Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Bioinspired, High-Stability, Nonaqueous Redox Flow Battery Electrolytes

Haobo Huang,[a] Rachael Howland,[a] Ertan Agar,[b] Mahnaz Nourani,[b] James A. Golen,[a] Patrick J. Cappillino*[a]

General:

Dowex 50WX4, zinc acetate dihydrate and tetramethylammonium hydroxide were purchased from Acros organics. Bromoacetic acid, hydroxylamine hydrochloride, calcium chloride and hydrochloric acid were purchased from Alfa Aesar. Vanadyl bis-acetylacetonate and ferrocene were purchased from Strem chemicals and 2-propanol and dimethylsulfoxide were purchased from Fisher Scientific. All reagents and solvents were used without purification except DMSO, which was distilled over 4A molecular sieves and degassed, and ferrocene, which was sublimated prior to use in electrochemical experiments. Tetrabutylammonium hexafluorophosphate was purchased from Alfa Aesar, recrystallized 3x from ethanol and water, and dried at 55°C under vacuum prior to use in electrochemical experiments. Tetraethylammonium hexafluorophosphate was purchased from Alfa Aesar, recrystallized 3x, from water and dried at 55° under vacuum before use.

Infrared Spectroscopy was performed with a ThermoFisher is5 using an ATR attachment. UV-vis spectra were measured using a ThermoFisher Evolution 220 spectrometer. Static cell electrochemical experiments and cyclic voltammetry was carried using a Princeton Applied Research Versastat 3 potentiostat. X-ray crystallography was carried out with a Bruker D8 Venture X-ray instrument. NMR spectroscopy was carried out using a 400 MHz Bruker Avance III spectrometer.

Synthetic Methods:

N-hydroxyiminodiacetic acid (H_3HIDA):

Zinc(ii) N-hydroxyiminodiacetate was synthesized using literature procedures and verified as matching published infrared spectra.[3] Subsequently, N'-hydroxyiminodiacetic acid was synthesized using a modification of published methods.[3] The zinc salt (16.0 g, 75.4 mmol) was added to 125 mL water and 12M HCl was added slowly until it dissolved (~50 mL). It was then loaded on an ion-exchange resin (Dowex 50WX4) and eluted with de-ionized water. Eluent was dried under reduced pressure to obtain a white, micro-crystalline product matching literature values for infrared[3] and NMR spectroscopy (1H, D_2O).[5] 45% Yield (36.5 g, 172 mmol).

Calcium(ii) vanadium(iv)bis-hydroxyiminodiacetate pentahydrate (CVBH):

CVBH was prepared by dissolving H_3HIDA (1.97 g, 13.2 mmol) in 50 mL of DI water followed by addition of vanadylbis-acetylacetonate (1.75 g, 6.60 mmol) and stirring for one hour. Calcium chloride (0.734 g, 6.60 mmol) was then dissolved in 25 mL of DI water and added, followed by another hour of stirring. Approximately 300 mL of 2-propanol was added to the reaction mixture, which was left at 9°C overnight to crystallize. A blue powder was collected by filtration to yield 1.53 g (3.23 mmol, 49% yield). The identity of the product was confirmed using X-ray crystallography, which matched that previously reported.[6] IR (ATR)/cm^{-1}: 3322 (NH), 2988 (CH), 1588 (CO); UV-vis (DMSO): 575 nm (27.6 $M^{-1}cm^{-1}$), 800 nm (24.1 $M^{-1}cm^{-1}$).

Bis-tetramethylammonium vanadium(iv)bis-hydroxyiminodiacetate pentahydrate:

The vanadium bis-hydroxyiminodiacetate dianion was prepared with two tetramethylammonium counter-cations by replacing 1.0 equivalents of $CaCl_2$ in the above procedure with 2.0 equivalents of tetramethylammonium hydroxide. A blue powder was collected by filtration to yield 0.3103 g (0.556 mmol, 21% yield). Crystals were obtained through slow diffusion of methanol into an aqueous solution. IR (ATR)/cm^{-1}: 3402 (NH), 3031, 2962 (CH), 1617 (CO), 1488 (CN).

Static Cell Electrochemistry:

Cyclic voltammetry was carried out in DMSO using a 3mm glassy carbon electrode as working electrode, a Pt wire counter electrode, a silver wire pseudo reference electrode and tetrabutylammonium hexafluorophosphate as supporting electrolyte. Ferrocene was used as an internal potential reference. Static cell cycling was carried out using graphite felt (Alfa Aesar, part # AA14630RR) which was heat-treated in a furnace at 250°C under air, overnight, before use.

Flow Cell Electrochemistry:

For the symmetric flow cell experiment, a flow cell with 3 layers of 250 µm carbon paper electrodes (AvCarb F250A – they were received as thermally activated using a proprietary cycle) and 2 layers of Teflon gaskets were used in each half-side. Electrodes with an active area of 10 cm^2 were compressed by ~33.3% in the assembled flow cell. Nafion 212 was selected as the membrane material. 25 mL of electrolyte (0.01 M of CVBH solution in DMSO) is used in each half-cell. This solution was prepared by oxidizing a 25 mL, 0.01M solution of CVBH from vanadium(iv) to vanadium(v) at 1.0 mA and mixing with a second 25 mL, 0.01 M solution of CVBH in the vanadium(iv) oxidation state (as synthesized) (Figure S4). A peristaltic pump (Masterflex L/S Series) with silicon tubing (Masterflex, 1.6 mm inner diameter) drove the electrolyte through the flow cell at 80 mL min^{-1}.

X-ray Crystallography:

Bis-tetramethylammonium vanadium(iv)bis-hydroxyiminodiacetate pentahydrate ($[TMA]_2[VBH]$)

A blue colored crystal was mounted on a Cryoloop with oil. Data were collected at 200K using Mo K alpha radiation and data were corrected for absorption with SADABS. Structure was solved by direct methods. All non-hydrogen atoms except oxygen O11 were refined anisotropically by full matrix least squares on F^2. Hydrogen atoms on oxygen atoms O11, O12, and O13 were found from a Fourier difference map and were allowed to refine isotropically with O-H distance of 0.86 (0.005, 0.01 or 0.02) angstroms and 1.50 Ueq of the parent oxygen atom. Oxygen atom O11 was disordered (0.55/0.45 ratio) and was refined isotropically.

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Highest peak    0.60  at  0.7139  0.0396  0.3157  [  1.07 A from O13 ]
Deepest hole   -0.57  at  0.8210  0.9006  0.3283  [  0.50 A from O11 ]
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Table S1. Crystal data and structure refinement for $[\mathrm{TMA}]_2[\mathrm{VBH}]$.

Empirical formula	C17 H40 N4 O13 V	
Formula weight	559.47	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0000(15) Å	α = 93.857(7)°.
	b = 10.601(2) Å	β = 102.755(7)°.
	c = 16.400(4) Å	γ = 101.878(6)°.
Volume	1318.2(5) $\mathrm{Å}^3$	
Z	2	
Density (calculated)	1.410 $\mathrm{Mg/m}^3$	
Absorption coefficient	0.443 mm^{-1}	
F(000)	594	
Crystal size	0.22 x 0.16 x 0.08 mm^3	
Crystal color / habit	blue / block	
Theta range for data collection	2.95 to 26.13°.	
Index ranges	-9<=h<=9, -13<=k<=12, -20<=l<=20	
Reflections collected	21592	
Independent reflections	5169 [R(int) = 0.0414]	
Completeness to theta = 25.25°	99.8 %	
Absorption correction	multi-scan / sadabs	
Max. and min. transmission	0.9654 and 0.9088	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5169 / 9 / 345	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1058	
R indices (all data)	R1 = 0.0583, wR2 = 0.1156	
Largest diff. peak and hole	0.604 and -0.571 $\mathrm{e.Å}^{-3}$	

Table S2. Crystal data and structure refinement for CVBH.

Identification code	CVBH	
Empirical formula	C8 H18 Ca N2 O15 V	
Formula weight	473.26	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.0175(3) Å	α= 90°.
	b = 8.3043(3) Å	β= 99.3610(10)°.
	c = 23.2909(8) Å	γ = 90°.
Volume	1720.89(10) Å^3	
Z	4	
Density (calculated)	1.827 Mg/m^3	
Absorption coefficient	8.237 mm^{-1}	
F(000)	972	
Crystal size	0.19 x 0.16 x 0.14 mm^3	
Crystal color / habit	blue / block	
Theta range for data collection	3.85 to 68.46°.	
Index ranges	-10<=h<=10, -10<=k<=10, -28<=l<=28	
Reflections collected	23941	
Independent reflections	3154 [R(int) = 0.0315]	
Completeness to theta = 68.25°	99.8 %	
Absorption correction	multi-scan / sadabs	
Max. and min. transmission	0.3918 and 0.3036	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3154 / 12 / 280	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0592	
R indices (all data)	R1 = 0.0244, wR2 = 0.0599	
Largest diff. peak and hole	0.257 and -0.412 e.Å^{-3}	

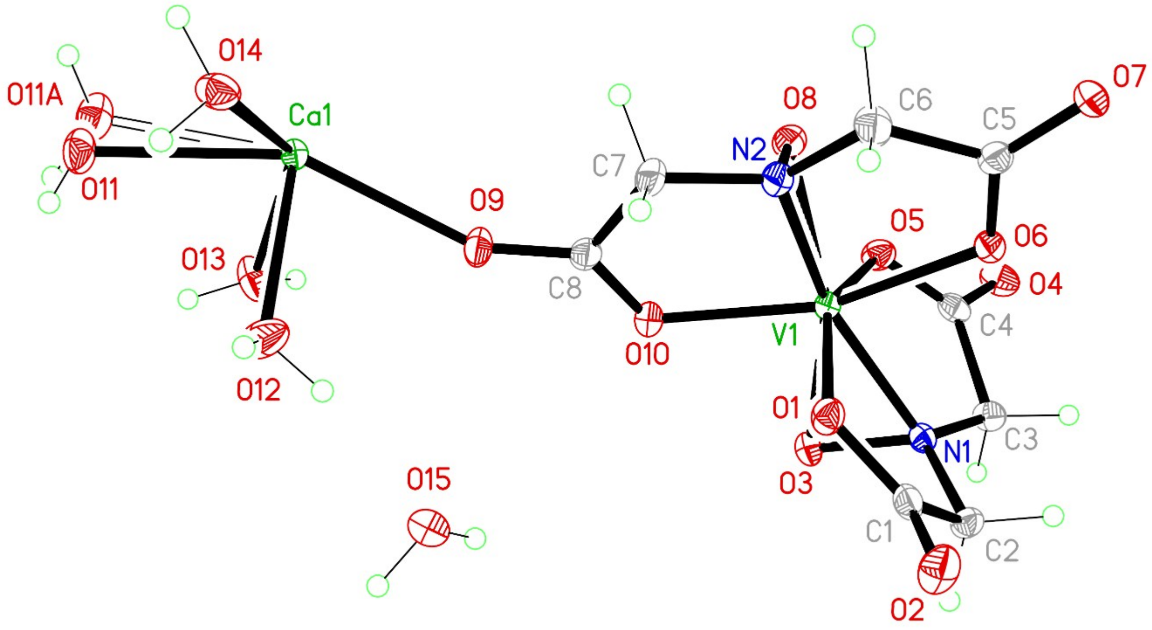

Figure S1. X-ray crystal structure of CVBH

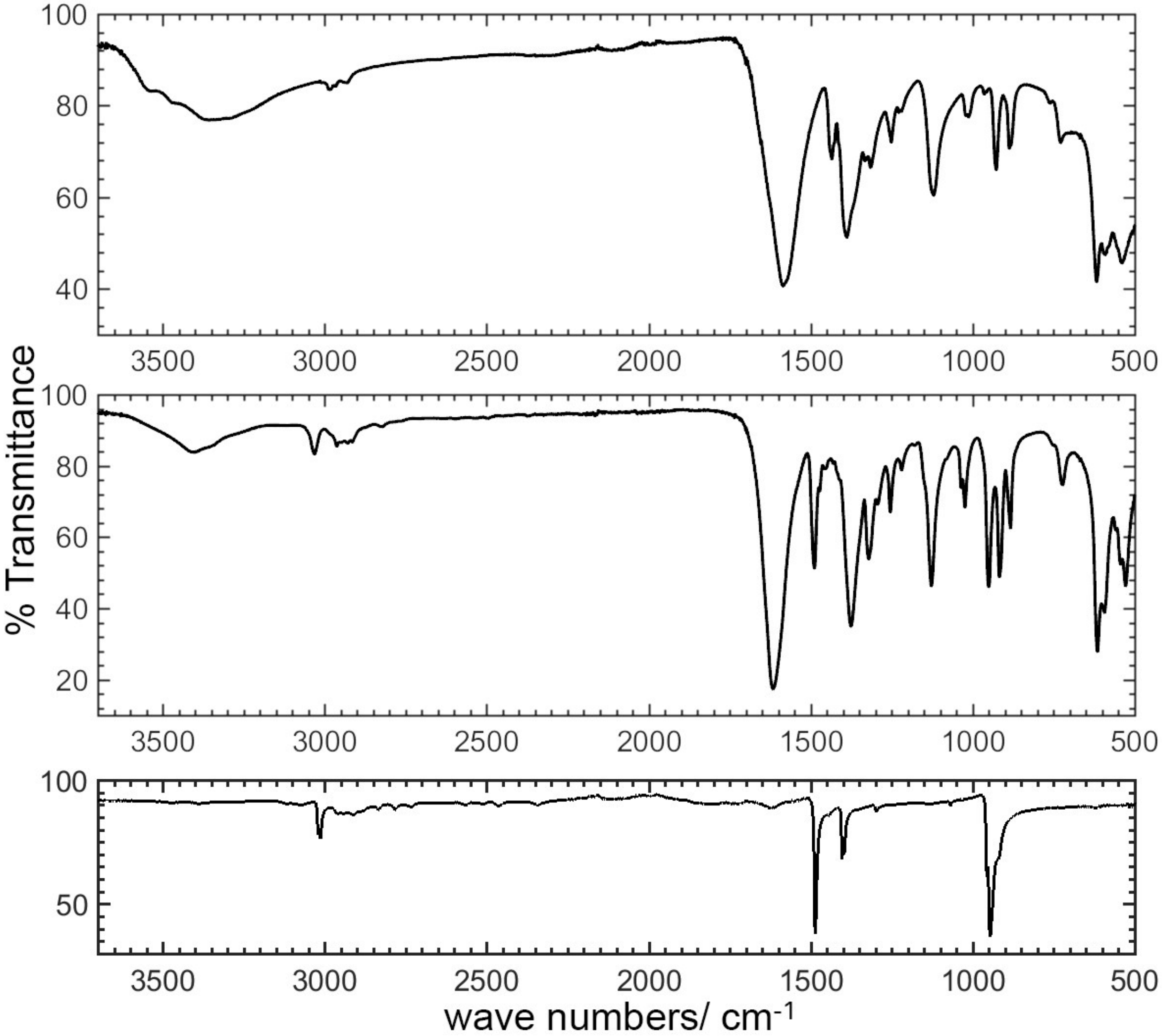

Figure S2. IR spectra of CVBH (top), [TMA]$_2$[VBH] (middle), and [TMA][Br]

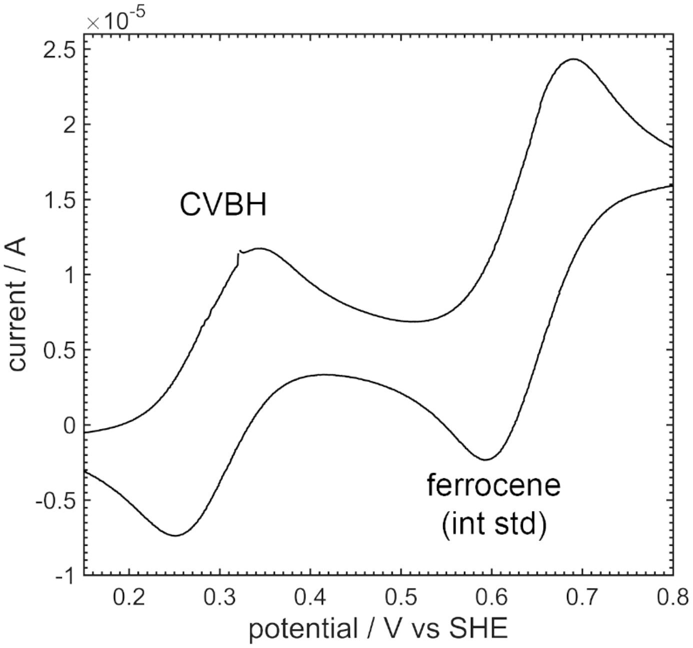

Figure S3. Cyclic voltammogram of 5 mM CVBH in DMSO with 0.1M TBAPF$_6$ supporting electrolyte, GC working electrode, silver wire reference electrode, platinum wire counter electrode and ferrocene (5 mM) as internal standard.

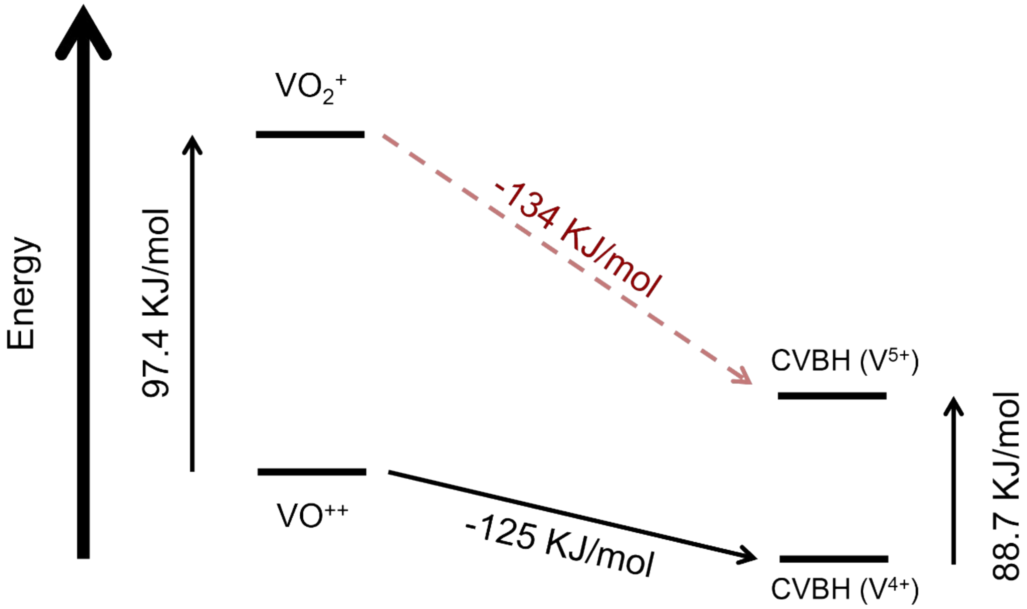

Figure S4. Thermodynamic cycle constructed from the IV/V reduction potentials of aqueous, acidic vanadium ions,[1] vanadium ions complexed with hydroxyiminodiacetate[2] and the ligand-binding equilibrium constant for aqueous vanadium(iv) ions in the presence of hydroxyiminodiacetate.[4]

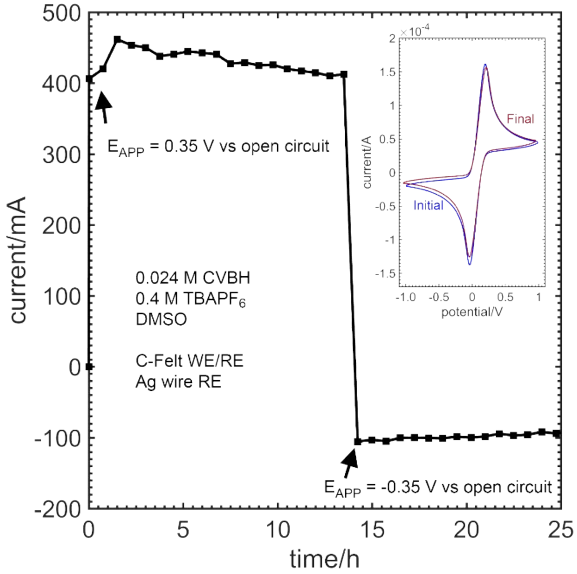

Figure S5. Current observed for CVBH solution in DMSO with +/- 0.35 V applied potential

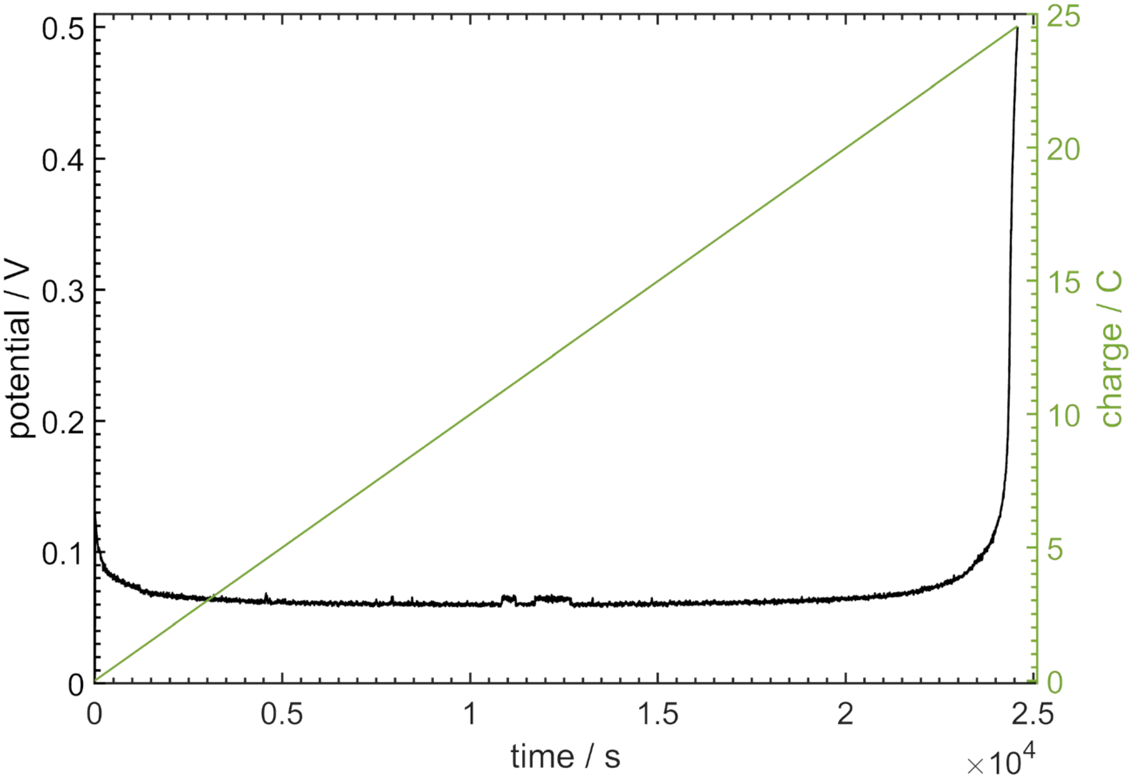

Figure S6. Oxidation of 0.01 M sample of CVBH in DMSO with 0.4M TEAPF$_6$ supporting electrolyte (25 mL), graphite felt working and counter electrodes and a silver wire reference electrode. Applied current was 1.0 mA and cutoff voltage was set to 0.5 V. Theoretical charge capacity was 24.1C.

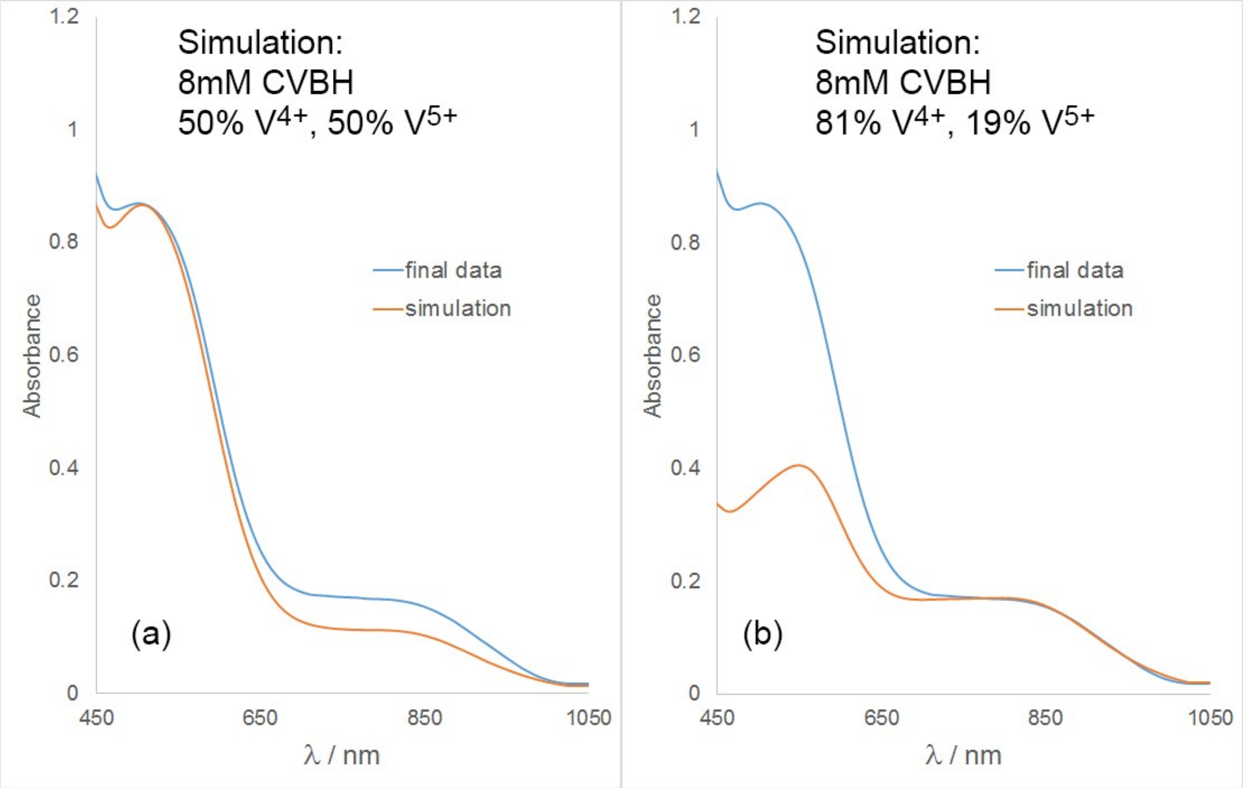

Figure S7. Simulated UV-vis spectra obtained by summing experimentally obtained vanadium(iv) and vanadium(v) spectra compared to the experimentally obtained UV-vis spectrum of CVBH after cycling in a symmetric flow cell. (a) Simulation assuming 20% decomposition and 1:1 vanadium(iv) and vanadium(v). (b) Simulation assuming 20% decomposition and 4:1 vanadium(iv) and vanadium(v).

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