

Supporting information for:

Temperature induced precipitation of V₂O₅ in vanadium flow batteries - revisited

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S1 – Datasheet for Oxkem vanadium solution



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Date of issue: 06 September 2017

Vanadium Sulphate Solution

Customer:

Batch No: B-09-3341

Quantity:

Customer Ref:

Oxkem Ref:

	$\text{VO}_2\text{SO}_4/\text{V}_2(\text{SO}_4)_3$	
Total Vanadium as V	1.60 M	82.6g/l
V (III)	50.7%	
V(IV)	49.3%	
Total Sulphate	4.1 M	
Density	1.330	
Phosphoric Acid	0.05M	
Ag	<0.5	ppm
Al	28	
As	<2	
B	<0.1	
Ba	<1.0	
Be	<0.1	
Bi	<1	
Ca	35	
Cd	<10	
Ce	<0.5	
Co	<0.5	
Cr	8	
Cu	<0.2	
Fe	18	
Ir	<0.1	
K	68	
Li	0.3	
Mg	<5	
Mn	<0.1	
Mo	<0.1	
Na	<10	
Ni	<20	
Os	<0.1	
Pb	<0.1	
Pd	<0.1	
Pt	<0.1	
Rh	<0.1	
Ru	<0.1	
Sb	0.3	
Se	<1.0	
Si	<2.5	
Sn	<1.0	
Sr	<0.5	
Te	<0.5	
Ti	<10	
Tl	<0.1	
Zn	<5.0	
Zr	<0.1	

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S2 – VOPO_4 precipitation



Figure S2.1: Photo showing VOPO_4 precipitation.

S3 – Detailed overview of all samples – Batch experiments SOC 84%

84%							
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
A1	3.00	1.60	2.00	0.050	0.000	46.0	0.0
A2	3.43	1.40	1.75	0.044	0.000	46.0	0.0
A3	4.00	1.20	1.50	0.038	0.000	47.3	1.2
A4	3.43	1.40	2.00	0.044	0.000	49.3	1.2
A5	4.00	1.20	2.00	0.038	0.000	55.3	1.2
A6	3.43	1.40	2.25	0.044	0.000	53.3	1.2
A7	4.00	1.20	2.50	0.038	0.000	62.0	0.0
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
B1	3.00	1.59	1.99	0.100	0.000	50.7	2.3
B2	3.43	1.39	1.74	0.088	0.000	50.7	2.3
B3	4.00	1.19	1.49	0.075	0.000	53.3	1.2
B4	3.43	1.39	1.99	0.088	0.000	53.3	1.2
B5	4.00	1.19	1.99	0.075	0.000	59.3	1.2
B6	3.43	1.39	2.24	0.088	0.000	55.3	1.2
B7	4.00	1.19	2.49	0.075	0.000	62.7	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
C1	3.00	1.57	1.97	0.049	0.050	45.3	1.2
C2	3.43	1.38	1.72	0.043	0.044	46.0	2.0
C3	4.00	1.18	1.48	0.037	0.038	47.3	1.2
C4	3.43	1.38	1.97	0.043	0.044	50.0	2.0
C5	4.00	1.18	1.98	0.037	0.038	54.7	1.2
C6	3.43	1.38	2.22	0.043	0.044	52.7	1.2
C7	4.00	1.18	2.48	0.037	0.038	61.3	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
D1	3.00	1.55	1.93	0.048	0.100	46.0	0.0
D2	3.43	1.35	1.69	0.042	0.088	46.7	1.2
D3	4.00	1.16	1.45	0.036	0.075	48.7	1.2
D4	3.43	1.35	1.94	0.042	0.088	50.0	0.0
D5	4.00	1.16	1.95	0.036	0.075	56.7	1.2
D6	3.43	1.35	2.19	0.042	0.088	55.3	1.2
D7	4.00	1.16	2.45	0.036	0.075	62.0	0.0
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
E1	3.00	1.56	1.94	0.112	0.093	49.3	1.2
E2	3.43	1.37	1.70	0.098	0.081	49.3	1.2
E3	4.00	1.17	1.46	0.084	0.070	50.0	2.0
E4	3.43	1.37	1.95	0.098	0.081	54.0	2.0
E5	4.00	1.17	1.96	0.084	0.070	58.0	0.0
E6	3.43	1.37	2.20	0.098	0.081	56.0	0.0
E7	4.00	1.17	2.46	0.084	0.070	62.0	0.0

S4 – Detailed overview of all samples – Batch experiments SOC 93%

93%							
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
A1	3.00	1.60	2.00	0.050	0.000	41.3	1.2
A2	3.43	1.40	1.75	0.044	0.000	41.3	1.2
A3	4.00	1.20	1.50	0.038	0.000	44.0	2.0
A4	3.43	1.40	2.00	0.044	0.000	45.3	1.2
A5	4.00	1.20	2.00	0.038	0.000	48.7	1.2
A6	3.43	1.40	2.25	0.044	0.000	48.0	0.0
A7	4.00	1.20	2.50	0.038	0.000	56.7	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
B1	3.00	1.59	1.99	0.100	0.000	46.0	0.0
B2	3.43	1.39	1.74	0.088	0.000	46.0	0.0
B3	4.00	1.19	1.49	0.075	0.000	48.0	0.0
B4	3.43	1.39	1.99	0.088	0.000	48.7	1.2
B5	4.00	1.19	1.99	0.075	0.000	50.7	2.3
B6	3.43	1.39	2.24	0.088	0.000	50.0	0.0
B7	4.00	1.19	2.49	0.075	0.000	58.0	2.0
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
C1	3.00	1.57	0.00	0.049	0.050	40.7	1.2
C2	3.43	1.38	1.72	0.043	0.044	41.3	1.2
C3	4.00	1.18	1.48	0.037	0.038	44.0	2.0
C4	3.43	1.38	1.97	0.043	0.044	45.3	1.2
C5	4.00	1.18	1.98	0.037	0.038	49.3	2.3
C6	3.43	1.38	2.22	0.043	0.044	47.3	1.2
C7	4.00	1.18	2.48	0.037	0.038	52.7	2.3
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
D1	3.00	1.55	1.93	0.048	0.100	42.0	0.0
D2	3.43	1.35	1.69	0.042	0.088	42.0	0.0
D3	4.00	1.16	1.45	0.036	0.075	43.3	1.2
D4	3.43	1.35	1.94	0.042	0.088	45.3	1.2
D5	4.00	1.16	1.95	0.036	0.075	50.7	1.2
D6	3.43	1.35	2.19	0.042	0.088	48.0	0.0
D7	4.00	1.16	2.45	0.036	0.075	55.3	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
E1	3.00	1.56	1.94	0.112	0.093	46.0	0.0
E2	3.43	1.37	1.70	0.098	0.081	48.0	1.2
E3	4.00	1.17	1.46	0.084	0.070	48.0	0.0
E4	3.43	1.37	1.95	0.098	0.081	50.0	1.2
E5	4.00	1.17	1.96	0.084	0.070	54.0	2.0
E6	3.43	1.37	2.20	0.098	0.081	50.0	0.0
E7	4.00	1.17	2.46	0.084	0.070	60.0	1.2

S5 – Detailed overview of all samples – Batch experiments SOC 100%

100%							
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
A1	3.00	1.60	2.00	0.050	0	40.0	0.0
A2	3.43	1.40	1.75	0.044	0	40.7	1.2
A3	4.00	1.20	1.50	0.038	0	42.7	2.3
A4	3.43	1.40	2.00	0.044	0	44.0	2.0
A5	4.00	1.20	2.00	0.038	0	48.7	1.2
A6	3.43	1.40	2.25	0.044	0	46.0	0.0
A7	4.00	1.20	2.50	0.038	0	51.3	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
B1	3.00	1.59	1.99	0.100	0	43.3	1.2
B2	3.43	1.39	1.74	0.088	0	43.3	1.2
B3	4.00	1.19	1.49	0.075	0	45.3	2.3
B4	3.43	1.39	1.99	0.088	0	46.7	1.2
B5	4.00	1.19	1.99	0.075	0	51.3	1.2
B6	3.43	1.39	2.24	0.088	0	48.7	1.2
B7	4.00	1.19	2.49	0.075	0	54.0	0.0
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
C1	3.00	1.57	0.00	0.049	0.050	40.0	0.0
C2	3.43	1.38	1.72	0.043	0.044	40.0	0.0
C3	4.00	1.18	1.48	0.037	0.038	42.0	2.0
C4	3.43	1.38	1.97	0.043	0.044	42.7	1.2
C5	4.00	1.18	1.98	0.037	0.038	47.3	1.2
C6	3.43	1.38	2.22	0.043	0.044	45.3	1.2
C7	4.00	1.18	2.48	0.037	0.038	51.3	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
D1	3.00	1.55	1.93	0.048	0.100	40.0	0.0
D2	3.43	1.35	1.69	0.042	0.088	40.0	0.0
D3	4.00	1.16	1.45	0.036	0.075	42.0	2.0
D4	3.43	1.35	1.94	0.042	0.088	43.3	1.2
D5	4.00	1.16	1.95	0.036	0.075	46.7	2.3
D6	3.43	1.35	2.19	0.042	0.088	45.3	1.2
D7	4.00	1.16	2.45	0.036	0.075	52.7	1.2
	Volume [ml]	V[M]	H ₂ SO ₄ [M]	H ₃ PO ₄ [M]	(NH ₄) ₂ SO ₄ [M]	Temp	Std
E1	3.00	1.56	1.94	0.112	0.093	44.0	0.0
E2	3.43	1.37	1.70	0.098	0.081	44.0	0.0
E3	4.00	1.17	1.46	0.084	0.070	44.0	1.2
E4	3.43	1.37	1.95	0.098	0.081	46.0	1.2
E5	4.00	1.17	1.96	0.084	0.070	46.0	2.3
E6	3.43	1.37	2.20	0.098	0.081	46.0	1.2
E7	4.00	1.17	2.46	0.084	0.070	54.0	0.0

S6 – Setup for batch experiments.



Figure S6: Photo of the batch temperature stability experimental setup. Box was sealed by a plastic cover and duct tape in order to minimize evaporation and ensure even temperature throughout the whole container.

S7 - Electrochemical cell for in-situ study of temperature stability

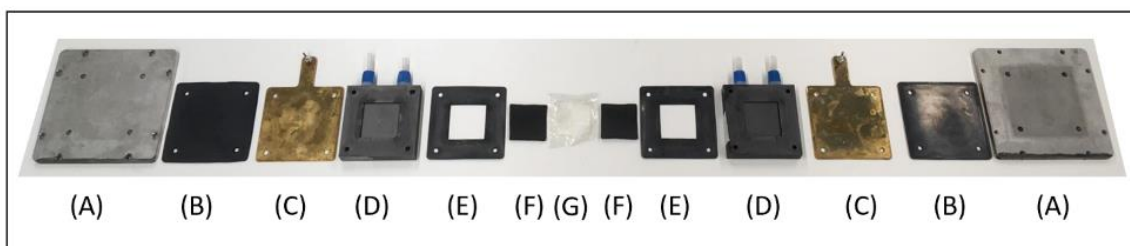


Figure S7.1 - Sequence of cell assembling: (A) End plate (B) Isolating plate (C) Current collector (D) Graphite plate (E) Gasket (F) Carbon Felt (G) Membrane

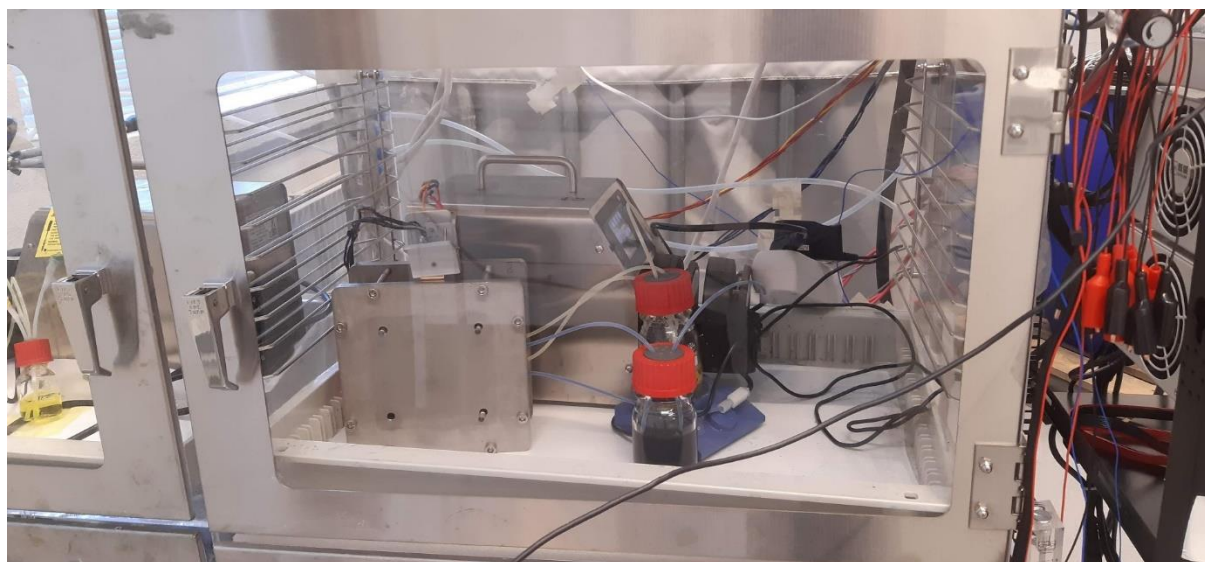


Figure S7.2: Combined experimental setup with pump, flow battery cell and bottles inside chamber. Shown without insulation and temperature control. Tubes enter into the glass bottles through sealed rubber septa.

S8 – Open circuit voltage as function of discharge capacity for different V_{state} values

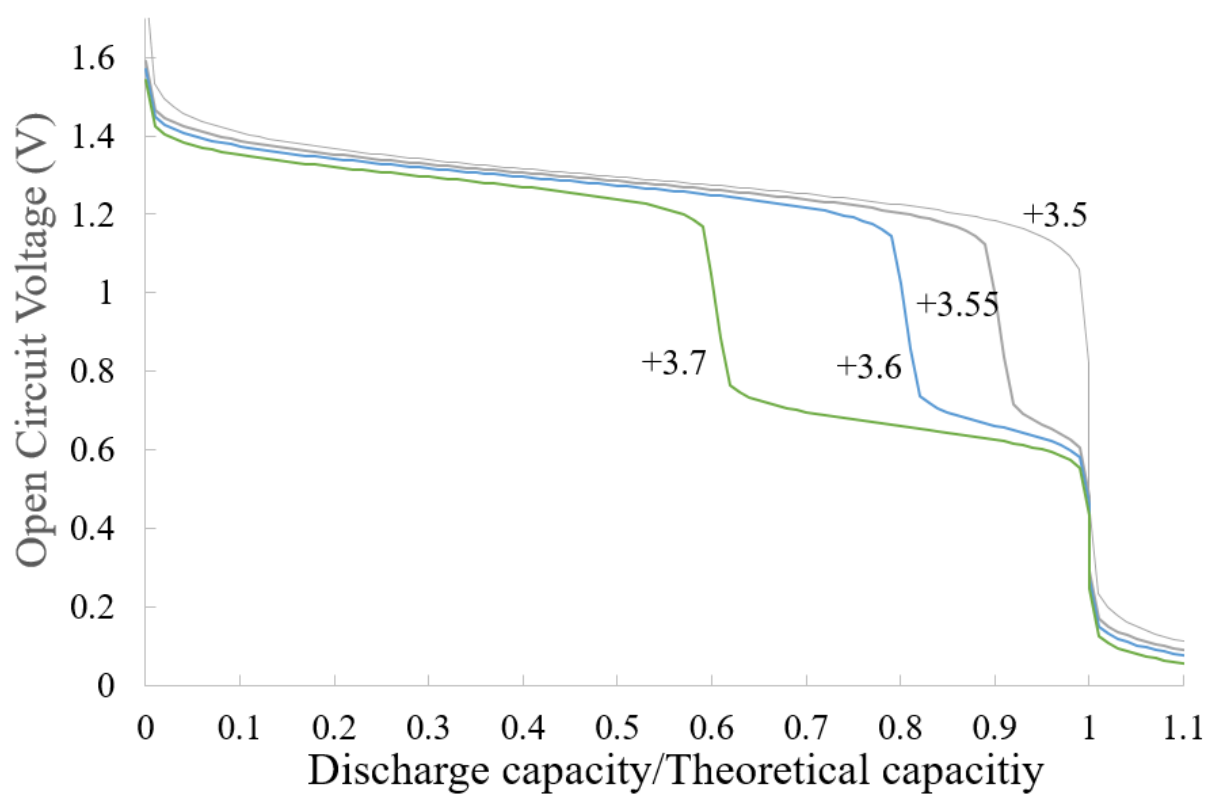


Figure S8.1: Graph shows open circuit voltage as function of normalised capacity. Numbers on graph refers to the V_{state} .

S9 – Performance of completely sealed flow battery cell in the presence of air

In the main text of the present paper an example of the influence of air on the capacity voltage curve during cycling is given (Figure 4). However, this experiment was conducted with the lids of the vanadium glass bottles completely opened in order to speed up the oxidation of the vanadium solution. Hence, it does not represent realistic conditions and an experiment where the battery was cycled completely sealed in the presence of air was also conducted.

The results can be seen in the figure below, which shows the charge/discharge voltage-capacity plot for an experiment that lasted for approximately 7 days and at a temperature of 44°C. Throughout the experiment, the lids of the vanadium bottles were sealed and the tubes introduced in the glass bottles through sealed rubber septa.

For the first two days the battery was cycled in N₂ (black data points). Thereafter, air was allowed into the chamber enclosing the experimental setup (red data points). After four days in air, N₂ was again continuously injected into the chamber (blue data points).

From Figures S9.1 and S9.2, it is obvious that despite the vanadium solution is sealed towards external atmospheres, the vanadium gets oxidised when the experimental setup is exposed to air.

A detailed investigation of the diffusion paths has not been conducted, but it can be either permeation through the graphite electrochemical cell, tubing or tiny leaks in the tube joints or septa. The main point is that testing in smaller flow battery cells for extended time (> 12-24 hours) must be conducted under oxygen free atmosphere.

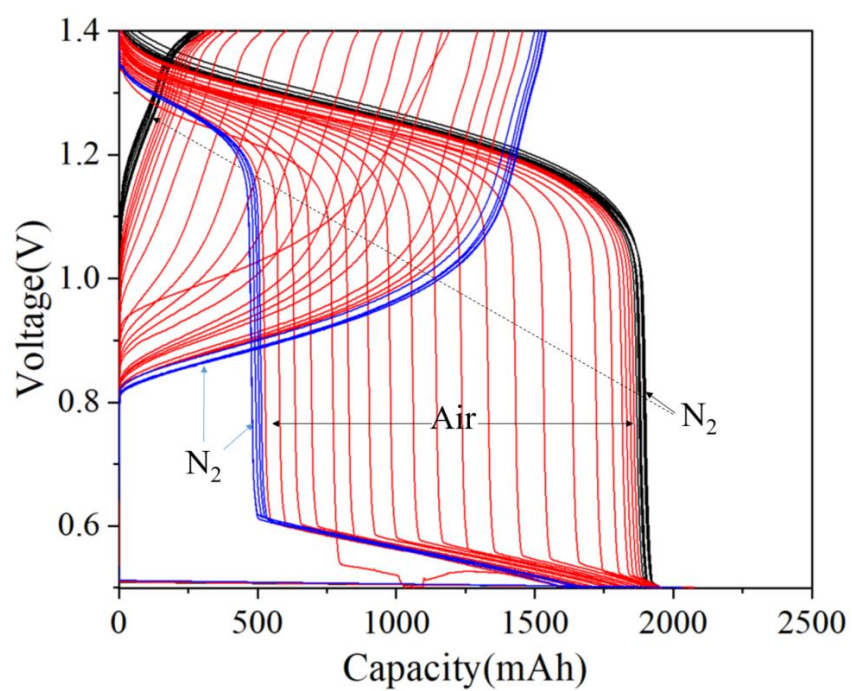


Figure S9.1: Voltage-capacity plot of battery cycling in N_2 and air.

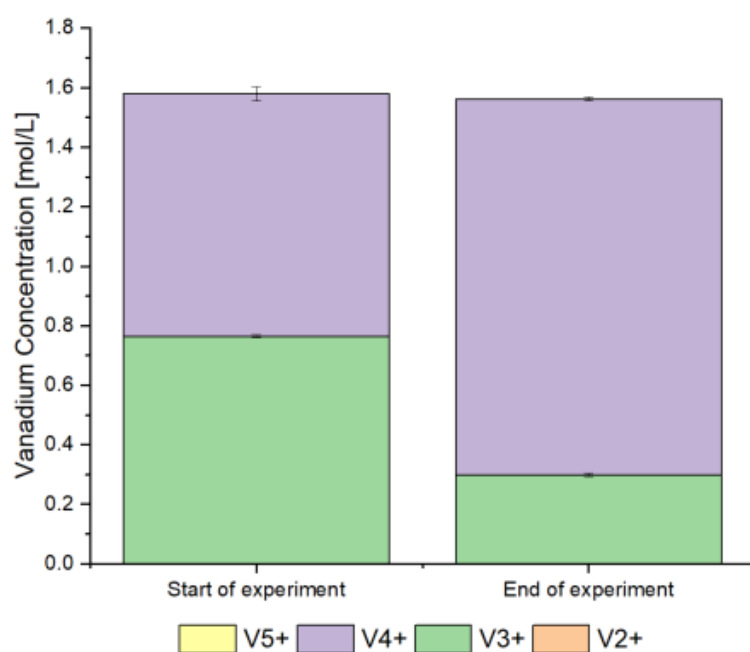


Figure S9.2: Vanadium concentrations before and after experiment. Measured with redox titration.

S10 – Supplementary flow battery test at elevated temperatures

The battery cycling procedure is described in Table S10.1. It follows a similar procedure to the one in the main text (Table 2). However, in order to induce precipitation, the maximum temperature was increased to 60°C instead of 50°C.

Figures S10.1 and S10.2 show the results of the whole battery cycling procedure. The experiment is divided into nine periods, from I to IX. V₂O₅ precipitation was formed during both periods of potential holds at 60 °C (period V and VIII). All precipitate formed after the first period V was redissolved by applying several charge-discharge cycles. (see figure S10.3). The precipitate formed during period VIII was only partially redissolved, as the membrane broke in the subsequent cycling and the experiment was stopped.

Although precipitation was observed at 60 °C, a few noticeable observations were made:

1. There is no apparent precipitation when cycled at 60 °C and combined with resting periods of 30 minutes between charge and discharge (II and IV)
2. Only for extended resting times (> 24 h) with potential holds of 1.6 V (~100 % SoC) precipitation could be observed.
3. Precipitate dissolved over a few cycles once the battery was cycled again.

The points above are discussed in more detail in the main article.

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Period	Temp- erature	Conditions	Notes

I	30°C	Cycle 1 - 23 -30 min pause between charge and discharge.	No precipitation observed during cycling.
II	60°C	Cycle 24 - 50 -30 min pause between charge and discharge.	No precipitation observed during cycling.
III	30°C	Cycle 51-66 -30 min pause between charge and discharge.	No precipitation observed during cycling.
IV	60°C	Cycle 67-78 - 30 min pause in between charge and discharge.	No precipitation observed during cycling.
V	60°C	Cycle 79 -30 h potential hold at 1.6V	Precipitation observed during the period of potential hold. 5 ml sample taken out after the period of potential hold.
VI	30°C	Cycle 80-107 -30 min pause between charge and discharge.	Precipitation immediately redissolved during the first discharge.
VII	60°C	Cycle 108-119 -30 min pause between charge and discharge.	No precipitation observed during cycling. 5 ml sample taken out end the end of this period.
VIII	60°C	Cycle 120 -70 h of potential hold at 1.6V	Precipitation observed during the period of potential hold.
IX	30°C	Cycle 121-124 -30 min pause between charge and discharge.	The precipitation was partially dissolved.

Table S10.1: Battery cycling procedure

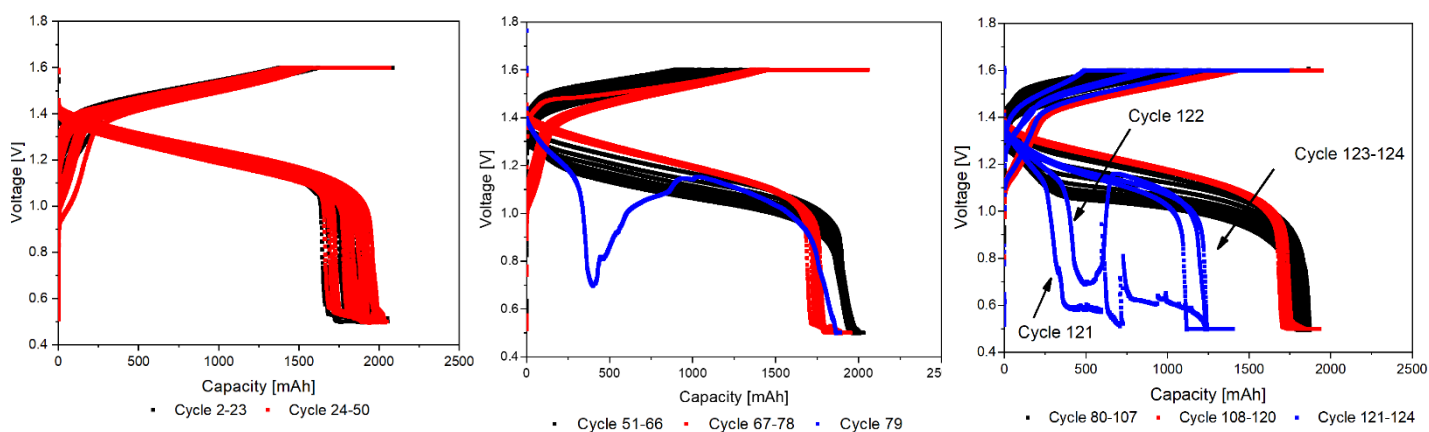


Figure S10.1: Capacity-voltage plot from different cycles of the experiment.

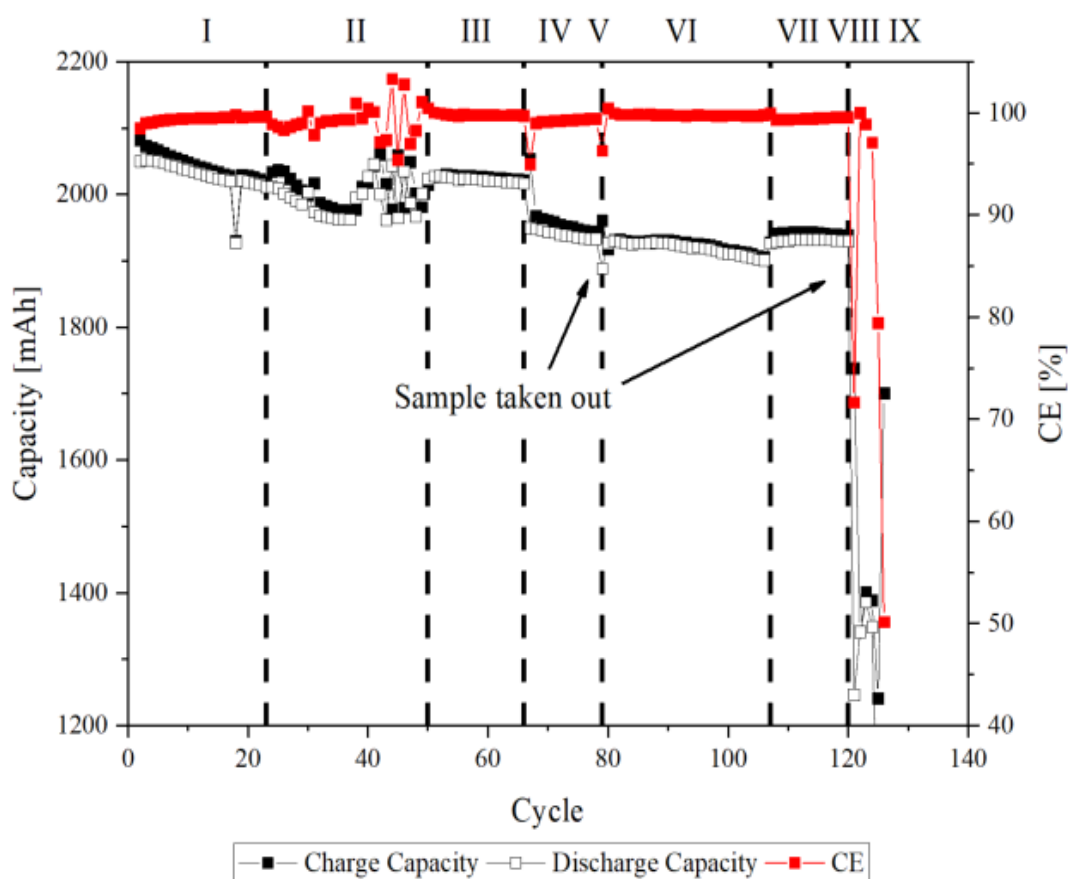


Figure S10.2: Charge/discharge capacity and coulomb efficiency (CE) as function of cycle number.

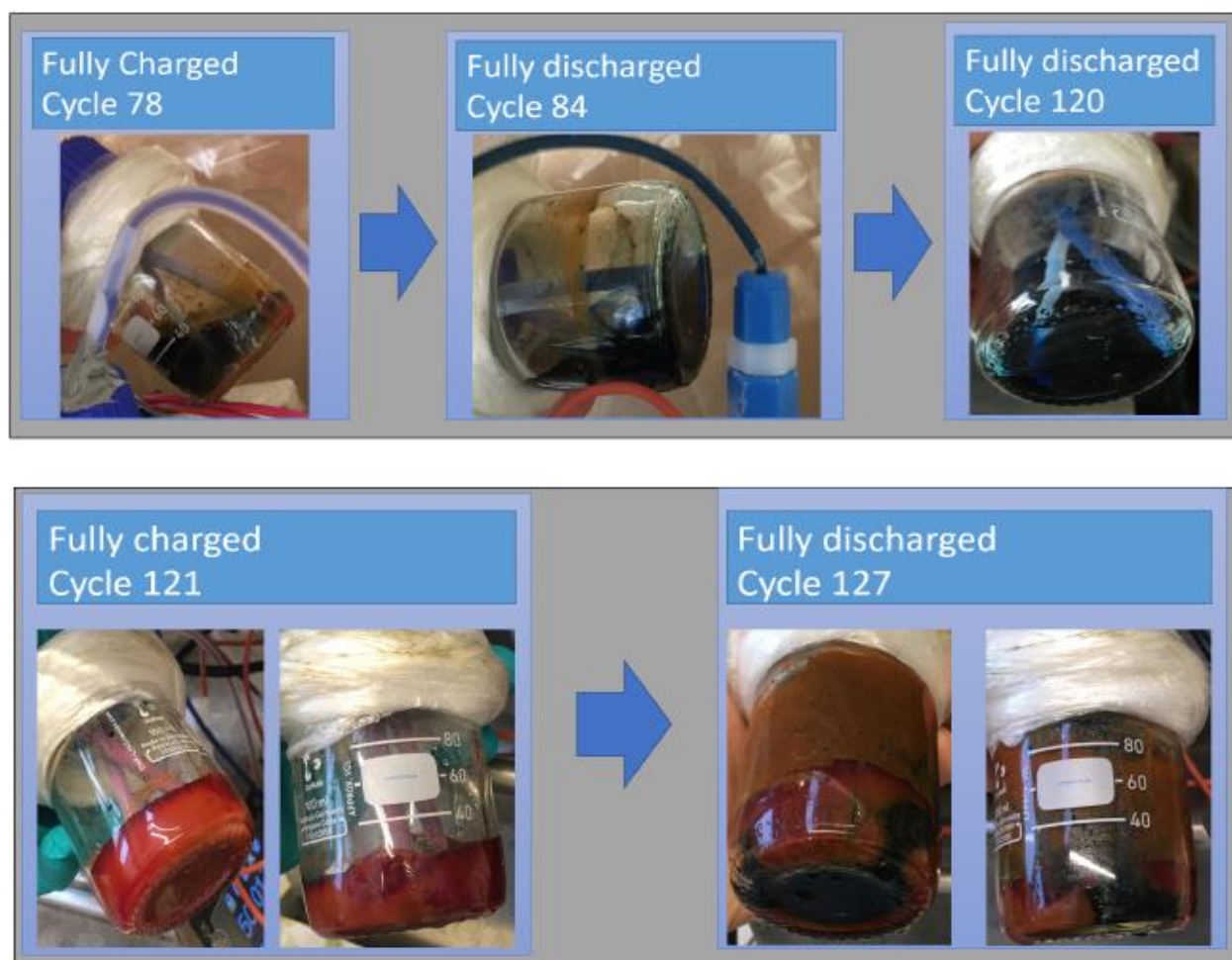


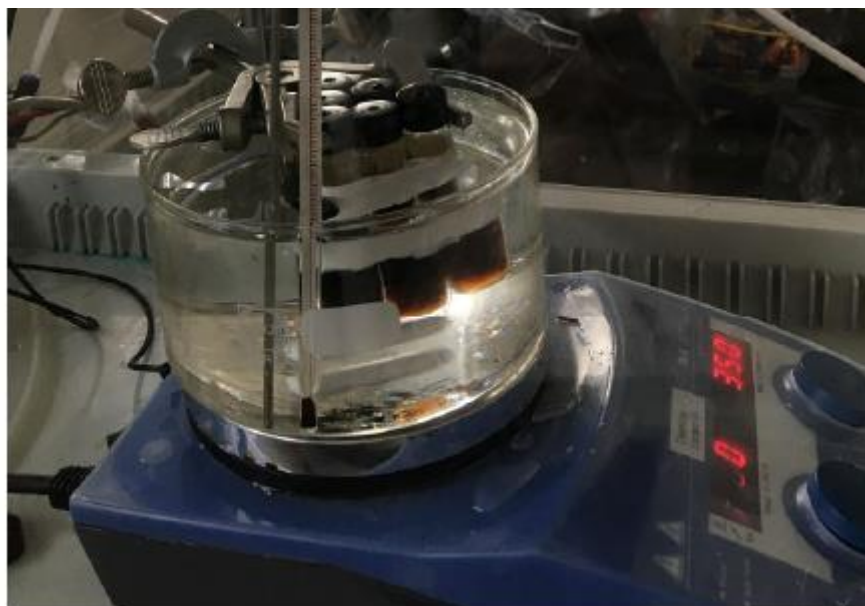
Figure S10.3: Overview of the formed precipitation and the dissolving of this over time for different cycles.

S11 – Effect of air and stirring on batch experiments

It cannot per se be ruled out that the lack stirring/aggregation/circulation of the vanadium solution during batch experiments can influence the (apparent) precipitation temperature. Furthermore, it can also be speculated that the precipitation process can be promoted by presence of oxygen (i.e. $2\text{VO}_2^+ + \text{H}_2\text{O} \xrightarrow{\text{O}_2 \text{ Cat}} \text{V}_2\text{O}_5 + 2\text{H}^+$). Hence, several experiments examining the influence of stirring and presence of oxygen on the precipitation process were carried out.

For these experiments, the temperature was controlled with an oil-bath and a combined magnetic stirrer and heater. A conventional mercury thermometer was used to verify the temperature in the oil bath, and a magnet to obtain uniform temperature distribution.

Figure S11.1: Photo of the batch temperature stability experimental setup with/without



stirring and presence of air.

The electrolyte solution used for the experiment consisted of 1.6 M vanadium, 2.1 M H_2SO_4 and 0.05 M H_3PO_4 . The electrolyte solution was fully charged (100 % SoC). 5.0 mL were put in six glass tubes and submerged into the oil-bath. Three of the tubes contained magnets for stirring, the other three did not. Holes were drilled in the lids of the glass vials, ensuring interaction between the electrolyte solution and the surrounding atmosphere. One batch of experiments was placed in a chamber that was constantly purged with N_2 , while the other batch experiments were conducted under ambient atmosphere.

Experiments were named according to the table below:

EXPERIMENT

A	N ₂	Stirring
B	Air	No stirring
C	Air	Stirring
D	N ₂	No stirring

Table S11: Overview of batch samples.

All samples were kept at 50 °C for 72 hours and were visually inspected for precipitation. In all four experiments precipitation was observed after 72 hours. Due to the different experimental conditions, (stirring/no stirring, nitrogen/air) different amounts of solvent could have evaporated from the different experiments and vanadium concentration above 1.6 M can be expected. Therefore, presence of precipitation does not by itself indicate low temperature stability. For this reason, by the end of the experiment, the total dissolved vanadium concentration in each solution was determined by titration and it is a measure of the ‘dynamic’ solubility after 72h. This is an indicator of the precipitation rate: the lower the total vanadium concentration, the higher the precipitation rate, and viceversa.

Data is shown in Figure S11.2 and it is seen that the samples without stirring have significantly higher vanadium concentrations than with stirring. Additionally, it appears as if the presence of both air and stirring leads to higher precipitation rate. It is speculated that this could be explained by supersaturation when no stirring is present.

Nonetheless, this observation disagrees with the higher precipitation temperature for the in-operando experiments (with circulation) compared to the batch experiments that are presented in the main article (no stirring). This difference is somehow surprising and does not lead to any clear conclusions about the different precipitation temperature observed for batch and in-operando experiments.

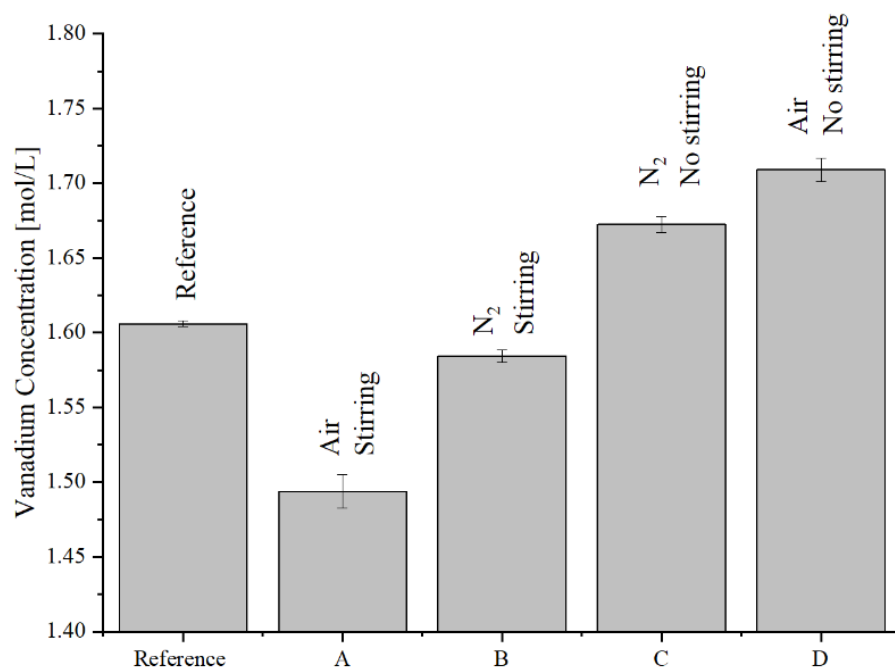


Figure S11.2: Total vanadium concentration in sample A-D after 72 h. Titrations are done as triplets and error bar is the standard deviation between the three samples.