Research Article

A polyoxometalate redox flow battery: functionality and upscale

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Abstract

While redox flow batteries carry a large potential for electricity storage, specifically for regenerative energies, the current technology-prone system—the all-vanadium redox flow battery—exhibits two major disadvantages: low energy and low power densities. Polyoxometalates have the potential to mitigate both effects. In this publication, the operation of a polyoxometalate redox flow battery was demonstrated for the polyoxoanions [SiW12O40]4– ([SiW12]) in the anolyte and [PV14O42]9– ([PV14]) in the catholyte. Emphasis was laid on comparing to which extent an upscale from 25 to 1400 cm² membrane area may impede efficiency and operational parameters. Results demonstrated that the operation of the large cell for close to 3 months did not diminish operation and the stability of polyoxometalates was unaltered.

Keywords: energy storage; redox flow battery; polyoxometalates; upscale

Introduction

Redox flow batteries (RFBs) are one of the few options to store energy from intermittent renewable-energy sources such as wind and solar electrochemically. The concept of the RFB has several advantages [1–3], such as the independent scalability of power and energy content. The former is determined by the size of the power converter, whereas the latter is given by the energy density of the electrolyte and the size of the tanks. Furthermore, as opposed to other battery types, the electrodes themselves are not redox-active and do not undergo conversion, intercalation or alloying reactions, which often lead to degradation. Instead, the energy is stored in redox-active species that are dissolved in the electrolyte.

Current challenges for RFB chemistry are their power density, their energy density and their costs [1–4]. According to Arenas et al., the development of new RFB technology can be described as follows [5]. As a first step, the fundamental electrochemistry is explored. Physical and chemical properties as well as important parameters, such as the equilibrium potential $U_0$ and the electron-transfer constant $k_0$ of the involved species, are investigated (Stage 1a). Following this, the cycling behaviour and stability of the novel RFB electrolytes are assessed in H-cells or laboratory-scale flow cells (Stage 1b). The next step then involves optimization of the electrochemical power converter according to the chemical and physical properties of the RFB electrochemistry. Potential and
current distribution, hydrodynamics, mass transport and cell geometry are optimized (Stage 2a), followed by the development of a pilot stack and a prototype RFB system (Stage 2b). The final stage according to Arenas et al. is a commercial implementation, which involves fabrication, testing, maintenance, marketing and many other tasks outside the realm of electrochemical engineering (Stage 3).

The properties of the used redox shuttles and employed solvents determine how the electron transfer and mass transport proceed within the power converter. Therefore, ideally, the power converter should be optimized for the specific redox shuttle. However, while many novel redox electrochemistries were proposed for RFBs in recent years, the literature focuses mostly on Stages 1a and 1b [6]. A recent literature review by our group showed that, of 24 published redox electrochemistries for RFBs, only 4 were demonstrated with a power rating of more than 100 W [3]. These are the all-vanadium RFB (VRFB) [7, 8], the zinc-bromine cell [9, 10], the iron-chromium cell [11, 12] and the bromine-poly sulphide RFB [1, 13, 14]. Of the remaining 20, 7 were tested in H-cell configurations only, all the others except for 2 in cells with less than 1-W power output. So, there is currently a knowledge gap between the laboratory Stage 1b and the electrochemical technology Stage 2a. This is one of the reasons for showing how a scale-up of a novel electrochemistry from a 25-cm² cell to a cell of 1400 cm² may affect important performance parameters of the RFB. The approach in our laboratory is to use polyoxometalates as redox shuttles. The redox electrochemistry described here is a polyoxometalate (POM) system, utilizing the polyoxoanions \( \text{SiW}_{12}^{4-} \) (SiW12) in the anolyte and \( \text{PV}_{14}^{2+} \) in the catholyte as nano-sized charge carriers [15].

Due to their structural and chemical properties, these metal-oxygen clusters have a number of advantages for energy-storage applications [15]. First, due to their large size, the interaction of the redox centres of the POM with solvent molecules is small. Therefore, the outer-sphere reorganization energy of the electron transfer is low, enabling fast kinetics and thus high power densities [16, 17]. Also, the inner-sphere reorganization energy is low due to the added electrons often being delocalized [18], causing only a minimal change in coordination upon reduction or oxidation [19]. This behaviour adds to the fast kinetics and thus high power densities. Their nature as large anions also prevents POMs from penetrating commercial cation-exchange membranes [15]. Size exclusion and electrostatic repulsion prohibit cross-over and mixing of the active species. Furthermore, some POMs exhibit high solubility, e.g. a concentration of 0.875 mol L⁻¹ can be obtained for SiW12 [15]. With multiple redox-active centres per molecule, this enables a high energy density in the battery. Moreover, both SiW12 and PV14 are stable during the operation of the battery. Losses in capacity only seem to stem from a parasitic reaction with residual oxygen, which could be avoided with an improved airtight setup [15].

Comparing the asymmetric POM system with the VRFB, one main difference is apparent: the electron transfer for the \( V^{2+/3+} \) and \( VO^{2+/3+} \) redox reactions is slow \( (k_0 \approx 10^{-6} \text{cm s}^{-1}) \) [7, 20], whereas electron transfer for the POMs is facile \( (k_0 \approx 10^{-2} \text{cm s}^{-1}) \) [15, 21]. The consequence is that the charge-transfer resistance \( R_{\text{CT}} \) for the POMs is considerably lower than for the VRFB. This leads to consequences for the design of the power converter, as the power-converter design aims to reduce the total resistance \( R_{\text{tot}} \), which is the sum of \( R_{\text{CT}}, R_{\text{diff}} \) and the Ohmic losses \( R_{\text{ohm}} \). The resistance of the cell determines the currents that can be drawn from a battery for a given voltage efficiency \( \eta_V \):

\[
\eta_V = \frac{\Delta U - R_{\text{ohm}} I}{\Delta U + R_{\text{int}} I}
\]

with cell voltage \( \Delta U \). In this study, we describe our findings of a novel flow battery electrochemistry for a laboratory-type cell of 25 cm² and the scale-up to a commercial cell of 1400 cm². Details on the basic electrochemistry of this novel RFB system can be found in a recent publication [15].

In this paper, we are describing the operational parameters such as charge–discharge cycles, coulombic and energy efficiencies, and stability of the electrolytes. Typical values such as \( R_{\text{ohm}}, R_{\text{CT}} \) and \( R_{\text{diff}} \) are determined using electrochemical impedance spectroscopy (EIS) and compared for the two cells.

1 Materials

1.1 Cells, sensors and parameters

Three electrode measurements were performed in custom-built glass cells with a polished glassy carbon working electrode (surface area \( A = 0.02 \text{ cm}^2 \)), a gold wire (diameter \( d = 0.5 \text{ mm} \)) counter electrode and a mercury/mercurous sulphate reference electrode in 1 M H₂SO₄ (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 SP-300 potentiostat was used for control and data acquisition.

The small flow cell used was a commercial cell (C-Tech 5x5, surface area \( A = 25 \text{ cm}^2 \)). Graphite felts (GFD, SGL Carbon) were used as electrodes and pre-treated at 400°C for 24 h in a laboratory atmosphere. In the cell, the 4.6-mm-thick electrodes were compressed to 3.5 mm. As the membrane, a cation-exchange membrane (FUMASEP—F-1075–PK) was used. During the experiment, the cell and the pump with tubing were kept in a polycarbonate box purged with nitrogen. The peristaltic pump could supply flow rates of 12–150 ml min⁻¹. Charge and discharge cycles were measured using a Bio-Logic BCS-810 battery tester. EIS measurements were performed using the Bio-Logic SP-300 (maximum supplied \( f = 7 \text{ MHz} \), measurement up to 200 kHz), as this could apply higher frequencies than the battery tester (\( f \) up to 10 kHz).

The large flow cell used was a commercial cell (J. Schmalz GmbH, surface area \( A = 1400 \text{ cm}^2 \)), originally designed for the VRFB chemistry. The same membrane as in the small cell was used. The flow rate was adjusted via the
pressure drop in the cell. Measured electrolyte flow and pressure drop were always proportional for both anolyte and catholyte. Flow rates from 450 to 1872 ml min⁻¹ were determined. Both the charge−discharge cycles and EIS were measured using a Bio-Logic BCS-815. In operando measurements of the pH values in the tanks were performed using Unitrode pH sensors from Metrohm. For data acquisition of the pH values, a National Instruments cDAQ-9175 was used in combination with a National Instruments Module 9205 and a current loop converter CLC-01 from company providing electronic measurement. Fig. 1 shows a photograph of a 1400-cm² cell with its periphery and containment. The cell itself is fixed in the top part of an acrylic glass container, the pumps are installed underneath and the electrolyte tanks are to the left and right of the pumps. The electrolyte tanks are continuously purged with nitrogen to avoid oxidation of the reduced redox species by atmospheric oxygen.

Tables 1 and 2 give an overview of the parameters used in this work. These quantities are used to discuss and compare the performance of the two cells.

1.2 Electrolytes and their electrochemistry

The electrochemistry and preparation of SiW₁₂ and PV₁₄ were described in detail in ref. [15]. In short, SiW₁₂ was bought from Sigma-Aldrich as tungstosilicic acid (H₅SiW₇O₂₈) and dissolved in de-ionised (DI) water with 1 M LiCl. Diluted LiOH was used for pH adjustment to 1.8 to prepare the anolyte. PV₁₄ was prepared following the synthesis for Na₅[H₄PV₁₄O₄₂]∙28 H₂O described in ref. [22]. To prepare the catholyte, Na₅[H₄PV₁₄O₄₂]∙28 H₂O was dissolved in DI water with 1 M LiCl and pre-reduced by addition of hydrazine (Sigma-Aldrich). This reduction was necessary, as otherwise both anolyte and catholyte would have been fully oxidized at the start of the battery operation, making cycling impossible. Cyclic voltammograms (CVs) of 1 mM PV₁₄ (red line) and 1 mM SiW₁₂ (blue line) are shown in Fig. 2a. PV₁₄ exhibits a multi-electron redox reaction in the range from 0.2 to 0.7 V vs. SHE. Experiments in a symmetric flow battery (PV₁₄ as both anolyte and catholyte) have shown that PV₁₄ transfers at least seven electrons [15]. SiW₁₂ shows two redox reactions at U°₁₁ = 0.0 V vs. SHE and U°₁₂ = -0.21 V vs. SHE. A third redox wave centred on U°₁₃ = -0.37 V vs. SHE is a two-electron redox reaction as opposed to the previous two, which are one-electron transfers. However, the third reaction is not used in the flow battery because the potential at which it takes place leads to an irreversible dimerization of the POM onto the carbon electrodes [23]. The polyhedral structures shown in Fig. 2b and Fig. 2c reveal that both SiW₁₂ and PV₁₄ are of the Keggin structure, with two additional V−O caps for the polyoxovanadate [24].

2 Results in a 25-cm² cell

In order to obtain data from a polyoxometalate redox flow battery, a commercial cell from C-Tech with a membrane area of 25 cm² was used. Heat-treated, compressed graphite felt (Sigracell GFD 4.6 EA) were used as electrodes as described earlier and a FUMASEP—F1075—PK membrane was employed. The electrolytes comprised 80 mM SiW₁₂ for the anolyte and 80 mM PV₁₄ for the catholyte in 1 M LiCl each. In charge−discharge cycles, the 25-cm² cell exhibited a coulombic efficiency ηC²5cm² of 96% and an energy efficiency ηE²5cm² of 64%. The theoretical capacity was Qth,25cm² = 214 mAh, of which 90% was reached. A study of the influence of the electrolyte concentration on the diffusion resistance Rdiff was conducted.

In Fig. 3, Rdiff is compared for the 25-cm² cell with 80 mM SiW₁₂ and 80 mM PV₁₄ as electrolytes (blue data) and a setup in which the anolyte was 600 mM SiW₁₂ and the catholyte 300 mM PV₁₄ (red data). To balance the charge, the PV₁₄ was pre-reduced by four electrons with hydrazine (instead of a pre-reduction by two electrons as for equal concentrations of POMs). The volume flow υ has been recalculated to normalized mass flow ε (see Table 2) by multiplying υ with the used concentrations of catholyte. It can clearly be seen that the mass flow, that is the amount of unreacted active material that is brought into the cell per minute, determines Rdiff.

3 Results in a 1400-cm² cell

3.1 Charge and discharge

An electrolyte solution with 80 mM SiW₁₂ was prepared as anolyte; a solution of 80 mM PV₁₄ was used as catholyte. With nₐn = nₐc = 2 L and Vₐn = Vₐc = 1.5 L, the theoretical capacity for both electrolytes was Qth = Qth = 6.4 Ah. Fig. 4a shows cycle 10 as an example for the cycling behaviour of the 1400-cm² cell. At a current density of 4 mA cm⁻², the cell reaches its upper voltage cut-off Umax = 1.4 V after ~3000 s; the successive discharge takes another 3000 s and stops at Ulow = 0 V. During cycle 10, the coulombic efficiency was ηC¹⁰ = 99.13 % and the energy efficiency was measured to be ηE¹⁰ = 86.13%. The pH probes reveal that the concentration of hydronium ions in the
During discharge, the reverse process of Equation 1 takes place: $\text{PV}_{14}$ takes up protons from the catholyte and the pH increases. This effect is restricted to the catholyte because the majority of the cations that cross the cation-exchange membrane are $\text{Li}^+$ ions. Fig. 4b compares the previously shown 10th cycle to the 1000th cycle. The latter was recorded 1508 h or 63 days after the former. As can be seen in the graph, the general shape of the charge and discharge curves is not changed, exhibiting similarly high efficiencies $\eta_{\text{1000}} = 99.2\%$ and $\eta_{\text{1000}} = 85.1\%$. The theoretical capacity $Q_{\text{an}} = Q_{\text{cat}} = 6.4\,\text{Ah}$ was not reached during cycling. In the 10th cycle, a discharge capacity of 4.6 Ah was measured, which corresponds to 72% of the theoretical capacity. Two plateaus can easily be distinguished and can be assigned to the first and second one-electron waves of $\text{SiW}_{12}$. The oxidation state of $\text{PV}_{14}$ does not influence the potential that much because of its multiple electron waves occurring at similar potentials. However, the plateau at higher voltages is shorter than the one at low voltages, which can be explained by an insufficient pre-reduction of $\text{PV}_{14}$ with hydrazine or oxidation by residual oxygen, respectively. Since the unit was not suited for applying a vacuum, it was impossible to completely empty the whole container of oxygen, so oxidation by air probably happened to a certain degree.

The long-term cycling behaviour of the 1400-cm² cell is shown in Fig. 5. The changes in pH of the anolyte and catholyte are given in Fig. 5a. The behaviour over 1400 cycles is in line with the pH changes shown in Fig. 4a for cycle 10; the hydronium concentration in the catholyte (green area) changes much more than that of the anolyte (blue area). The pH of the catholyte is stable; the pH of the anolyte increases slightly from 1.5 to 2 during 1400 cycles (pH data were not continuously recorded). Fig. 5b shows the capacity retention (red data) and the current density (blue line) of the 1400-cm² cell during 1400 cycles. The discharge capacity dropped from $Q_{\text{ch}}^{10} = 4.70\,\text{Ah}$ to $Q_{\text{ch}}^{1400} = 3.95$...
Ah, which equals an average capacity loss of \(0.53 \times 10^{-3}\) Ah/ cycle or 0.011% per cycle. The capacity loss of 0.75 Ah may be due to slow ingress of atmospheric oxygen, taking up protons while being reduced to water. This is supported by similar numbers of charges involved: 0.75 Ah is equal to 28 mmol of transferred electrons while the pH shift from 1.5 to 2 mentioned earlier corresponds to 32 mmol of used-up protons.

When the current density was increased from 4 to 43 mA cm\(^{-2}\) (cycles 185 to 240), the discharge capacity dropped to \(Q_{\text{dch}} \approx 3.2\) Ah. Comparing Fig. 5a and Fig. 5b, one can notice that the pH of the anolyte decreases from approximately 1.5 to 1.0 when the current density is increased from 4 to 43 mA cm\(^{-2}\). This observation can currently not be explained. Fig. 5c shows the coulombic efficiency \(\eta_C\) (black data) and energy efficiency \(\eta_E\) (red data). For the 1400 cycles measured, \(\eta_C\) is at approximately 99%.

During the cycles with higher current density (cycles 185 to 240), \(\eta_C\) increases to 100%. The coulombic efficiency \(\eta_C\) of the PV\(_{14}\)-SiW\(_{12}\) system in the 1400-cm\(^2\) cell is higher than it is for typical VRFB cells (\(\eta_C^{\text{VRFB}} \approx 0.9\ [1, 25, 26]\)). While the VRFB loses charge through cross-mixing of the electrolytes and by the parasitic hydrogen evolution reaction (HER) [27], the POM system experiences no cross-over and the HER has not been observed due to more positive potentials in the anolyte compartment. An energy efficiency \(\eta_E \approx 86\%\) during the cycles at 4 mA cm\(^{-2}\) and only \(\eta_E \approx 40\%\) during the cycles at 43 mA cm\(^{-2}\) was achieved. An EIS study was conducted to determine which resistance, \(R_{\text{Ohm}}\), \(R_{\text{CT}}\) or \(R_{\text{diff}}\), contributes most to the overvoltage and therefore the decrease in \(\eta_E\) at higher rates.

### 3.2 EIS

Impedance spectra were recorded at different volumetric flow rates \(\vec{V}\) in the 1400-cm\(^2\) cell; Nyquist plots of these spectra are shown in Fig. 6a. The volumetric flow rates \(\dot{V}\) (ml min\(^{-1}\)) were normalized to volumetric flow rates per surface area of the cell \(\dot{V}_{\text{norm}}\) (ml min\(^{-1}\) cm\(^{-2}\)).

To obtain \(R_{\text{Ohm}}\), \(R_{\text{CT}}\) and \(R_{\text{diff}}\), semicircles were fitted to the spectra. The intercepts of these semicircles with the abscissa determine the resistances. The first intercept at the highest frequencies is \(R_{\text{Ohm}}\), then \(R_{\text{CT}}\) followed by \(R_{\text{diff}}\). As can be seen in Fig. 6a, especially in the inset Fig. 6b, the first semicircle (at high frequencies) is relatively independent of the normalized flow rate. The second semicircle (at lower frequencies) becomes smaller with higher normalized flow rates. Determined values for \(R_{\text{Ohm}}\) (red segment), \(R_{\text{CT}}\) (blue segment) and \(R_{\text{diff}}\) (green segment) are shown in Fig. 6c. The Ohmic resistance \(R_{\text{Ohm}}\) represents Ohmic losses in the leads, the current collector, the contact resistance between the current collectors and the electrodes, the resistance of the solution and the ionic resistance in the membrane [28].

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is independent of flow rate and with $R_{\text{Ohm}} = (2.806 \pm 0.021) \ \Omega \ \text{cm}^2$ higher than typical values for the VRFB system, $R_{\text{Ohm}} \approx 0.5 \ \Omega \ \text{cm}^2$ [29]. We assume that this high resistance stems mostly from the ionic resistance of the membrane. Due to a lack of protons ($pH > 1$), Li$^+$ cations are used to enable charge balance by their transport through the membrane and the diffusion coefficient for Li$^+$ through a perfluorosulphonated polymer membrane is smaller than that of H$^+$ [30]. The charge-transfer resistance $R_{\text{CT}}$ is also independent of the flow rate and, at $R_{\text{CT}} = (0.382 \pm 0.015) \ \Omega \ \text{cm}^2$, smaller than $R_{\text{Ohm}}$. The explanation for this small value of $R_{\text{CT}}$ is that it is inversely proportional to the electron-transfer constant $k_0$ and $k_0$ is large for the POMs [15, 31]. The resistance invoked by mass-transport limitations depends on $\dot{v}$ because the flow rate governs at which rate fresh electrolyte is transported to the electrodes, which can then undergo electron transfer. Even at the highest flow rate ($\dot{v} = 1.34 \ \text{ml cm}^{-2} \ \text{min}^{-1}$), $R_{\text{diff}} = 4.4 \ \Omega \ \text{cm}^2$ and therefore diffusion presents a larger resistance than $R_{\text{Ohm}}$ and $R_{\text{CT}}$ combined. At lower flow rates, this problem is aggravated. There are two ways to bring more unreacted electrolyte to the electrode in a given time: (i) Increase the concentration of the redox species to increase the amount of reactant per pumped volume. This approach can be done without changing the power converter and has been shown earlier in this work using the 25-cm$^2$ cell (see Fig. 3). (ii) Increase the pump rate and thereby the flow of electrolyte. In order to increase the pump rate, the cell
3.3 Post-cycling analysis of electrolytes

After 1400 cycles, the electrolytes used were extracted from the battery and investigated by $^{51}$V NMR and CV studies, the results of which are shown in the supporting information. Supplementary Fig. 1a (see the online supplementary data) gives the $^{51}$V NMR spectra of the anolyte and the catholyte. The signal of the catholyte (red curve) shows the typical fingerprint signal of PV$_{14}$ [15, 22]. Two small additional peaks at a chemical shift of approximately 505 ppm and 525 ppm are attributable to [V$_{13}$O$_{28}$]$^{6-}$, a polyoxovanadate that forms from PV$_{14}$ at pH > 2.3 but is in a pH-dependent dynamic equilibrium with PV$_{14}$ [22]. We investigated the formation of [V$_{13}$O$_{28}$]$^{6-}$ and the time and pH dependency of this process earlier via $^{51}$V NMR and found that a pH value as low as 1.7 can be tolerated permanently and even lower values are acceptable for short periods of time [15]. All observed conversions are reversible and do not cause permanent capacity loss. This indicates that PV$_{14}$ in the catholyte was stable during the cycling and did not decompose to single vanadium species. The anolyte (blue curve) shows no vanadium signal, indicating that no PV$_{14}$ has crossed over into the anolyte reservoir during the 1400 cycles. This result is in line with our earlier results that showed that the negatively charged POMs do not cross cation-exchange membranes [15]. CVs of both electrolytes were recorded to check the state of health of the anolyte and to confirm the result of the $^{51}$V NMR for the catholyte. Supplementary

4 Comparison of the two cells

In order to compare the cycling performance of the two cells under investigation, both the flow rate and the capacity are normalized, as shown in Fig. 7a. The 25-cm$^2$ cell reached a discharge capacity of Q$_{dch}$,25cm$^2$ = 192 mAh, which is 90% of its theoretical capacity of Q$_{theo}$,25cm$^2$ = 214 mAh. For the 1400-cm$^2$ cell, the 10$^{th}$ cycle that was described in Fig. 4b is given for comparison. At a similar flow rate and the same current density (4 mA cm$^{-2}$), the coulombic efficiency of the larger cell is higher: $\eta_{E}$,1400cm$^2$ = 86% as compared to $\eta_{E}$,25cm$^2$ = 64%. Therefore, the voltage efficiency of the 1400-cm$^2$ cell must be higher than that of the 25-cm$^2$ cell (as $\eta_{E} = \eta_{V} \cdot \eta_{C}$). While the coulombic efficiency is mainly given by the redox electrochemistry and the electrode materials, cell construction and its materials determine the voltage efficiency. To identify the loss mechanism(s) that contribute to the difference in voltage efficiency, we compare $R_{\text{Uml}}$, $R_{\text{CT}}$, and $R_{\text{diff}}$ for both cells versus the normalized flow rate. Data points for the 1400-cm$^2$ cell in Fig. 7b are the same as shown in Fig. 6b, but here the resistances for the smaller cell are shown in
The small cell. The concentration of electrolyte is a possible approach to reduce $R_{\text{diff}}$.

5 Summary and conclusion
In this study, we have shown that a recently developed POM electrochemistry for flow batteries can work effectively in a redox flow battery. Data obtained for a 25-cm$^2$ laboratory cell were quite satisfying, with a coulombic efficiency of 64%. The energy efficiency of 96% was considerably lower, probably due to specifications in the cell design. It was also demonstrated that a large single cell of 1400 cm$^2$ can be successfully employed. While the cell was designed for the VRFB chemistry, it still shows good performance for the investigated SiW$_{12}^-$/PV$_{14}^-$ electrolytes. During 88 days, the 1400-cm$^2$ cell was charged and discharged 1400 times. The initial discharge capacity of $Q_{\text{dch}}$ was 4.70 Ah dropped to $Q_{\text{dch}}^{1400}$ = 3.95 Ah, which equals an average capacity loss of 0.53 10$^{-3}$ Ah/cycle. During the cycling at 4 mA cm$^{-2}$, a coulombic efficiency of $\eta_C \approx 99\%$ and an energy efficiency of $\eta_E \approx 86\%$ were reached—both values larger than in the small laboratory cell. A post-cycling analysis was performed on the electrolytes. Both $^{51}$V NMR and cyclic voltammetry showed that the polyoxoanions in the electrolyte were not damaged during the battery operation and that the molecules had not crossed the membrane. Using pH sensors in the electrolyte tanks, we could show that the pH value of the catholyte changes during cycling, but that the average pH of the catholyte does not shift over 1400 cycles.
The average pH of the anolyte increases slightly during the experiment, from pH 1.5 to 2 during 1400 cycles.

While the cell showed a high energy efficiency at low current densities, this value dropped to \( \eta_e \approx 40 \% \) at 43 mA cm\(^{-2}\). Using impedance spectroscopy, we found that both the Ohmic resistance \( R_{\text{ohm}} \) and the charge-transfer resistance \( R_{\text{CT}} \) were independent of the electrolyte flow rate, but that high flow rates decreased the mass-transport resistance \( R_{\text{diff}} \). At the highest volumetric flow rate (1.34 ml cm\(^{-2}\) min\(^{-1}\)), the measured resistances were as follows: \( R_{\text{ohm}} = 2.78 \), \( R_{\text{CT}} = 0.39 \) and \( R_{\text{diff}} = 4.4 \Omega \ cm^2 \) . Comparing the first electron transfer of SiW\(_{12}\) (\( k_0 = 4.2 \times 10^9 \) cm s\(^{-1}\)) and the VO\(^{2+}/\text{VO}_2^+\) redox reaction (\( k = 3 \times 10^7 \) cm s\(^{-1}\)), the electron transfer of the POM is more than five orders of magnitude faster than that of the latter [15, 35]. This confirms the assumption from the introduction that, for redox couples with fast electron-transfer kinetics, the total resistance \( R_{\text{total}} \) depends more on the cell parameters \( R_{\text{diff}} \) and \( R_{\text{ohm}} \) than on the electrochemical parameter \( R_{\text{CT}} \). For higher concentrations, this will also remain true, with a larger influence from \( R_{\text{ohm}} \). While the above resistances were recorded at an electrolyte concentration of \( c_{\text{an}} = c_{\text{cat}} = 80 \) mM, we have shown in Fig. 3 that \( R_{\text{diff}} \) decreases with higher mass flows (mol min\(^{-1}\)cm\(^{-2}\)) and therefore concentrations. Simultaneously, \( R_{\text{CT}} \) will decrease with higher concentrations, as it is inversely proportional to the concentration of redox species [7]. The Ohmic drop \( R_{\text{ohm}} \), which is governed by the membrane, will remain unchanged by a change in the concentration of active material.

This indicates that, in order to increase the performance of the presented asymmetric POM RFB, the cell, specifically parameters related to \( R_{\text{ohm}} \) and \( R_{\text{diff}} \) need to be the main focus for improvements. Components to work on are:

- **Membrane/separatior:** The Ohmic drop \( R_{\text{ohm}} \), which is dominated by the membrane resistance, is likely to be the highest resistance in a cell, with a higher concentration of active material, as \( R_{\text{ohm}} \) does not scale with the concentration of the electrolyte. To reduce \( R_{\text{ohm}} \) incurred from the membrane, two measures can be taken:
  - Use a membrane thinner than the currently used FUMASEP—F-1075-PK (thickness 75 \( \mu \)m), as the ionic resistance of the membrane increases with thickness of the membrane. For the VRFB, it was found that a sulfonated fluorinated poly(arylene ether) membrane with 45-\( \mu \)m thickness enabled a higher power density than the same type of membrane with 28 or 80-\( \mu \)m thickness [36]. The 45-\( \mu \)m-thick membrane was found to be the optimum due to the combined effects of Ohmic losses and cross-over. We found that SiW\(_{12}\) does not cross perfluorosulfonic acid (PFSA) membranes as thin as 40 \( \mu \)m due to size exclusion and electrostatic repulsion [15]. The minimum membrane thickness that still prevents cross-over should be determined.
  - Reduce the specific Ohmic resistance of the membrane. We assume that the high value for \( R_{\text{ohm}} \) stems from the fact that Li\(^+\) cations are used for charge balance instead of protons. The cell chemistry could either be transferred into a more acidic solvent, which allows the use of protons, or the membrane could be optimized for the use of Li\(^+\) cations. A lower pH than currently employed might lead to stability issues for PV\(_{14}\) [22].

- **The geometry of the power converter and its flow design** [5, 37]: Neglecting an effect of \( R_{\text{ohm}} \), there are two limiting cases for the type of rate control in an electrochemical converter: charge-transfer control and mass-transport control [37]. In the former case, the rate of electron transfer limits the current that can be drawn from the cell; a larger overpotential or a larger surface area for the electrode can increase the rate. Under mass-transport control, the supply of active species and its removal after reaction determine the current; a limiting current \( I_{\text{cat/an}} \), \( c_{\text{an}}/c_{\text{cat}} \) and \( c \) can be defined. Assuming that \( R_{\text{diff}} \) is a measure for 1/\( L \), the connection between \( I \) and \( c \) is empirically shown in Fig. 3. The proportionality depends on the geometry and typically turbulent flow allows higher \( I \) than laminar flow. As the POMs exhibit fast electron transfer, and judging from Fig. 6c, \( I \) needs to be increased to enhance the performance of the cell, which can be done in two ways:
  - Increase the concentration \( c_{\text{an}}/c_{\text{cat}} \). This approach was tested for the small cell with the result shown in Fig. 3. Clearly, a higher concentration of active species reduces \( R_{\text{diff}} \) and increases \( I_L \).
  - Increase the rate at which fresh active material is supplied to the electrodes. This can be done by increasing the pump rate or by enhancing the spatial distribution of the mass flow in the cell to maximize electrolyte utilization.

### Supplementary data

Supplementary data is available at Clean Energy online.

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