot 5 H_2O$ (DMA{V₁₀})

V₂O₅ (5 g, 27.5 mmol, 1 eq.) were dissolved in water (50 ml) and basified with 4 M aqueous LiOH until pH 11 was reached. The solution was stirred for 1 h at 50 °C, which yielded a colorless solution. After cooling the solution to rt, the pH was decreased to 4.5 using 4 M HCl. To this solution, a solution of DMA·HCl (4.2 g, 51.5 mmol, 2 eq.) in water (10 ml) was added dropwise under stirring. Diffusion of ethanol into the reaction mixture gave orange plate crystals of DMA{V₁₀} suitable for X-ray diffraction.

Elemental analysis for C₁₀H₅₀N₅LiV₁₀O₃₃ in wt.-% (calcd.): C 9.27 (9.35), H 3.81 (3.92), N 5.49 (5.45).

ICP-OES for (C₂H₈N)₅Li[V₁₀O₂₈] · 5 H₂O in wt.-% (calcd.): Li 0.542 (0.54), V 39.85 (39.65).

Characteristic IR bands (in cm⁻¹): 3438 (m, b), 3157 (s, b), 2762 (m), 1600 (w), 1456 (m), 1014 (m), 988/974/944 (s), 838 (s), 805 (s), 731 (s), 579 (s).

Characteristic Raman bands (in cm⁻¹): 3029 (w), 2966 (m), 1466 (w), 994 (s), 956/949 (s), 889 (w), 879 (w), 840 (w), 594 (w, b), 456 (w, b), 313 (s), 255 (s), 210 (m), 187 (s), 175 (s), 150 (m), 102 (m).

PXRD diffractions (in °): 8.940 (s), 9.240 (s), 9.600 (s), 10.425 (s), 10.530 (s), 10.875 (m), 11.085 (m), 11.385 (s), 11.925 (w), 13.440 (m), 26.355 (w), 27.060 (w), 27.255 (w).

Thermogravimetric analysis (TGA):

Between 70 and 120 °C a weight corresponding to four water molecules is lost (observed: 5.6%, calc.: 5.6%). A weight loss between 145 and 360 °C corresponds to the loss of the remaining water molecule and all five DMA molecules (observed: 19.8%, calc.: 19.3%).

DMA{V₁₀}-120 and DMA{V₁₀}-145 were obtained by heating the sample under vacuum for 12 h at 120 °C and 145 °C, respectively.

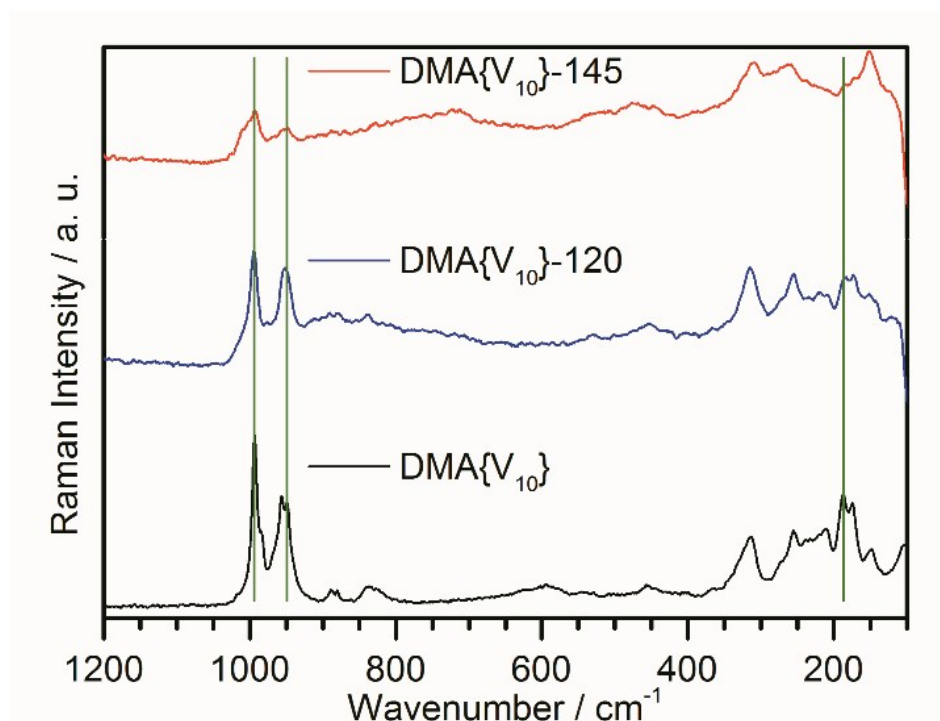


Figure S 1 Raman spectra of $\text{DMA}\{\text{V}_{10}\}$ (black), $\text{DMA}\{\text{V}_{10}\}$ -120 (blue) and $\text{DMA}\{\text{V}_{10}\}$ -145 (red) showing the structural stability at 120 °C and the starting decomposition at 145 °C.

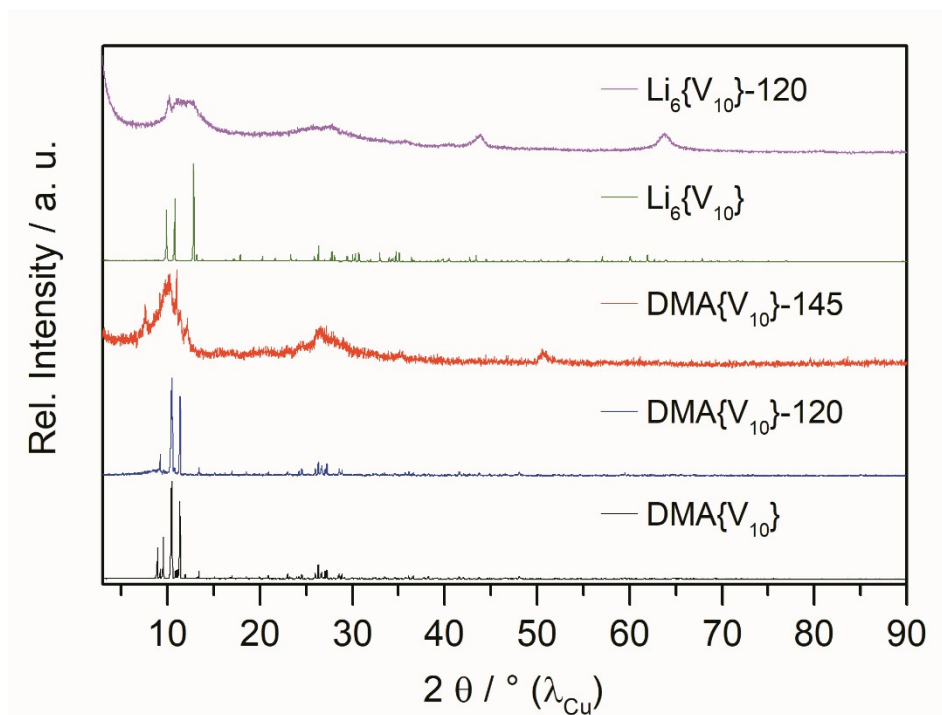


Figure S 2 Powder X-ray diffraction pattern between 3 and 94 ° of $\text{DMA}\{\text{V}_{10}\}$ (black), $\text{DMA}\{\text{V}_{10}\}$ -120 (blue) and $\text{DMA}\{\text{V}_{10}\}$ -145 (red) showing the structural stability at 120 °C and the starting decomposition at 145 °C. The pXRD pattern of $\text{Li}_6\{\text{V}_{10}\text{O}_{28}\} \cdot 16 \text{H}_2\text{O}$ before ($\text{Li}_6\{\text{V}_{10}\}$, green) and after ($\text{Li}_6\{\text{V}_{10}\}$ -120, pink) heating to 120 °C are shown for comparison.

3. Heat treatment of $\text{DMA}\{\text{V}_{10}\}$

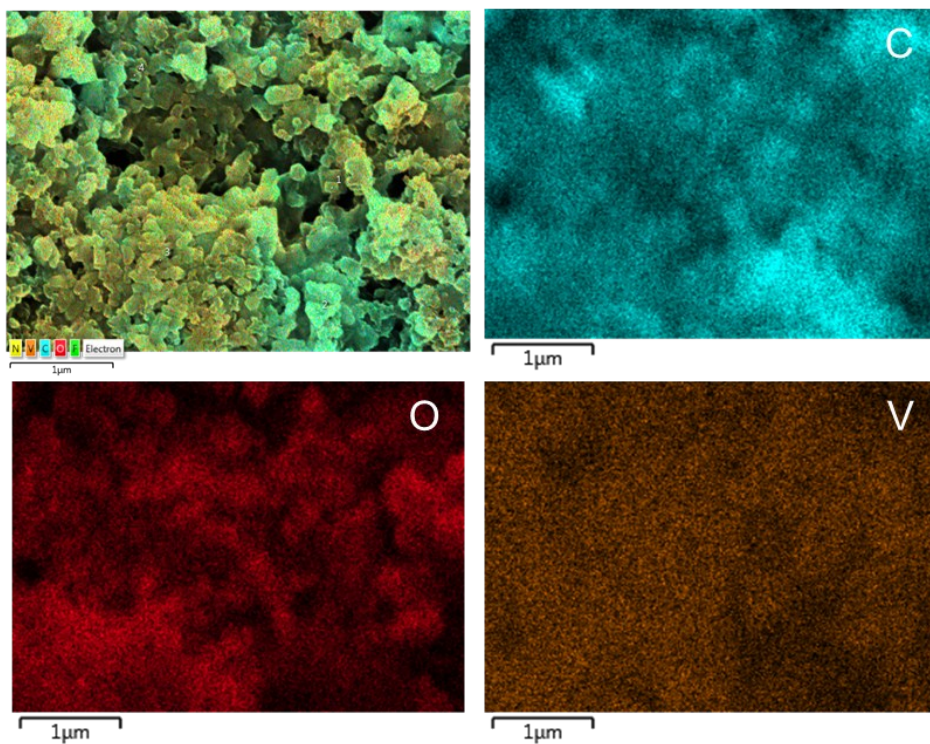


Figure S 3 EDX mapping of vanadium, carbon and oxygen and a layered image of the electrode surface showing the well dispersed distribution of the active material on the electrode surface.

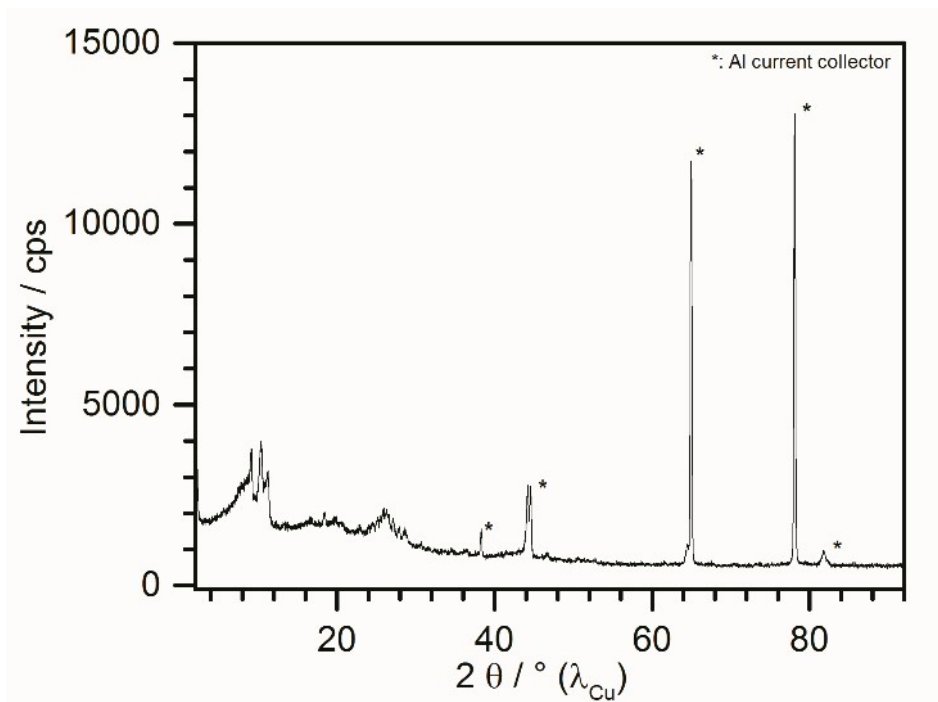


Figure S 4 Powder XRD spectrum of the as-prepared electrode.

4. Electrode Fabrication and Characterization

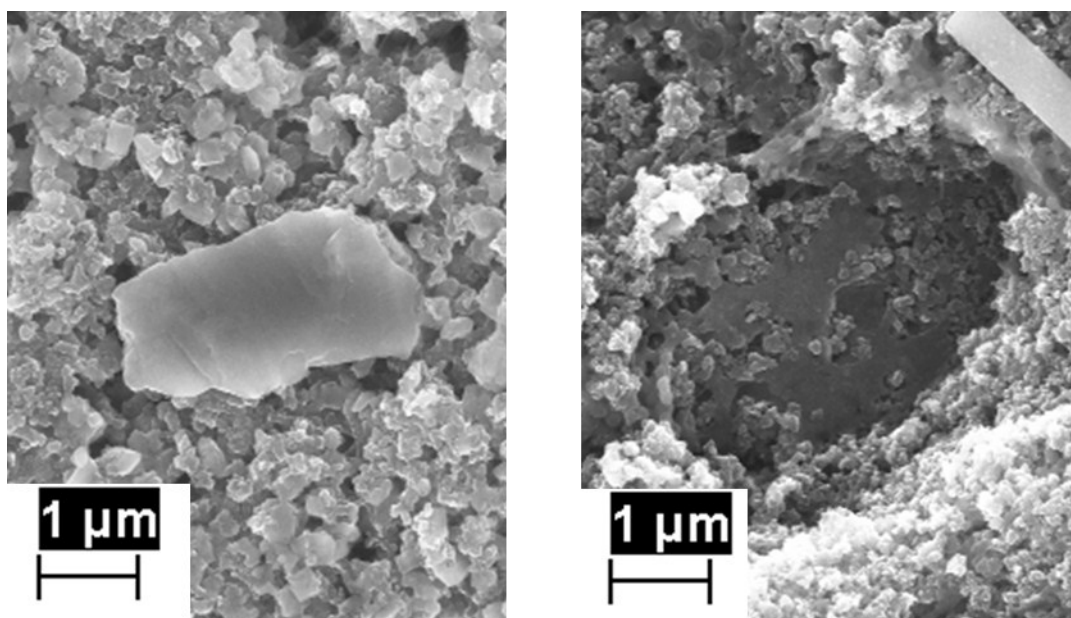


Figure S 5 Scanning electron micrographs of the electrode before (left) and after (right) cycling, indicating the disconnection of the observed microparticles.

5. Electrochemical Impedance Spectroscopy

Table S1 Fitting Values of the Electrochemical Impedance Spectroscopy.

	1
I	3.3E-7
R_e	3.0
A_w	285
τ	11
α	0.4
C	0.01
CPE₁	8.53E-4
n₁	0.29
R_{CT}	49
CPE_{DL}	2.2E-5
n_{DL}	0.84

6. Crystallographic Data of DMA{V₁₀}

Crystallographic data for: C₁₀H₃₇N₅O₃₁V₁₀, Mw = 1233.85 g mol⁻¹, triclinic, space group P-1, *a* = 11.228 Å, *b* = 16.754 Å, *c* = 20.784 Å, α = 81.27, β = 83.96, γ = 82.44 V = 3816.5 Å³, Z = 4, $\mu(\text{Mo-K}\alpha)$ = 2.436 mm⁻¹, 163183 reflections collected, 14440 unique which were used in all calculations; structure solution and refinement as done using OLEX2.³² Final R₁ = 0.0664 and wR₂ = 0.1613 (all data). Note that due to disorder, some of the dimethyl ammonium cations were refined over several positions and in part restrained using SIMU, DELU, and SADI commands. This caused some alerts in the CIF report which are typically found under these circumstances. CCDC 1955646 contains the crystallographic information. CIF files are available free of charge from the Cambridge Crystallographic Data Centre.

Data parameter	Value
CCDC no	1955646
Empirical formula	C ₁₀ H ₃₇ N ₅ O ₃₁ V ₁₀
Formula weight / g mol ⁻¹	1233.85
Temperature / K	150.0
Wavelength / nm	0.71073
Crystal system	Triclinic
Space group	P-1
<i>a</i> / Å	11.2284(4)
<i>b</i> / Å	16.7543(6)
<i>c</i> / Å	20.7837(7)
α / °	81.2690(14)
β / °	83.9623(14)
γ / °	82.4443(16)
Volume / Å ³	3816.5(2)
Z	4
Density (calc.) / g cm ⁻³	2.147
Absorption coefficient / mm ⁻¹	2.436
F(000)	2444.0
2 θ range for data collection	6.914 ° ≤ 2 σ ≤ 51.362 °
Index range	-13 ≤ <i>h</i> ≤ 13, -20 ≤ <i>k</i> ≤ 20, -25 ≤ <i>l</i> ≤ 25
Reflection collected	163183
Independent reflections	14440 [R(int) = 0.0374, R(σ) = 0.0171]
Refinement method	ShelXL Least Square Minimization
Data / restraints / parameters	14440 / 23 / 1072
Goodness-of-fit on F ²	1.131
Final R indices [I > 2 σ (I)]	R ₁ = 0.0572, wR ₂ = 0.1538
R indices (all data)	R ₁ = 0.0664, wR ₂ = 0.1627
Largest diff. peak and hole / e Å ⁻³	1.74 / -1.34

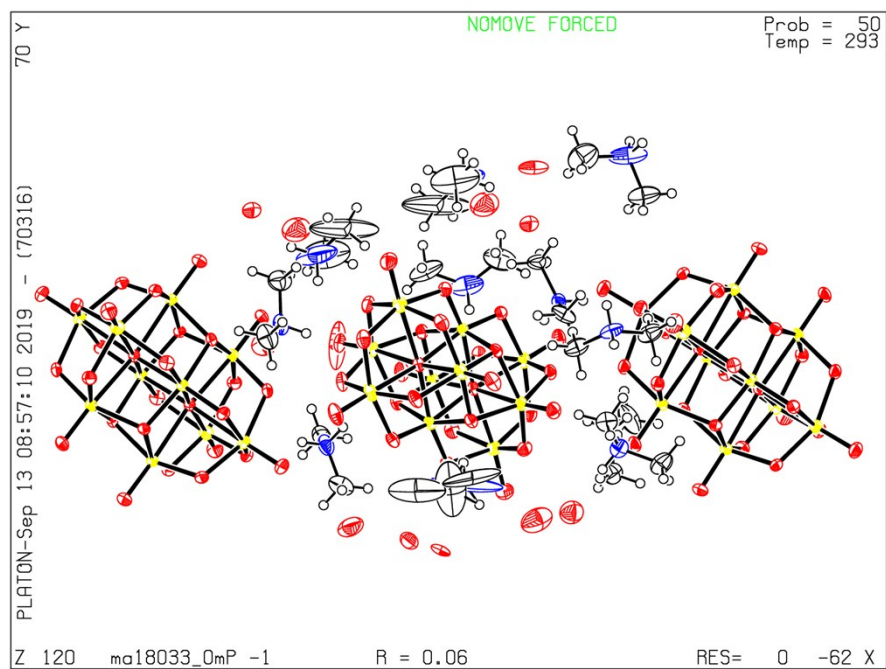


Figure S 6 ORTEP representation of **DMA{V₁₀}**, probability ellipsoids shown at 50%.

7. Author contribution

All authors conceived the experiments. S.G. and M.H.A. performed synthesis, characterization and thermal stability tests. S.G. performed battery performance tests and data analysis. All authors co-wrote the manuscript. S.G. and M.H.A. contributed equally to this study.