

Highly reduced and protonated aqueous solutions of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ for on-demand hydrogen generation and energy storage

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As our reliance on renewable energy sources grows, so too does our need to store this energy to mitigate against troughs in supply. Energy storage in batteries or by conversion to chemical fuels are the two most flexible and scalable options, but are normally considered mutually exclusive. Energy storage solutions that can act as both batteries and fuel generation devices (depending on the requirements of the user) could therefore revolutionize the uptake and use of renewably generated energy. Here, we present a polyoxoanion, $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, that can be reversibly reduced and protonated by 18 electrons/ H^+ per anion in aqueous solution, and that can act either as a high-performance redox flow battery electrolyte (giving a practical discharged energy density of 225 Wh l^{-1} with a theoretical energy density of more than $1,000 \text{ Wh l}^{-1}$), or as a mediator in an electrolytic cell for the on-demand generation of hydrogen.

Our increasing reliance on renewable energy sources brings with it a need to store this energy to smooth out peaks in demand and troughs in supply^{1–3}. Among the solutions proposed for this challenge, two stand out in terms of their flexibility and scalability: storage of energy as electrical charge in batteries^{4–7} and storage of energy via conversion to chemical fuels, like H_2 (refs^{8–12}). Both approaches bring their own unique set of advantages and drawbacks, and it is often not obvious as to which would make the better choice in any given circumstance^{13,14}. Against this background, energy storage solutions such as battolysers, which can act as both batteries and fuel generation devices, could have a transformative effect on how renewable energy is used^{15,16}. Soluble redox mediators are the cornerstone of these promising devices, but the electron storage capacity of the mediators considered hitherto is limited to only 1–2 electrons per molecule. As the number of electrons that can be stored in the mediator places a fundamental limit on the energy and capacity density of these energy storage systems, there is a great need to search for new mediator systems that can store as many electrons per molecule as possible.

Polyoxometallates show tremendous promise in this regard because of their ability to store multiple electrons in a reversible manner^{17,18}. For example, Launay reported that silicotungstic acid ($[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$) can be highly reduced in aqueous solution¹⁹, and Bond and co-workers have reported that the polyoxometallates $\alpha\text{-}[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ is capable of taking part in extensive redox processes on the voltammetric timescale in mixed acetonitrile/water solutions^{20,21}. In many of these cases, the effects of adding protons or other small cations (such as Li^+) have been shown to be crucial for modifying the redox potentials of the polyoxometallates, facilitating the generation of reduced species at less cathodic potentials compared to when these cations are absent^{22–24}.

On account of the ability of polyoxometallates to undergo a large number of redox processes in a reversible fashion, polyoxometallates have been investigated as potential energy storage devices²⁵, including solid-state batteries (and battery electrodes) with Li^+ (refs^{26–30}) and Na^+ (refs^{30,31}) as charge carriers, and in redox flow batteries^{32–35}. In these latter cases, however, the achieved power and energy

densities have hitherto been rather low, with the current champion specific energy density for a polyoxometallates-based redox flow battery being 15.4 Wh l^{-1} (ref.³⁶). This is because polyoxometallates have not yet lived up to their potential in terms of storing a large number of electrons in a reversible manner, and hence we hypothesized that it should be possible to produce more highly reduced systems that display reversibility.

Here, we show that the polyoxoanion $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ displays notable proton-coupled electron redox activity, which allows this molecule to reversibly accept up to 18 protons and electrons in aqueous solution, allowing the construction of polyoxometallates-based redox flow batteries with energy densities of 225 Wh l^{-1} , or the rapid on-demand generation of hydrogen from water as part of a decoupled electrolysis system.

Results

The first suggestion of the intriguing redox chemistry displayed by $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (prepared according to a modified literature procedure³⁷, see Supplementary Sections I and II and Fig. 1a) in aqueous solution was provided by cyclic voltammetry (CV) experiments in a thin-layer electrochemical cell (Supplementary Fig. 3), such as those shown in Fig. 1b,c. Hence at a low concentration (2 mM), $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ displays four reversible waves within the range +0.6 to -0.6 V (versus standard hydrogen electrode, SHE). At pH 7, each of these waves is a simple one-electron process (black line in Fig. 1b), as determined by controlled potential bulk electrolysis and by UV-vis titration, which agrees with literature reports for this compound (Supplementary Figs. 4 to 8)³⁸. However, as the pH is lowered to 4, both peaks below 0 V become two-electron processes, as previously observed^{39–43}. Importantly, on moving to higher concentrations of the polyoxometallates (100 mM), there is a significantly enhanced redox wave for $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ below -0.3 V , when compared to the control studies at 2 mM concentration or the CV of 1 M H_2SO_4 in the absence of polyoxometallates (Fig. 1c and Supplementary Fig. 9).

This behaviour suggested to us that the storage of electrons in the polyoxometallates was proton-coupled, and that as the concentration of polyoxometallates in solution increased (and the pH

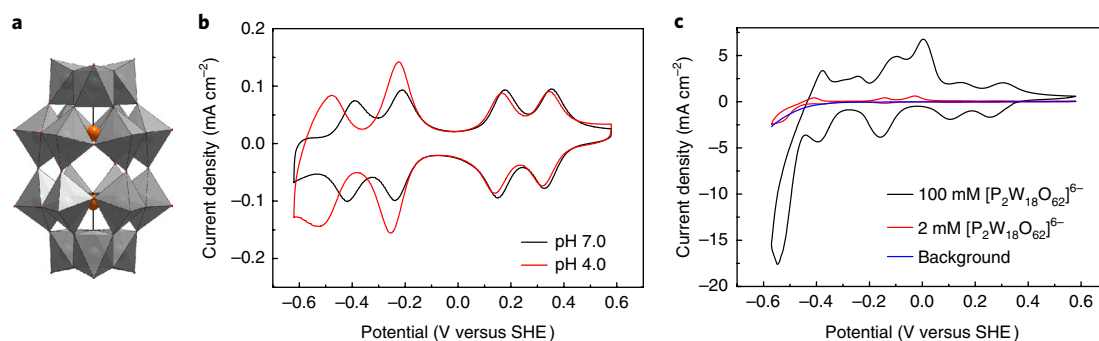


Fig. 1 | Structure and basic electrochemistry of $[P_2W_{18}O_{62}]^{6-}$. **a**, Structure of $[P_2W_{18}O_{62}]^{6-}$ (tungsten, grey; phosphorus, orange). **b**, Cyclic voltammograms of a 2 mM solution of $Li_6[P_2W_{18}O_{62}]$ in 1 M Li_2SO_4 (pH 7, black line) and in 1 M Li_2SO_4/H_2SO_4 (pH 4, red line) at a scan rate of 10 mV s^{-1} , showing the reversible nature of these waves. **c**, Cyclic voltammograms of a 2 mM solution (red line) and 100 mM solution (black line) of $Li_6[P_2W_{18}O_{62}]$ in 1 M H_2SO_4 , and a CV of just 1 M H_2SO_4 for comparison (blue line), showing the effects of increasing solution pH and polyoxometallates concentration on the redox profile. Scan rate, 10 mV s^{-1} .

decreased) it might be possible to store an increasing number of electrons in the polyoxometallates. Encouraged by these results, a three-electrode electrochemical flow cell with an $Hg/HgSO_4$ reference electrode was constructed to quantify the number of electrons that the polyoxometallates could store in a reversible fashion (Fig. 2a; see Supplementary Section III for details concerning the membrane⁴⁴, materials and assembly).

In this device (Fig. 2a), water was oxidized on the iridium oxide catalyst (left-hand side of left-hand cell), producing O_2 , protons and electrons. These electrons and protons were used to reduce and protonate an aqueous solution of $[P_2W_{18}O_{62}]^{6-}$ on the right-hand side of the cell, forming more reduced polyoxoanions ($[P_2W_{18}O_{62}]^{(6+n)-}$). Once a desired amount of charge had been passed, the reduced polyoxometallates solution was then reoxidized electrochemically by recirculation of the solution to a carbon anode in a cell like that shown on the right-hand side of Fig. 2a. The charge stored reversibly in the polyoxometallates solution could then be gauged by comparing the charge originally used to reduce the polyoxometallates with the charge obtained when it was reoxidized.

The key to dramatically increasing the amount of charge in terms of protons and electrons that can be reversibly stored on the $Li_6[P_2W_{18}O_{62}]$ cluster is to increase the concentration of the cluster in aqueous solution at low pH, as shown in Fig. 2b (note that these studies were conducted without any supporting electrolyte in the polyoxometallates solution). In each case, the charge passed equated to that which would be expected (in the absence of other reactions) to bring about an 18-electron reduction of the polyoxometallates (red dashed line in Fig. 2b). At low polyoxometallates concentrations, it is apparent that most of the charge passed during the reduction process cannot be extracted during reoxidation of the polyoxometallates solution. For example, at a concentration of cluster of 2 mM, only 4 of the 18 electrons passed during the reduction process can be recovered. By increasing the concentration of $Li_6[P_2W_{18}O_{62}]$ to 50 mM, the amount of charge recovered increased to around 16 of the 18 electrons. Analysis of the headspace of the polyoxometallates holding tank indicates that the charge that is not recovered by electrochemical reoxidation is instead liberated as hydrogen (Supplementary Section IV). By increasing the concentration further (to 100 mM), 96% of the charge used during the reduction process can now be extracted by electrochemical reoxidation, implying that each polyoxometallates molecule is reversibly storing an average of 17.2 electrons under these conditions (Supplementary Table 1 and Supplementary Section V).

Flow cells with low ohmic polarization resistances ($\sim 20\text{ m}\Omega$ in our case) are essential for the efficient operation of this system because reduction of the polyoxometallates anions happens at only

slightly less cathodic potentials than hydrogen evolution (Fig. 1). Hence, we employed high flow rates of the polyoxometallates solution (100 ml min^{-1}) to minimize mass transport overpotentials. We also found it expedient to use galvanostatic electrolysis methods to control the current density so that the polyoxometallates could be reduced without causing excessive hydrogen evolution. Using traditional static electrochemical cells (that is, without any continuous flow of electrolyte) led to much higher resistances (usually at least several dozen ohms), which were found to be too high for the polarization potential to be sufficiently controlled when using galvanostatic methods. Conversely, the use of potentiostatic methods in static electrochemical cells was found to lead to depletion of the polyoxometallates at the electrode and therefore gave rise to large hydrogen evolution currents. Hence flow cells seem essential if excessive hydrogen evolution is to be avoided when performing the reduction of $[P_2W_{18}O_{62}]^{6-}$ by more than around six electrons.

The ability of the $Li_6[P_2W_{18}O_{62}]$ cluster to store large numbers of electrons under flowed redox conditions was then explored by passing charge equivalent to 32 electrons per cluster at a concentration of 100 mM and measuring the difference between the reduction and reoxidation processes in terms of coulombic efficiency, as shown in Fig. 2c (also Supplementary Figs. 10 to 13). This shows that the efficiency of polyoxometallates reduction and reoxidation remains at or above 95% up to a reduction level of 18 electrons per polyoxometallates molecule. The maximum number of electrons that can be recovered electrochemically from the reduced polyoxometallates under these conditions appears to be 20 per polyoxometallates molecule, although there are considerable parasitic losses at this maximum value. Hence, we consider 18 electrons to be the maximum number of electrons that can be stored per polyoxometallates molecule under these conditions without appreciable losses to other processes.

The stability of $[P_2W_{18}O_{62}]^{6-}$ during the 18-electron redox process was probed electrochemically with successive galvanostatic reduction/reoxidation cycles (Fig. 2d,e), with the coulombic efficiency of this process being $>95\%$ with a capacity retention of 97.3% over 100 cycles. In addition, high-resolution mass spectrometry analysis of a 100 mM solution of $[P_2W_{18}O_{62}]^{6-}$ after such redox cycling serves as further evidence that the polyoxometallates is stable under these conditions (Supplementary Section VI).

Given that $[P_2W_{18}O_{62}]^{6-}$ can be reversibly reduced by 18 electrons with high coulombic efficiency, we decided to assess the performance of this highly reduced polyoxometallates for proton-electron storage for on-demand hydrogen generation. Accordingly, we reduced a 100 mM solution of $[P_2W_{18}O_{62}]^{6-}$ by 18 electrons per polyoxometallates using the electrochemical flow system (left-hand

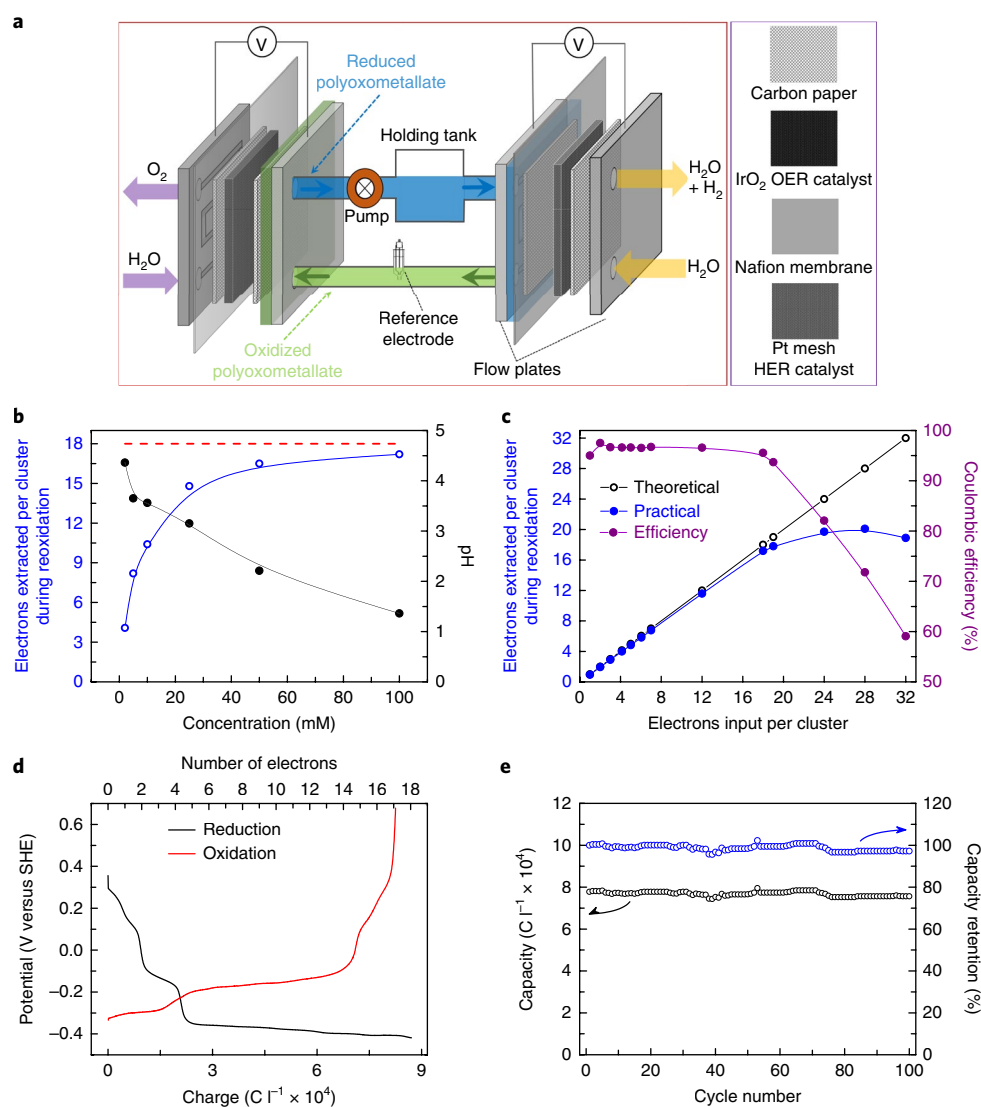


Fig. 2 | Reversible multi-electron redox chemistry of $[P_2W_{18}O_{62}]^{6-}$. **a**, Flow cell device used for the reduction and oxidation of $[P_2W_{18}O_{62}]^{6-}$. HER, hydrogen evolution reaction; OER, oxygen evolution reaction. **b**, Relationship between polyoxometallates concentration, solution pH (measured before electro-reduction, black filled circles) and the number of electrons that can be extracted from a reduced solution of the polyoxometallates (blue open circles). The number of electrons used to reduce the polyoxometallates was limited at 18 per molecule (red dashed line). **c**, Total number of electrons that can be extracted from a 100 mM solution of polyoxometallates after reduction by various numbers of electrons per polyoxometallates molecule. Under these conditions, 18 electrons represents the upper limit above which competitive hydrogen evolution becomes significant. **d**, Representative 18-electron reduction/reoxidation curves of a 50 mM solution of $[P_2W_{18}O_{62}]^{6-}$. **e**, Plot of 100 successive 18-electron reduction/reoxidation cycles of a 50 mM solution of $[P_2W_{18}O_{62}]^{6-}$, showing near-quantitative capacity retention. In **d** and **e**, a current density of $\pm 50 \text{ mA cm}^{-2}$ was applied and 1M H_2SO_4 was used as a supporting electrolyte.

side of Fig. 2a), and then exposed this to Pt/C (see Supplementary Section VII for a description of the apparatus used). An initial rate of 3,500 mmol of hydrogen per hour per mg of Pt was achieved (Fig. 3a), which is a significantly higher rate per mg of Pt than that achieved in conventional proton exchange membrane electrolyzers (where rates in state-of-the-art systems are on the order of 50–100 mmol of hydrogen per hour per mg of Pt)^{45,46}. Supplementary Fig. 22 relates the amount of hydrogen that is evolved to the number of electrons used to reduce the polyoxometallates initially: after 400 s, around 14 of the initial 18 electrons (per polyoxometallates anion) are recovered as hydrogen, and hydrogen evolution is still ongoing (albeit at a much slower rate than initially). Given that Fig. 1 shows that the final two reoxidation potentials of the reduced polyoxometallates are anodic of the reversible hydrogen potential (0V versus SHE), then contact with Pt/C would only ever be expected to yield hydrogen

until the two-electron reduced species is reached. Hydrogen evolution would then be expected to cease, leaving a two-electron-reduced anion, $[P_2W_{18}O_{62}]^{8-}$ (with appropriate charge-balancing cations). Hence, under these conditions, 16 is the maximum number of electrons that can be obtained spontaneously as hydrogen by contacting the reduced polyoxometallates with Pt/C, in very good agreement with the data in Supplementary Fig. 22.

Interestingly, spontaneous hydrogen evolution from solutions of $[P_2W_{18}O_{62}]^{(n+6)-}$ can be achieved without any electrochemical bias and without the need for any catalyst, by simply diluting the solution. This is shown in Fig. 3b, where 50 mM solutions of $[P_2W_{18}O_{62}]^{6-}$ (pH 2) were first reduced by 16 electrons per polyoxometallates molecule, before then being diluted to a final concentration of 2 mM with various solutions. When this dilution is carried out with water (red circles), hydrogen

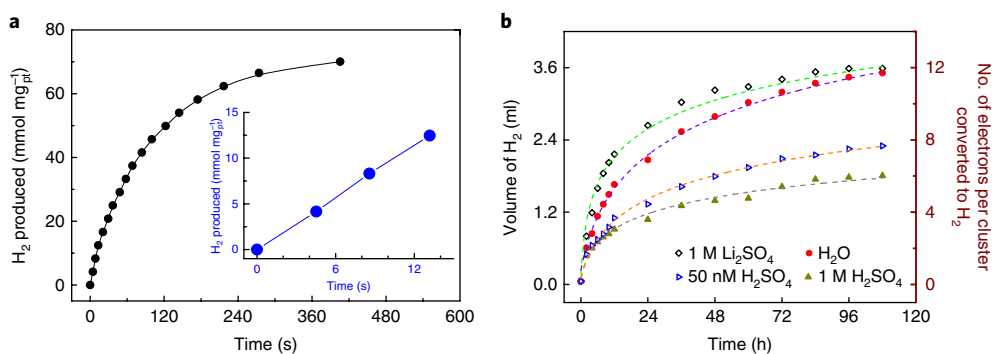


Fig. 3 | Hydrogen production, on demand, from solutions of reduced polyoxometallates. **a**, H_2 production from a 10 ml sample of 0.1 M 18-electron reduced polyoxometallates solution under an argon atmosphere in the presence of 10 mg Pt/C catalyst (1% Pt by weight). **b**, Dilution of 0.5 ml aliquots of 50 mM 18-electron reduced polyoxometallates solution with 1 M Li_2SO_4 (pH7), H_2O (pH7), 50 mM H_2SO_4 (pH1.5) and 1 M H_2SO_4 (pH1.0). The greater the rise in pH on dilution, the greater the extent of spontaneous hydrogen evolution.

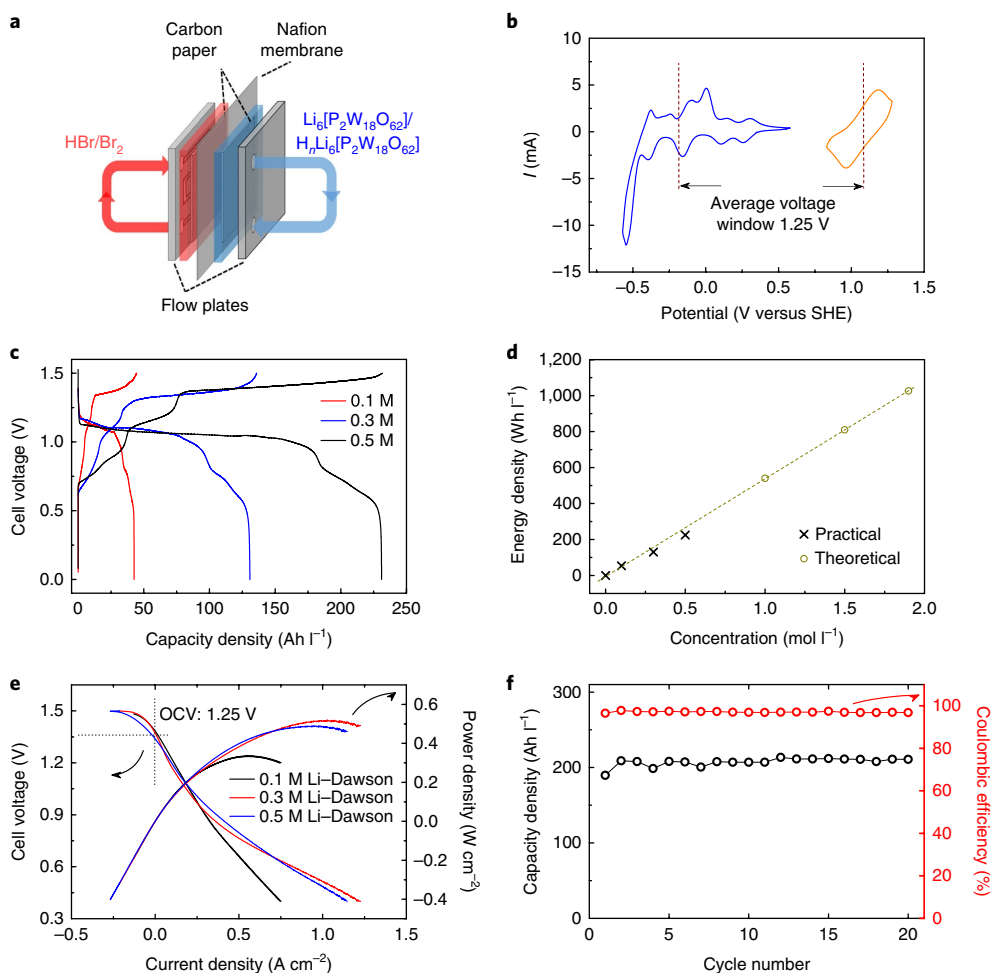


Fig. 4 | Application of $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ in a redox flow battery. **a**, Schematic of the redox flow cell. **b**, Cyclic voltammograms of 100 mM $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ in 1 M H_2SO_4 (blue) and 0.5 M HBr in 1 M H_2SO_4 (orange) at a scan rate of 10 mV s^{-1} using the set-up described in Supplementary Fig. 3. **c**, Cell voltage versus capacity density with different concentrations of $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ in aqueous solution on the negative side and 4 M HBr + 0.1 M Br_2 on the positive side at a current density of 50 mA cm^{-2} at 20°C , showing how the capacity density increases with polyoxometallates concentration. **d**, Relationship between energy density and concentration of $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ in a redox flow battery, showing how the energy density increases with polyoxometallates concentration. **e**, Polarization curves showing power density versus current density over the voltage range 0.4–1.5 V at 20°C at 100% state of charge (OCV, open-circuit voltage). **f**, Discharge capacity density and coulombic efficiency versus cycle number obtained by applying a constant current of 0.1 A cm^{-2} over the voltage window 0–1.65 V at 20°C , using 4 M HBr + 0.1 M Br_2 on the positive side and 0.5 M $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ in 0.1 M H_2SO_4 on the negative side. The coulombic efficiency is nearly quantitative.

gas is observed to evolve spontaneously (albeit slowly) from the solution until the cluster is reduced by only four electrons. Meanwhile, when diluted with acidic media (50 mM H₂SO₄ and 1 M H₂SO₄, blue and green triangles in Fig. 3b respectively), the spontaneous hydrogen evolution happens much more slowly. An enhanced kinetic effect is seen when the dilution is undertaken with a non-buffering electrolyte, which still allows the pH to rise (Li₂SO₄, black diamonds). Hence, raising the pH causes more rapid spontaneous hydrogen evolution during the dilution process.

In our next set of studies exploring the properties of the highly reduced Li₆[P₂W₁₈O₆₂], we investigated its performance as an electrolyte in a redox flow battery. We therefore constructed a system with the cluster as the negative redox couple and using HBr/Br₂ as the positive electrolyte (Fig. 4a,b). A discharge capacity density of 42.6 Ah l⁻¹ can be achieved at a concentration of 0.1 M at 50 mA cm⁻² with a coulombic efficiency of 96%, as well as an energy density of 43.2 Wh l⁻¹. On increasing the concentration of Li₆[P₂W₁₈O₆₂] to 0.3 M and 0.5 M, higher capacities of 131 Ah l⁻¹ and 230 Ah l⁻¹ can be achieved at 20 °C, corresponding to practical energy densities of 130 Wh l⁻¹ and 225 Wh l⁻¹ respectively (Fig. 4c). Meanwhile, the energy efficiency at each of these concentrations is 76% (Supplementary Figs. 23 to 25). These results are exciting because they show that this system, at the solubility limit of the cluster, could yield a flow battery with an energy density of more than 1,000 Wh l⁻¹ (Fig. 4d). The polarization curves of this redox flow battery (Fig. 4e) exhibit a peak galvanic power density of 0.52 W cm⁻² at a concentration of Li₆[P₂W₁₈O₆₂] of 0.3 M at 20 °C, which falls off slightly at higher concentrations due to the increased viscosity of the solution. Figure 4f presents cycling data for this redox flow battery with 0.5 M Li₆[P₂W₁₈O₆₂] at 0.1 A cm⁻² within the voltage cutoffs of 0 V and 1.65 V. The galvanic discharge capacity during cycling is highly stable at around 210 Ah l⁻¹ over 20 cycles with a coulombic efficiency of 98%. Cycling data using 0.1 M Li₆[P₂W₁₈O₆₂] at 0.1 A cm⁻² is provided in the Supplementary Information (Supplementary Fig. 26). Compared to current state-of-the-art negative electrolytes for redox flow batteries^{47–50}, Li₆[P₂W₁₈O₆₂] has a much higher energy density, as shown in Supplementary Table 5.

Conclusion

This work shows that polyoxometallates clusters like Li₆[P₂W₁₈O₆₂] can achieve very high proton–electron storage capacities in aqueous solution. This is illustrated by the ability of this cluster to reversibly accept 18 electrons and protons. This corresponds to ~9 g of hydrogen stored per litre, or a flow battery with a practical discharge energy density of 225 Wh l⁻¹ (with an open-circuit voltage of 1.25 V and an energy efficiency of 76%) at room temperature at 0.5 M. Extrapolating to the limits of the solubility of this polyoxometallates (1.9 M l⁻¹ in aqueous solution)³⁷, an effective storage potential of 34.2 g H₂ l⁻¹ could be achieved, which compares with that of pure cryogenic liquid hydrogen (71 g H₂ l⁻¹ at 20 K), and which would also yield a flow battery with an energy density breaking the 1,000 Wh l⁻¹ barrier. Thus, we believe that this system will lead to new flexible energy production systems with the ability to switch between hydrogen or electrical power that could redefine the energy storage landscape. Moreover, such extremely high capacities could transform how redox flow batteries are used, potentially allowing electric vehicles to be powered by these electrolytes^{51,52}.

Data availability. All relevant data are available from the authors, and requests for data sets should be addressed to L.C. or M.D.S.

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Author contributions

L.C. conceived the concept and, together, L.C., J.J.C. and M.D.S. expanded the hypothesis, planned experiments and wrote the paper. J.J.C. performed all the electrochemistry experiments and analysis.

Additional information

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