Enhanced Charge Storage of Nanometric ζ-V_2O_5 in Mg Electrolytes

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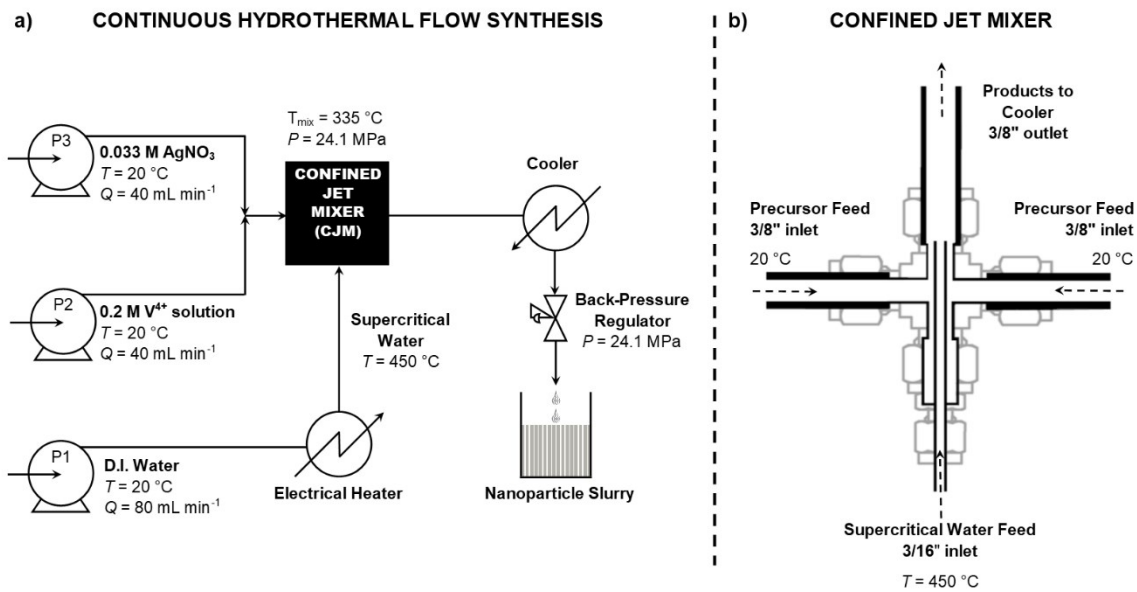

Figure S1. a) A schematic of the Continuous Hydrothermal Flow Synthesis (CHFS) apparatus; b) a schematic of the Confined Jet Mixer (CJM).

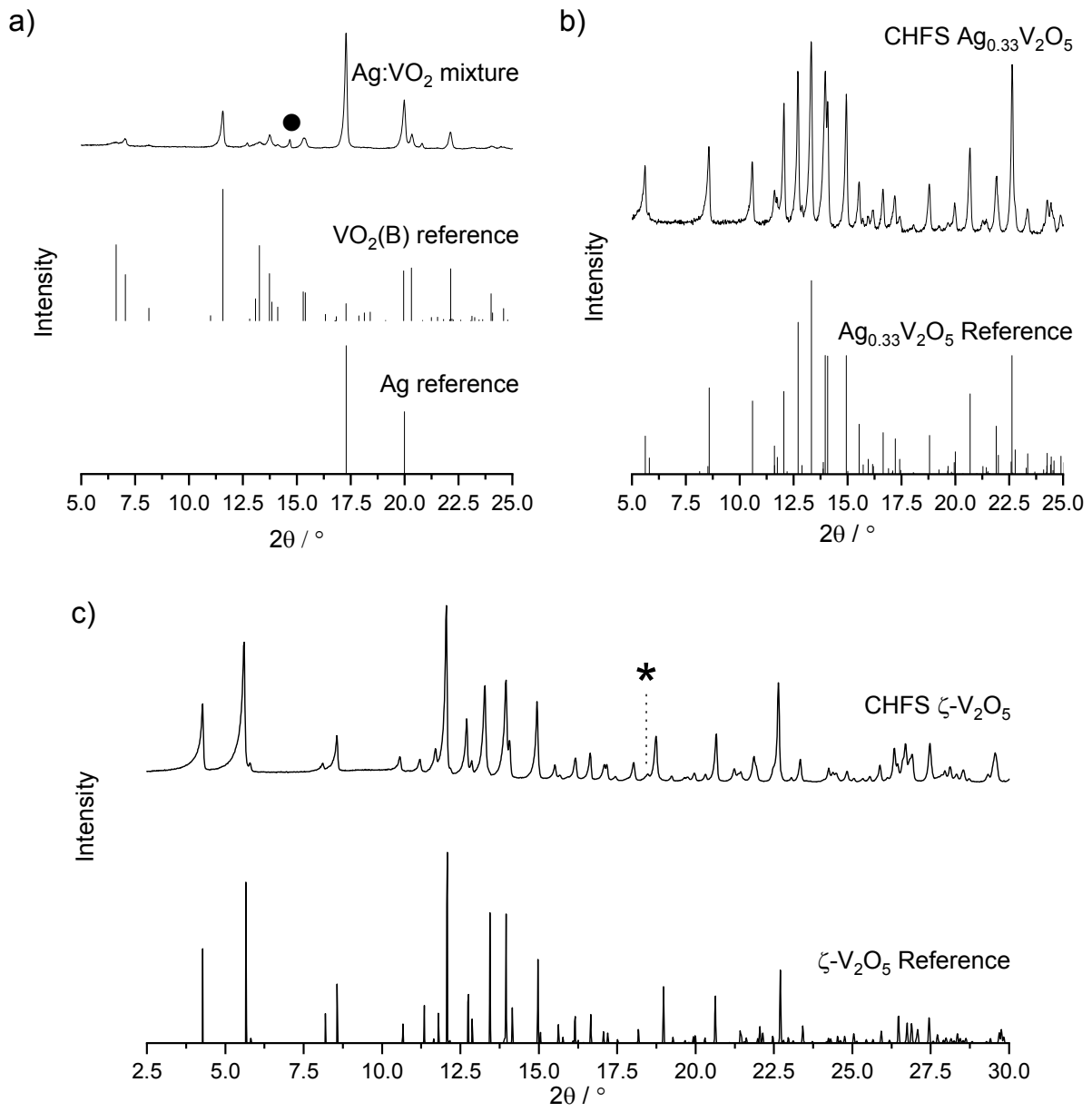

Figure S2. XRD patterns (Mo-Kα radiation) of a) the direct product of the CHFS process, which appeared to be a mixture of VO_2(B) and Ag (PDFs 00-081-2392 and 01-089-3722 respectively, although an additional diffraction peak was present as indicated with ● symbols), b) the annealed product CHFS $Ag_{0.33}V_2O_5$, which matched the $Ag_{0.33}V_2O_5$ reference pattern (PDF 01-082-1177), and c) the product of acid leaching, Nano ζ-V_2O_5, which matched a simulated diffraction pattern from parameters described in reference 30, although an additional feature was observed at 18.5° 2θ from the collimator, and is marked with a * symbol.

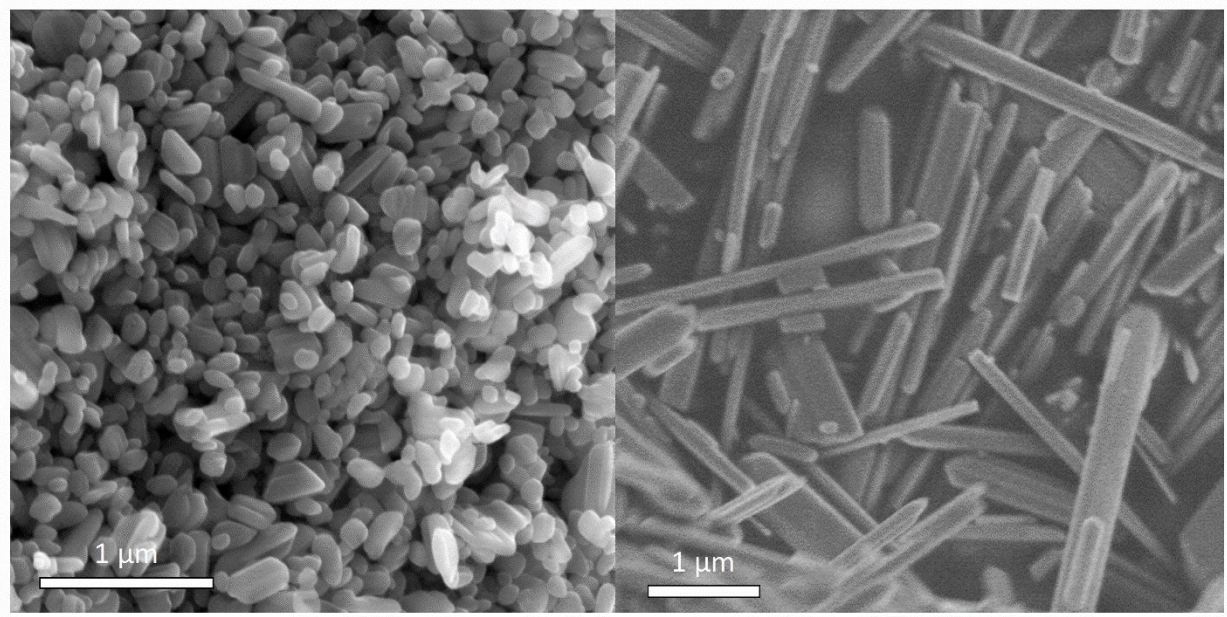

Figure S3. a) SEM image of the Nano ζ-V_2O_5 sample, displaying sub-100 nm semi-spherical crystallites with a small population of faceted rods up to 500 nm in length. b) SEM image of the Bulk ζ-V_2O_5 sample, displaying rod-morphology, with lengths in the µm-scale and an average width of ~150 nm.

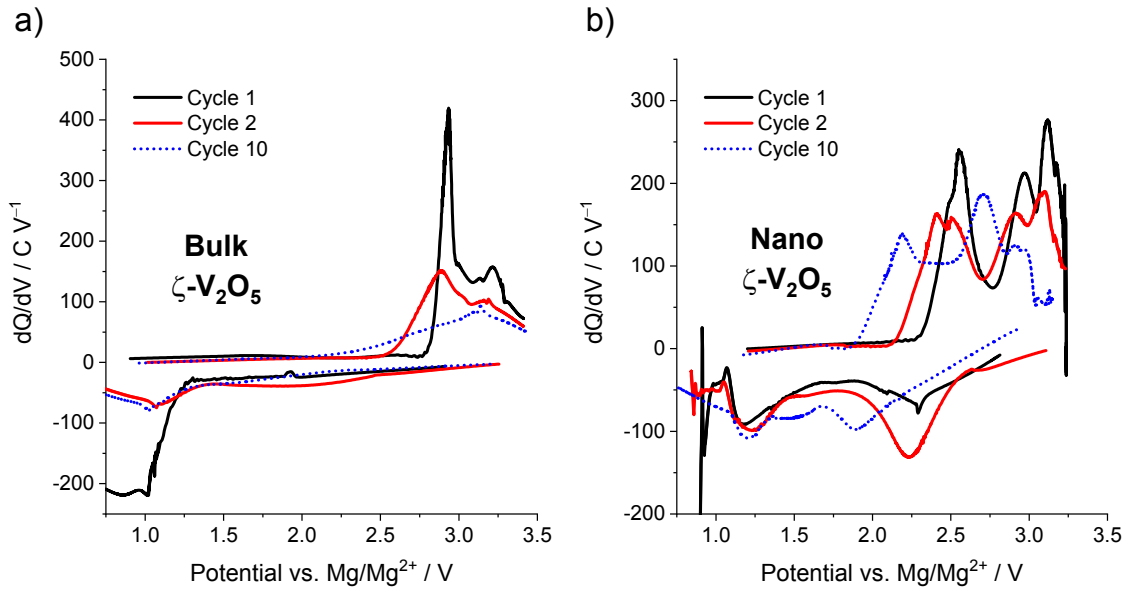

Figure S4. dQ/dV profiles of the first, second, and tenth cycles of a) Bulk ζ-V_2O_5 and b) Nano ζ-V_2O_5.

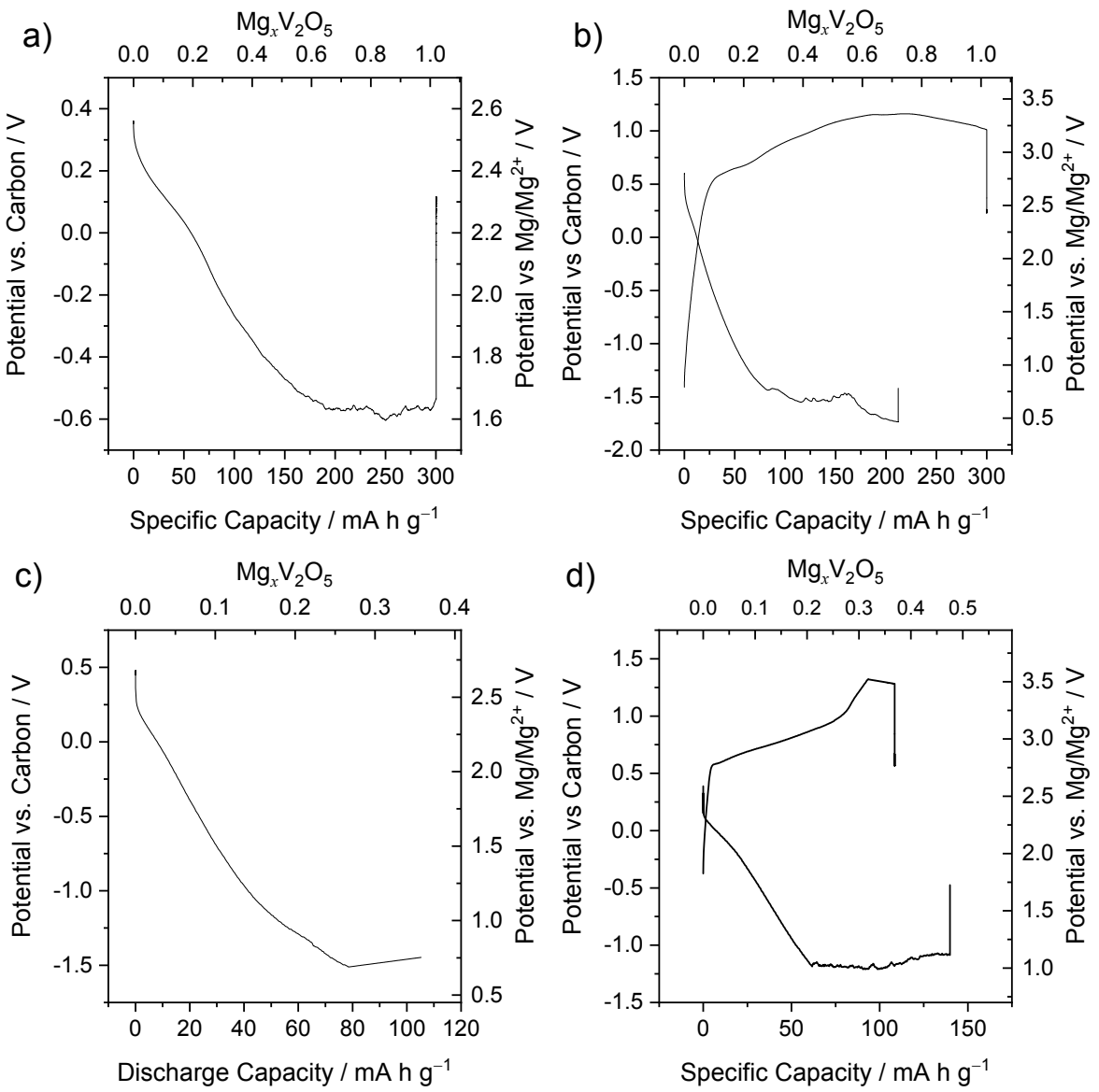

Figure S5. Discharge curves for the a) discharged and b) charged electrodes used for the XAS analysis. Discharged curves for the c) discharged and d) charged electrodes used for the XRD, EDS, and HAADF-STEM analysis.

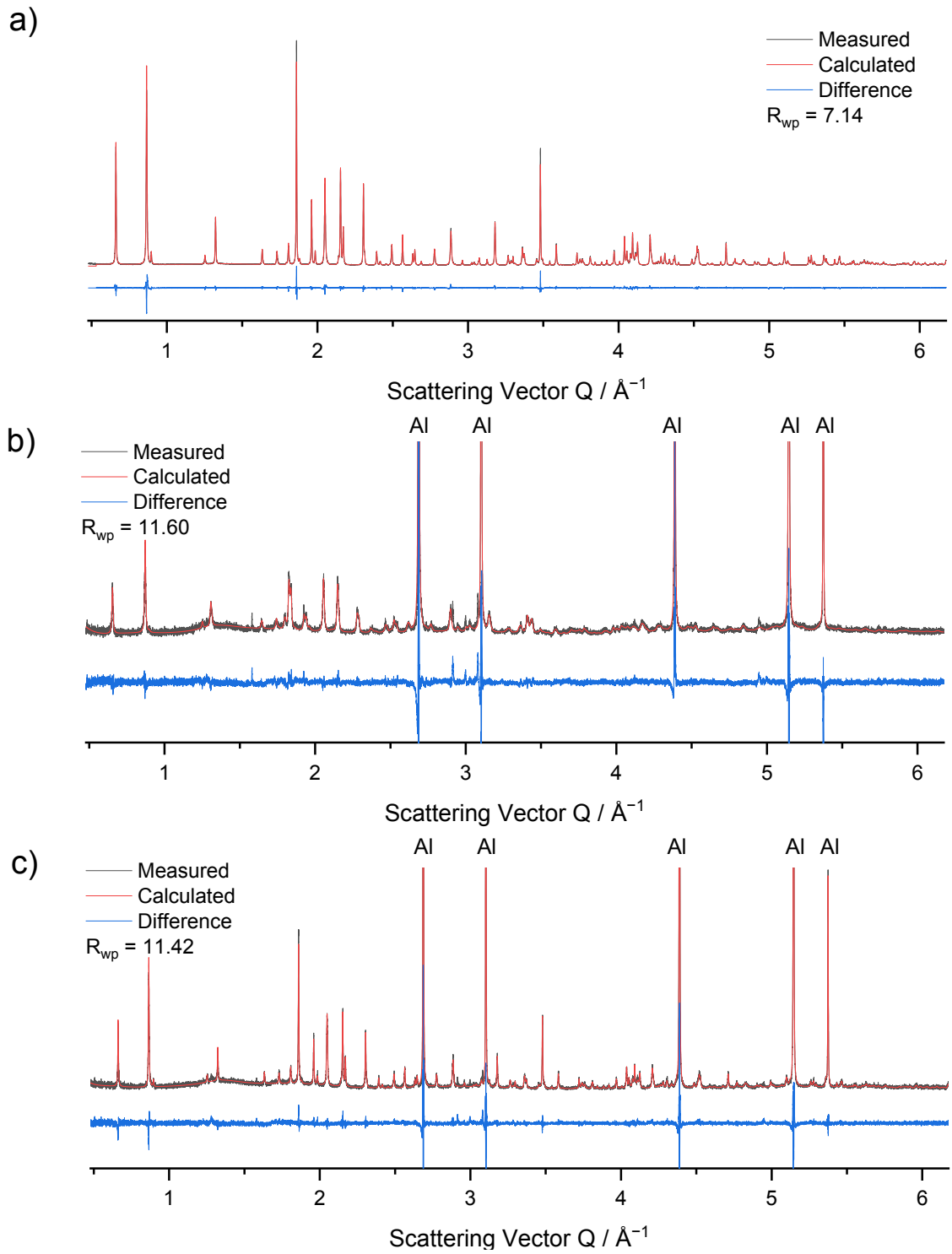

Figure S6. Rietveld refinement plots of the a) Pristine, b) Discharged and c) Charged electrodes, with Al electrode substrate diffraction peaks indicated within the plots. The diffraction angle was normalized to scattering vector Q to ensure consistent comparison between the diffraction patterns, as the wavelength λ varied slightly between measurements.

Table S1. Unit cell parameters and atomic coordinates for the pristine Nano ζ-V_2O_5 sample.

a = 15.40841(4) Å, b = 3.610815(6) Å, c = 10.078048(20) Å, β= 109.56366(17)°, V = 528.342(2) Å^3 Space Group *C12/m1*, R_{wp} = 7.14, χ^2 = 1.23					
Atom	***x***	***y***	***z***	**Occupancy**	**B_{eq}**
V1	0.33790(3)	0	0.10134(4)	1	0.378(8)
V2	0.11646(3)	0	0.11866(4)	1	0.380(8)
V3	0.28803(3)	0	0.40974(5)	1	0.414(9)
O1	0	0	0	1	0.52(4)
O2	0.10629(11)	0	0.27069(15)	1	0.76(3)
O3	0.13377(11)	0.5	0.07729(14)	1	0.18(3)
O4	0.26295(10)	0	0.22174(15)	1	0.31(3)
O5	0.43610(10)	0	0.21925(15)	1	0.90(3)
O6	0.31506(10)	0.5	0.05500(14)	1	0.27(3)
O7	0.39754(11)	0	0.47083(16)	1	1.10(3)
O8	0.25742(10)	0.5	0.42610(15)	1	0.45(3)
Na	0.00128(17)	0	0.4067(2)	0.4430(18)	1.89(6)

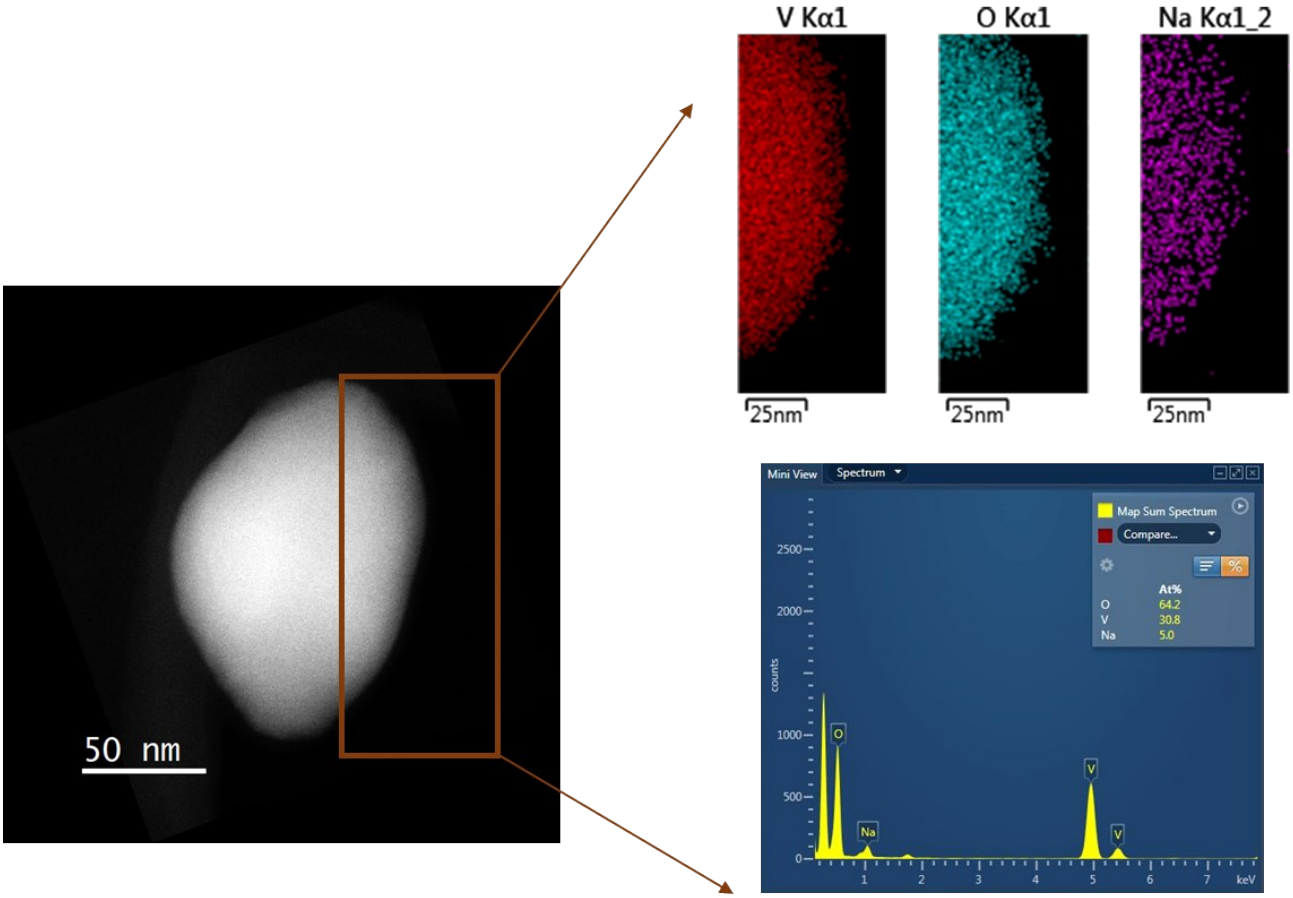

Figure S7. EDS analysis of a particle within the Pristine electrode.

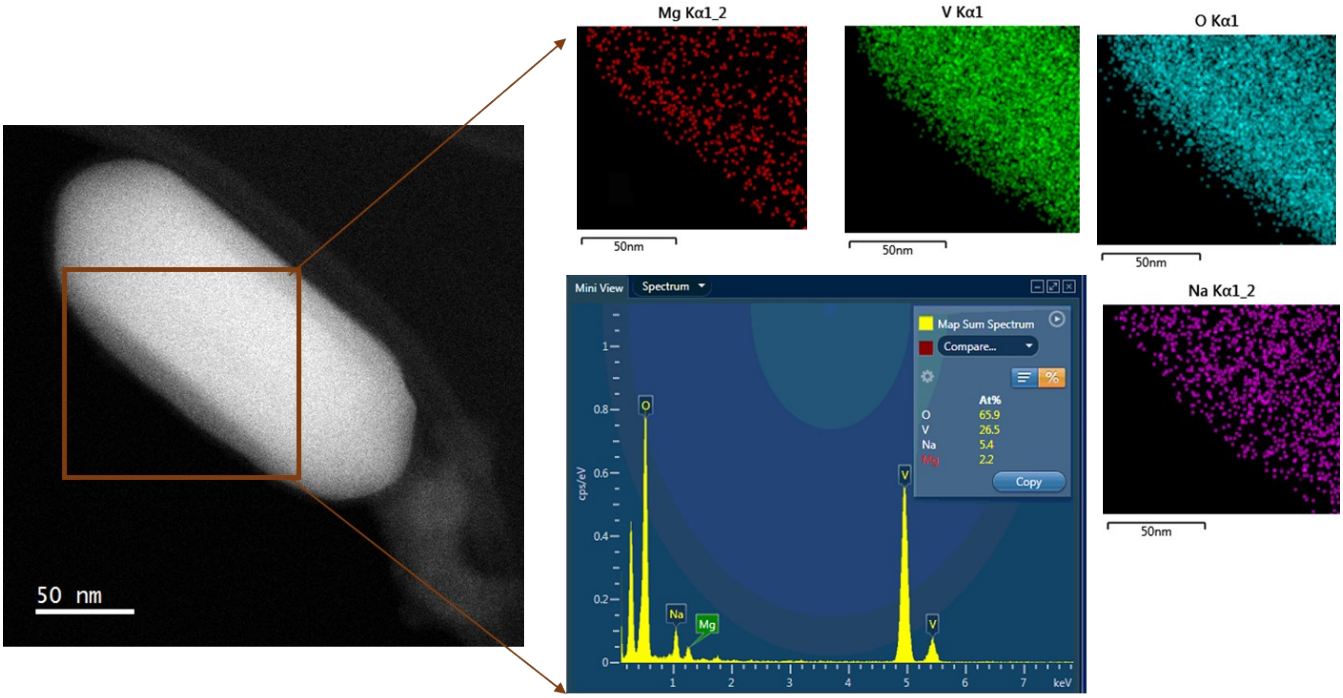

Figure S8. EDS analysis of a particle within the Discharged electrode.

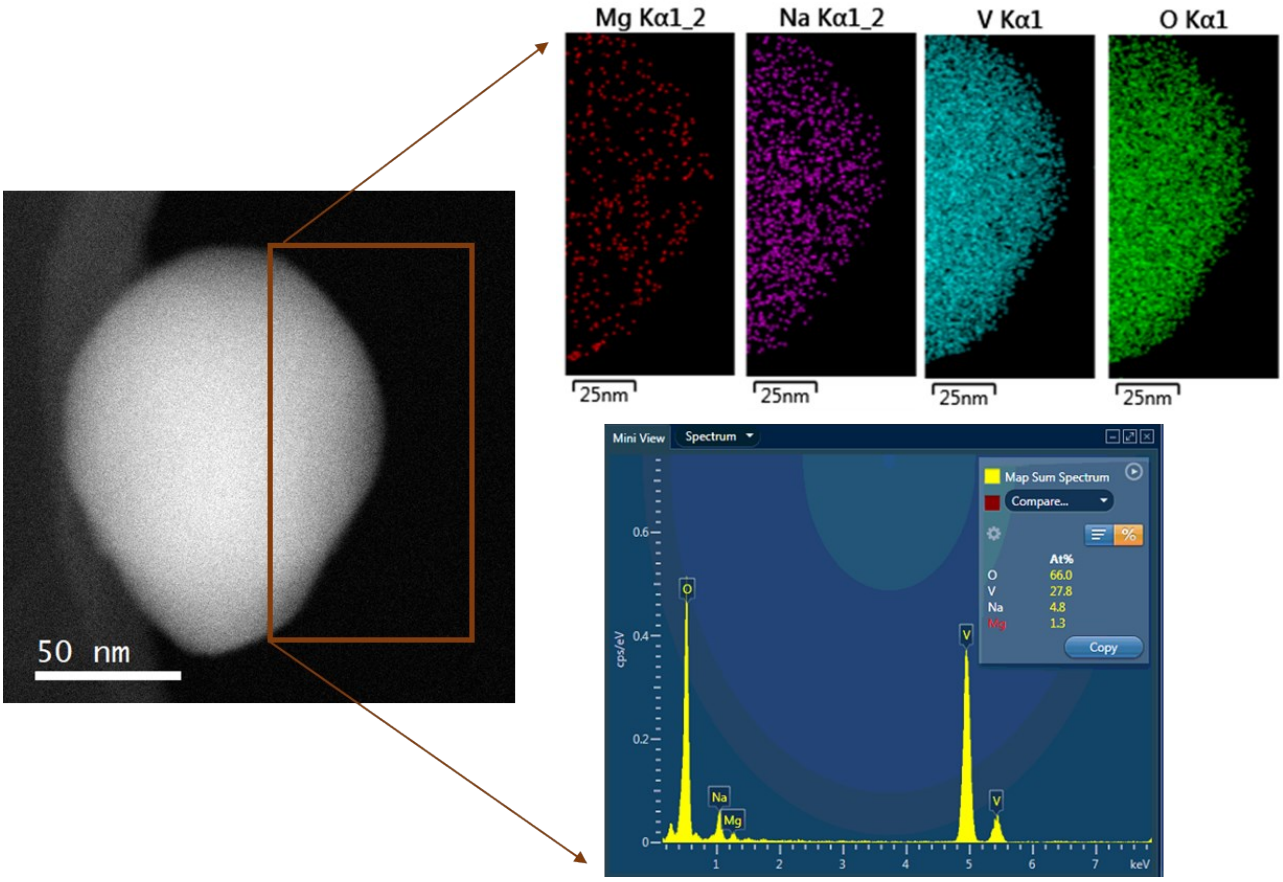

Figure S9. EDS analysis of a particle within the Charged electrode.

Table S2. Elemental composition found by EDS characterization.

Material	Na content	Mg content	V content[a]
Pristine[b]	0.31(5)	0	2
Discharged[b]	0.45(14)	0.18(11)	2
Charged[b]	0.40(13)	0.09(5)	2

[a] The atomic content has been normalized such that V = 2 in all cases, allowing facile stoichiometric comparison between the pristine, discharged and charged states. [b] Elemental composition averaged over a minimum of 5 particles.

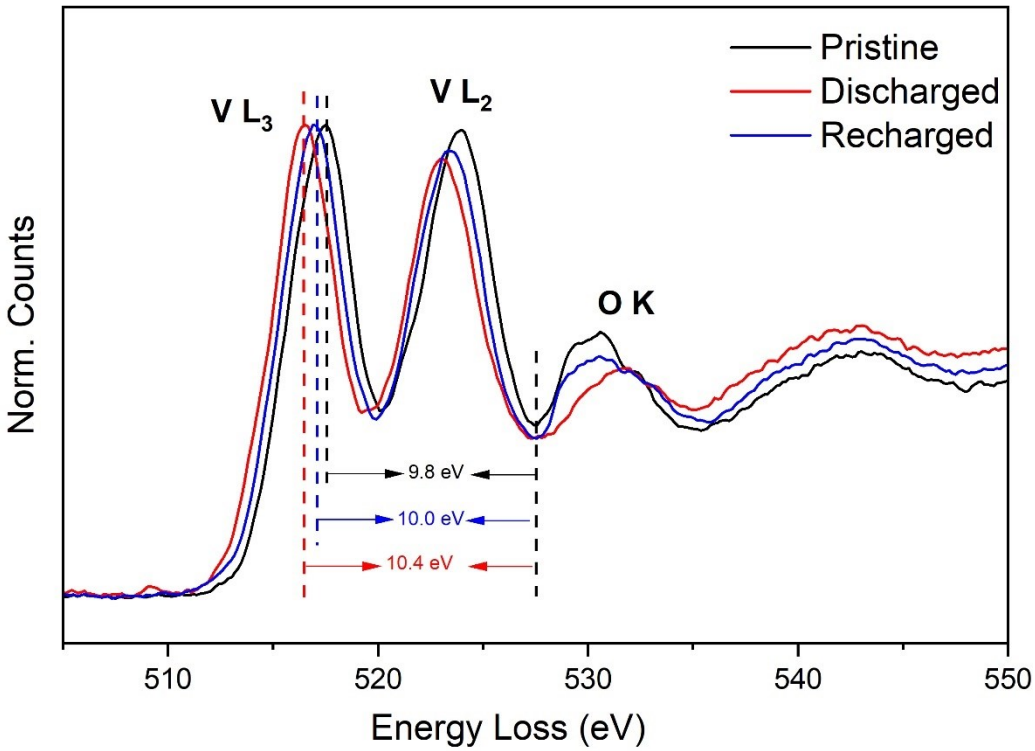

Figure S10. a) Electron Energy Loss Spectroscopy (EELS) spectra of the pristine, discharged and charged electrodes of Nano ζ-V_2O_5.