Energy & Environmental Science

Supplementary Information

Supplementary Information: Asymmetric Polyoxometalate Electrolytes for Advanced Redox Flow Batteries

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1. Materials and Methods

1.1. Synthesis of PV_{14}

All reagents and solvents were purchased from Sigma Aldrich and used without further purification. The hydrated sodium salt of $[PV_{14}O_{42}]^{9-}$ (**PV_{14}**), $Na_{4.75}H_{4.25}[PV_{14}O_{42}]$ was obtained by a modification of the preparation by Selling *et al*. [1] The identity of **PV_{14}** was confirmed by dissolving the product in water and taking a ^{51}V NMR spectrum that showed the three distinct peaks of **PV_{14}**.

Selling *et al*. measured the numbers of protons attached to **PV_{14}** anions in solution by ^{31}P and ^{51}V NMR.[1] They found that there are multiple $[H_xPV_{14}O_{42}]^{(9-x)-}$ species with x = 1-6 in a *pH* range from 1.5 < *pH* 6.5. The lower the *pH*, the higher the number of protons per **PV_{14}** polyoxoanion. As each of the species has its own pK_a value, we assume that **PV_{14}** can act as buffer. Therefore, a titration curve was measured during the formation of **PV_{14}** from $NaVO_3$ as shown in Fig. S1. Initially, 300g $NaVO_3$ were dissolved in 1 L of ultra-pure type 1 water (ELGA Option- Q) with 70 mL conc. (85%) phosphoric acid added. Then the *pH* was measured (Mettler Toledo, Lab 850 benchtop pH meter) while adding concentrated (35%) hydrochloric acid. The protons taken up per **PV_{14}** polyoxoanion *p* were calculated by subtracting the "free protons" H^+_{free} from the added protons H^+_{added}:

$$H^+_{added} = c_{HCl} \cdot v \quad (1)$$

$$H^+_{free} = 10^{-pH} * (v + 1.07L) \quad (2)$$

$$p = (H^+_{added} - H^+_{free}) / n_{PV_{14}} \quad (3)$$

With concentration of concentrated (35%) HCl c_{HCl} = 12.1 M, volume of added HCl *v*, amount of **PV_{14}** $n_{PV_{14}} = 0.176$ mol.

Fig. S1 shows that the *pH* of the solution drops from *pH* 5.8 to *pH* 2.0 upon addition of 101 mL of concentrated (35%) HCl. The number of protons per **PV_{14}** rises linearly from 0 to 7. The measured *pH* value exhibits two plateaus during the measurement, indicating that the **PV_{14}** solution acts as a buffer in these regions. Addition of 32 mL of concentrated HCl (35%) changed the *pH* by one unit, from 3.0 to 2.0.

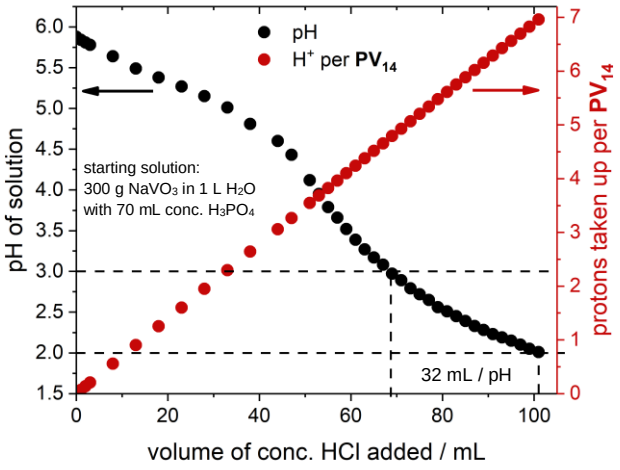

Fig. S1 Titration curve measured during the synthesis of **PV_{14}**. The abscissa gives the volume of added HCl, the left ordinate (black data points) the measured *pH* values and the right ordinate the calculated number of protons taken up by each **PV_{14}** in solution.

1.2. ^{51}V NMR and in-situ NMR

^{51}V (*I* = 7/2, nat. abund. 99.76%) NMR spectra were measured at 78.94 MHz without proton decoupling on a Bruker Avance III 300 Spectrometer in 5 mm o.d. tubes at a temperature of 298 K. Chemical shifts are relative to neat $VOCl_3$ as an external reference. 90º excitation pulses of 9.2 µs duration were used, and rapid T_1 relaxation as a result of the nuclear quadrupole led to line widths of 1000 – 2000 Hz. For the in-situ NMR measurements the spectral width was 1188 ppm and the FID was acquired into 1024 data points, leading to an acquisition time of 0.00546 s, so that with a relaxation delay of 0.001 s it was possible to acquire 2048 transients in less than 14 s. Measurements were made at intervals of 85 seconds over a period of 10 hours, and the individual FIDs were transformed

into 32678 points after multiplication by a 50 Hz exponential window.

1.3. Electrochemistry

Three electrode measurements were performed in custom-built glass cells with a polished glassy carbon working electrode (surface area A = 0.02 cm²), a gold wire (diameter d = 0.5 mm) counter electrode and a Mercury/Mercurous Sulfate reference electrode in 1 M H_2SO_4 (MSE, 0.668 V vs. Standard Hydrogen Electrode) (SHE)). Prior to the measurements the electrolyte was purged with nitrogen, and the cell was kept under nitrogen pressure during the experiment. A Bio-Logic SP300 potentiostat was used for control and data acquisition. The flow battery experiments were conducted in a commercial cell (C-Tech 5x5, surface area A = 25 cm²). Graphite felts (GFD, SGL Carbon) were used as electrodes and pre-treated at 400 °C for 24 h in the laboratory atmosphere. In the cell the 4.6 mm thick electrodes were compressed to 3.5 mm. As membrane a cation exchange membrane (FUMASEP - F1040, thickness 40 µm) was employed. During the experiment the cell and the pump with tubing were kept in a polycarbonate box purged with nitrogen.

2. Three electrode studies of SiW_{12}

2.1. pH stability of SiW_{12} measured by cyclic voltammetry

pH-stability was assessed by preparing a series of 0.1 M solutions of **SiW_{12}** and adjusting their *pH* to values in the range 1 – 6 by addition of 3 M LiOH. These solutions were stored for 24 h and were then diluted to a common *pH* and concentration (1 mM) by addition of 1 M H_2SO_4. The CVs are shown in Fig. S2 and indicate that exposure for 24 h to an electrolyte with *pH* up to 6 does not affect **SiW_{12}** detrimentally as the CV pattern is very similar for each curve, similar to the CV of freshly prepared **SiW_{12}** shown in Fig. 1a and is in accord with CV data published in the literature.[2–4]

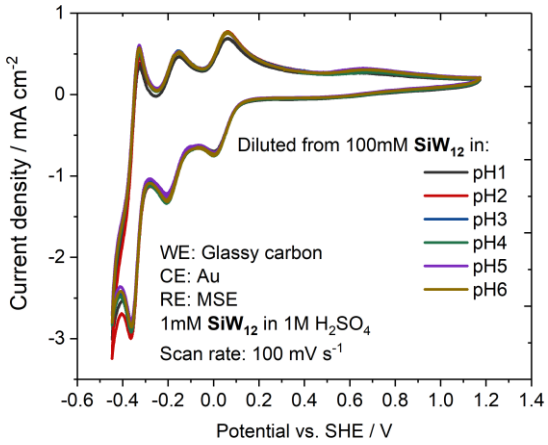

Fig. S2 Cyclic voltammogram of 1 mM **SiW_{12}** after storage for 24 h in aqueous solution ranging in *pH* from 1- 6. Measured in 1 M H_2SO_4 aqueous solution.

2.2. Electrochemical impedance spectroscopy of SiW_{12}

In order to determine the redox kinetics of **SiW_{12}** electrochemical impedance spectroscopy (EIS) measurements were performed in a solution with 20 mM **SiW_{12}**. This solution was reduced by 0.5 electrons per **SiW_{12}** polyoxoanion by bulk electrolysis. The solution then contained 10 mM **SiW_{12}** and 10 mM **SiW_{12}^-** and the measured open circuit potential (OCP) was equal to the measured standard potential of $U^{\theta,1}_{SiW_{12}}$ = 0 V for the first reduction. EIS was measured at the OCP with an amplitude of 10 mV from 1 MHz to 100 mHz. The obtained spectra were fitted to a Randles Circuit (shown in Fig. S3)

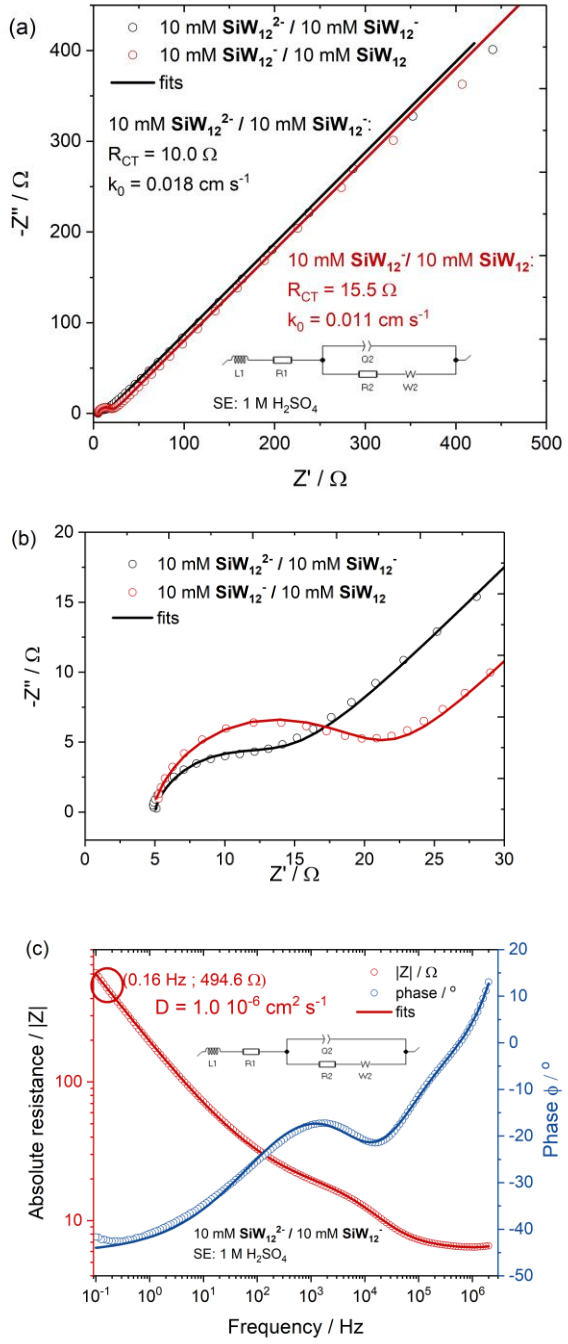

Fig. S3 Electrochemical impedance spectroscopy measurements of the first two redox reactions of **SiW_{12}**. (a) Nyquist plots of 10 mM **SiW_{12}**/10 mM **SiW_{12}^-** and 10 mM **SiW_{12}^-**/10 mM **SiW_{12}^{2-}** with fits and the used equivalent circuit shown. (b) Detail of (a) showing the semicircle. (c) Bode plot of 10 mM **SiW_{12}^-**/10 mM **SiW_{12}^{2-}** with fits.

Table S1 Parameters for first two redox reactions of SiW_{12} determined by fitting the experimental data to the equivalent circuit given in Fig. S3 or by reading the impedance at 0.16 Hz.

	R_{ohm} / Ω	R_{CT} / Ω	CPE/ F $s^{(a-1)}$	a	k_0 / cm s^{-1}	C_{DL} / µF	$\|Z\|$ at 0.16 Hz/Ω	D / cm^2 s^{-1}
SiW_{12}/SiW_{12}^-	4.8	15.5	2.6 10^{-6}	0.85	0.011	0.31	510	1.0 10^{-6}
SiW_{12}^-/SiW_{12}^{2-}	4.6	10.0	21.2 10^{-6}	0.76	0.018	1.0	494	1.1 10^{-6}

with added inductance accounting for the inductivity of the setup.[5] The electron transfer constant k_0 was then calculated from the charge transfer resistance R_{CT} obtained from the fit. All fitted parameters are given in Table S1, the double layer capacitance was calculated from the constant phase element (CPE) with the formula given by Hirschorn *et al*. for a surface distribution.[6] The measurement described above was repeated to measure the kinetics of the second electron transfer of **SiW_{12}**; 1.5 electrons were added to fully oxidised **SiW_{12}**, the composition of the solution is then 10 mM **SiW_{12}^-** and 10 mM **SiW_{12}^{2-}** and the OCP was $U^{\theta,2}_{SiW_{12}}$ = -0.21 V. Nyquist plots for both measurements with their fits are shown in Fig. S3a and S3b. R_{ohm} is very similar for both measurements, the double layer capacitance C_{DL} is lower for **SiW_{12}/SiW_{12}^-** than for **SiW_{12}^-/SiW_{12}^{2-}**. For the latter measurement a specific capacitance c_{DL} = 14 10^{-6} F cm^{-2} is reasonable for a glassy carbon electrode.[7]

The determined electron transfer constants are on the order of $k_0 \approx 10^{-2}$ cm s^{-1}. It appears that the second redox reaction **SiW_{12}^-/SiW_{12}^{2-}** is faster than the first redox reaction **SiW_{12}/SiW_{12}^-**. To the best of our knowledge, this has not been investigated in the literature and could be an interesting research topic.

Diffusion coefficients D can be determined from the magnitude of the admittance ($1/|Z|$) at a frequency of 0.16 Hz (for details see electrochemistry text books such as ref[8]). The calculations yield a very similar diffusion coefficient for **SiW_{12}^-/SiW_{12}^{2-}** and **SiW_{12}/SiW_{12}^-** at D = 1.1 10^{-6} cm^2 s^{-1} and D = 1.1 10^{-6} cm^2 s^{-1} respectively. The literature value for D of $[SiW_{12}O_{40}]^{4-}$ in 0.9 M Na_2SO_4, 0.1 M H_2SO_4 at 25 °C is higher at 2.6 10^{-6} cm^2 s^{-1}.[3]

2.3. Cyclic voltammograms of the V^{2+}/V^{3+} redox reaction

Fig. 1a in the main manuscript shows a CV of 12 mM V^{3+} on a polished glassy carbon (GC) electrode. The current which is associated with the reduction of V^{3+} and the subsequent reoxidation of V^{2+} is very small, current from the hydrogen evolution reaction appears to be larger. Fig. S4 compares the previously shown CV of 12 mM V^{3+} in 1 M H_2SO_4 on a polished GC electrode with a CV of 12 mM V^{3+} on a GC electrode which has been electrochemically oxidised. For this the potential of the GC electrode was stepped to 2 V vs. SHE for 10 s in 1 M H_2SO_4. The much higher current on the oxidised GC indicates that the electrochemical pretreatment produced a catalytic electrode surface. This is in accordance with other studies that attributed catalytic properties for the V^{2+}/V^{3+} redox reaction to oxygen functional groups.[9–12] The reason for this catalytic effect is most likely a bridge activated electron transfer, as for Fe^{2+}/Fe^{3+}.[7,13,14]

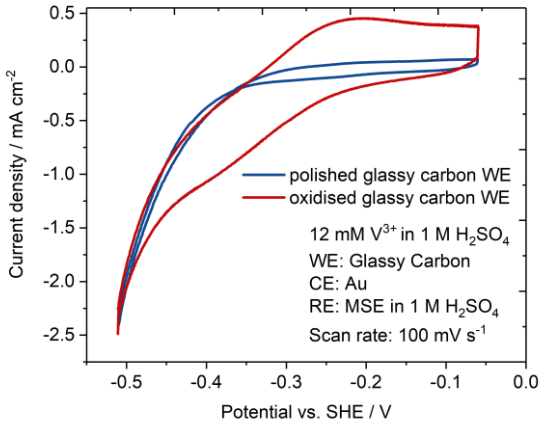

Fig. S4 Comparison of the V^{2+}/V^{3+} redox reaction on a polished and on an oxidised (2 V vs. SHE for 10 s in 1 M H_2SO_4) glassy carbon working electrode.

3. Investigation of proton coupled electron transfer of PV_{14}

To confirm that the electron transfer of **PV_{14}** is coupled to proton transfer, the polyoxovanadate was reduced and oxidized in a flow battery while the *pH* was measured in the tank. The other half-cell consisted of an excess of Fe^{2+}. The result is shown in Fig. S5. Upon reduction the *pH* increases, as **PV_{14}** takes up electrons and protons. This behaviour is reversible, and depends on the concentration of **PV_{14}** as expected.

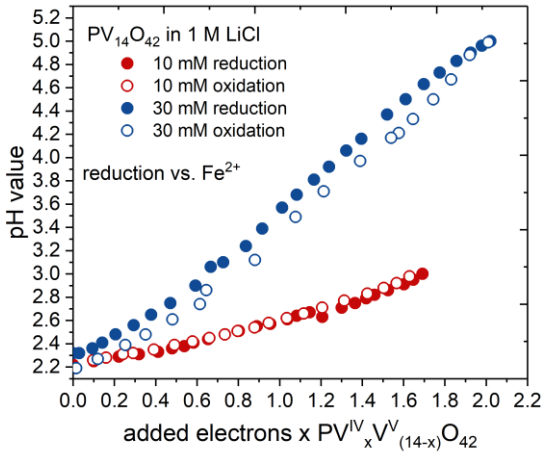

Fig. S5 Evolution of *pH* value during reduction and oxidation of **PV_{14}** against an excess of Fe^{2+}. The measurement is shown for two concentrations: 10 mM (red circles) and 30 mM (blue circles) **PV_{14}** for reduction and oxidation.

4. ^{51}V NMR investigation of PV_{14} to measure pH stability

The *pH* stability of **PV_{14}** was measured by ^{51}V NMR. For this purpose spectra in electrolytes ranging in *pH* from 1.1 to 2.1 were recorded immediately after adjusting the *pH*, and again after 3, 6 and 78 hours. The ratio of free vanadium (VO_2^+) to **PV_{14}** was determined by integrating the intensities of the peaks labelled PV_{14}^3 and VO_2^+. The signal PV_{14}^3 arises from two vanadium sites in **PV_{14}**, and so its integrated intensity was divided by 2 for comparison with the single vanadium site in VO_2^+.

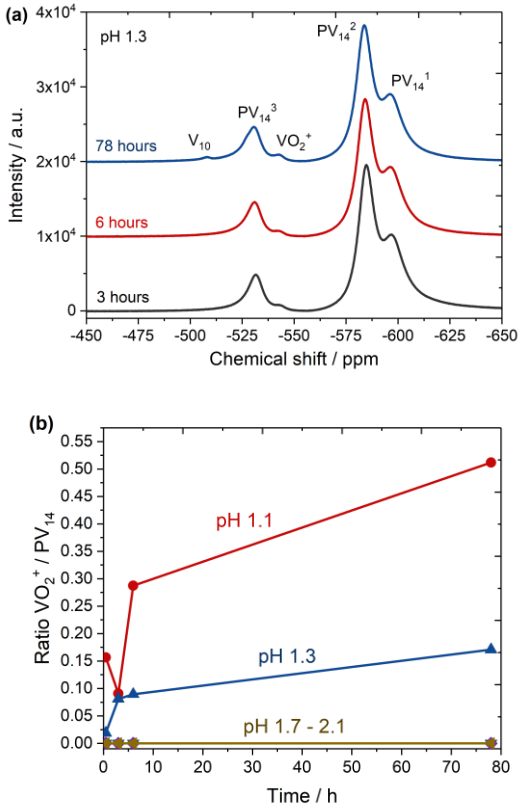

Fig. S6 (a) Typical ^{51}V NMR spectra for 50 mM **PV_{14}** in water with *pH* 1.3: 3 hours after adjusting the *pH* (black curve), after 6 hours (red curve) and after 78 hours (blue curve). (b) Development of VO_2^+ to **PV_{14}** ratio evaluated over time. The three lines for *pH* 1.7, 1.9 and 2.1 overlap.

5. Battery studies

The cross-over studies were performed by separating two half-cells each with a volume of 32 cm^3 by a membrane with a surface area of 16 cm^2. One of the half-cells contained a concentration *c* of 100 mM of the species under investigation (Fe^{2+} or **SiW_{12}**) in 1 M H_2SO_4, the electrolyte in the other half-cell was *c* = 20 mM of V^{3+} in the case of Fe^{2+} and *c* = 20 mM of Fe^{2+} in the case of **SiW_{12}**. The half-cell with the high concentration was stirred. In the half-cell with the lower concentration a working-, counter- and reference electrode were used to measure CVs periodically. The measured peak currents for Fe^{2+} and **SiW_{12}** were then converted to concentrations and plotted as seen in Fig. S7.

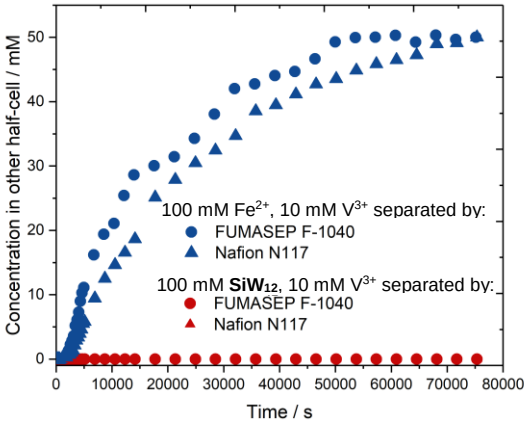

Fig. S7 Time dependent concentration of Fe^{2+} (blue data) and **SiW_{12}** (red data) measured by CVs in a half-cell that did not contain these species at t = 0s.

Electrochemical impedance spectroscopy was employed at an open circuit voltage of 1 V with an amplitude of 10 mV and in a frequency range 10 kHz $\leq f \leq$ 50 mHz. The resulting Nyquist plot is shown in Fig. S8.

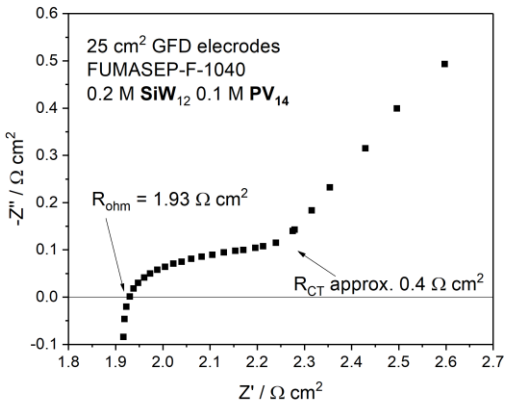

Fig. S8 Nyquist spectrum of the flow cell after 155 cycles at an open circuit voltage of 1 V with values for R_{ohm} and R_{CT} given.

A ^{51}V NMR spectrum of the catholyte was obtained after the 155 charge and discharge cycles shown in Fig. 5 at a moment when it was fully charged. The *pH* of the solution was 1.2. This spectrum is shown in Fig. S9 and is very similar to the spectra shown in Fig. S6a. Most of the vanadium is present as **PV_{14}**, however, a contribution from VO_2^+ at -544 ppm is also visible. Fitting of the peaks and data analysis revealed that the ratio of VO_2^+ to PV_{14}^3 signals is 0.10, and therefore the presence of VO_2^+ is as expected for the measured *pH*. This indicates, that degradation due to electrochemical processes does not contribute to the decomposition of **PV_{14}**. A ^{51}V NMR spectrum of the anolyte after 155 charge and discharge cycles gave no signal, indicating that no vanadium containing species had crossed through the membrane.

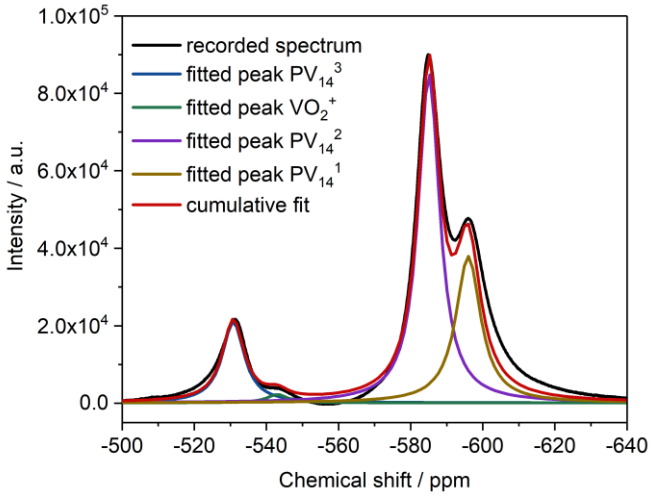

Fig. S9 ^{51}V NMR spectra of the catholyte after 155 charge and discharge cycles which took 14 days. The individual contributions were fitted to Lorentzian curves.

Table S2. Peak positions and integrated intensities for the curves fitted to the ^{51}V spectrum shown in Fig. S9.

Peak	Chemical shift / ppm	Integrated Intensity	Ratio to PV_{14}^3
PV_{14}^3	-530.8	240000	1
VO_2^+	-543.0	23500	0.10
PV_{14}^2	-585.1	960000	4.0
PV_{14}^1	-596.0	495000	2.1

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