

Supplementary Materials for the manuscript:

Hydrogen/manganese hybrid redox flow battery

Javier Rubio-Garcia ¹, Anthony Kucernak ^{*1}, Dong Zhao ¹, Danlei Li¹, Kieran Fahy, ¹ Vladimir Yufit ²,

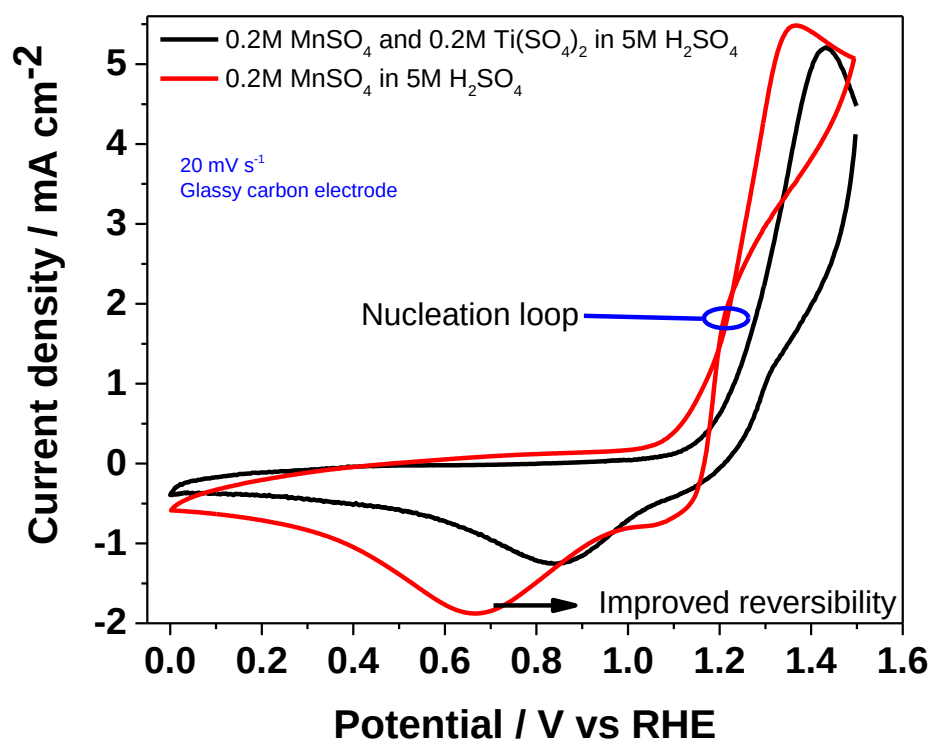
Nigel Brandon ² and Miguel Gomez-Gonzalez ³

1. Department of Chemistry, Imperial College London, SW7 2AZ, UK.

2. Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, UK.

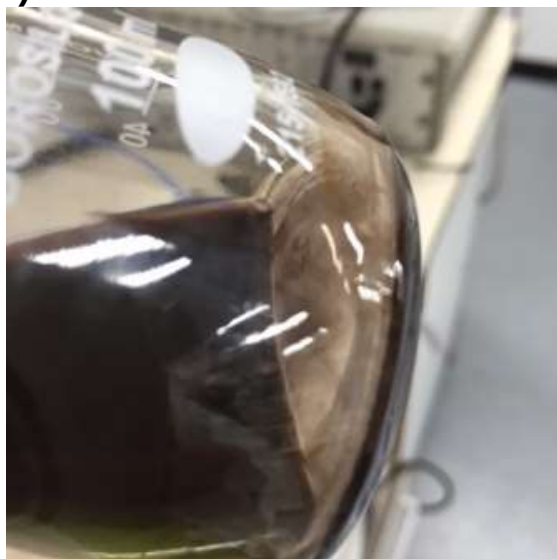
3. Department of Materials, Imperial College London, SW7 2AZ, UK.

(*corresponding author e-mail: anthony@imperial.ac.uk)



Supplementary Figure 1. Stabilisation of Mn^{3+} in solution by Ti(IV) . Voltammetry on a carbon disk showing electrochemical cycling of a 0.2 M MnSO_4 in $5\text{M H}_2\text{SO}_4$ in the presence and absence of $0.2\text{M Ti(SO}_4)_2$.

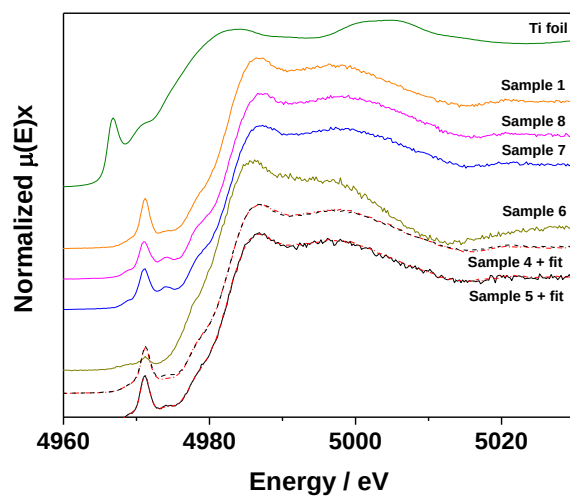
A)



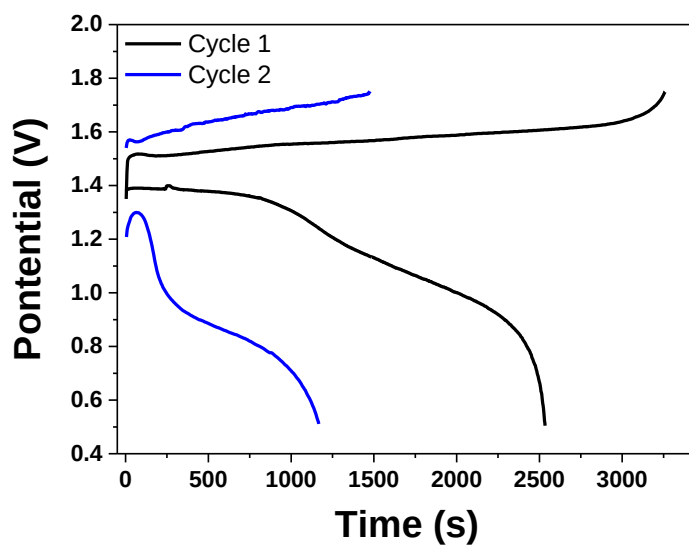
B)



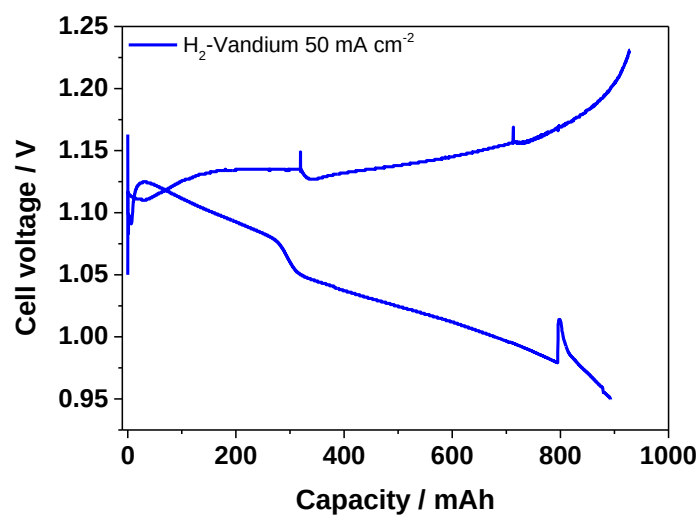
Supplementary Figure 2. Images of electrolyte formulations immediately after bulk-electrolysis at 100 mA cm^{-2} with *in-situ* production of Mn(III) from an initial composition of 1M MnSO_4 in 3M H_2SO_4 , (A) without metal additive and (B) with 1M $\text{Ti}(\text{SO}_4)_2$.



Supplementary Figure 3. Normalized Ti K-edge XANES spectra (black line) of Sample 4 ($0.2\text{M MnSO}_4 + 0.2\text{M Ti}(\text{SO}_4)_2 + 5\text{M H}_2\text{SO}_4$), and 5* ($0.2\text{M Ti}(\text{SO}_4)_2$) and their corresponding linear combination fittings (red dashed line). XANES spectra of the standards included in the LCF analyses are also displayed at the top of the figure (*Sample 5 was also used as standard for the LCF of sample 4). The labeling of the standards corresponds to sample 6 ($0.2\text{M Ti}_2(\text{SO}_4)_3$ in $5\text{M H}_2\text{SO}_4$), sample 7 (0.1M TiOSO_4 in $5\text{M H}_2\text{SO}_4$) and sample 8 ($0.1\text{M MnSO}_4 + 0.1\text{M TiOSO}_4 + 5\text{M H}_2\text{SO}_4$), sample 1 ($0.2\text{M MnSO}_4 + 0.2\text{M Ti}(\text{SO}_4)_2 + 5\text{M H}_2\text{SO}_4$) and Ti foil.

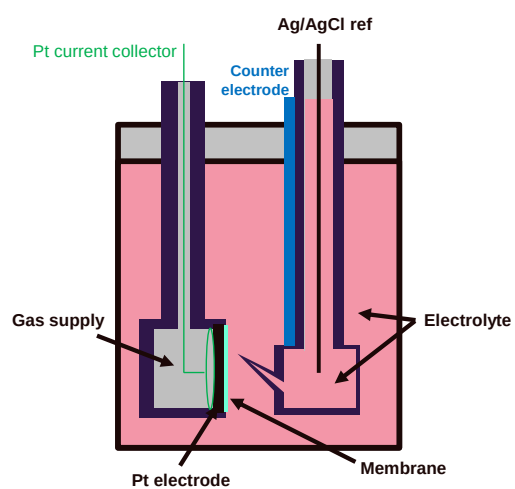


Supplementary Figure 4. Hydrogen/manganese hybrid RFB galvanostatic charge and discharge utilizing an un-stabilized electrolyte of 1M MnSO_4 in 3M H_2SO_4 . Unlike previous experiments where 3 layers of SGL carbon paper were used at the positive electrode, here a single layer was utilized (current density 20 mA cm^{-2}). A liquid flow rate of 50 mL min^{-1} and a gas flow rate of 100 mL min^{-1} was used.

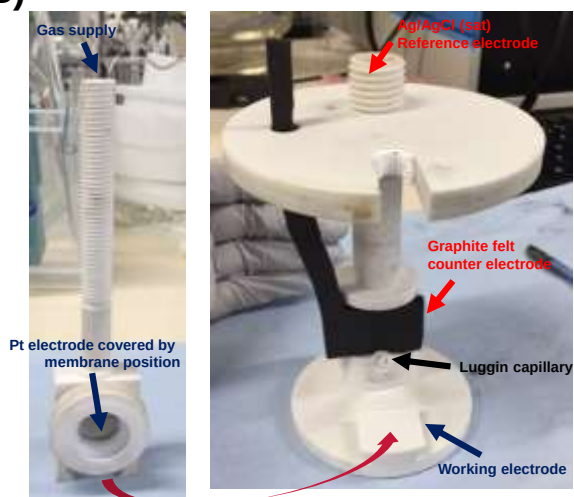


Supplementary Figure 5. Hydrogen/vanadium hybrid RFB galvanostatic charge and discharge at 50 mA cm^{-2} utilizing exactly the same cell assembly as for the hydrogen/manganese one (using 3 layers of SGL carbon paper). Electrolyte 2.5M VOSO_4 in 6M HCl which promotes enhanced V(V) stability. Liquid flow rate 50 mL min^{-1} and gas flow rate 100 mL min^{-1} .

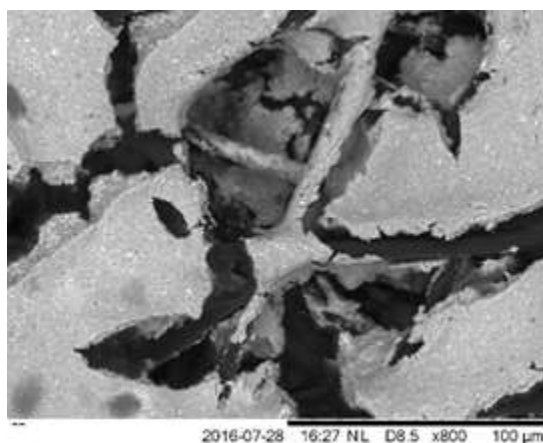
A)



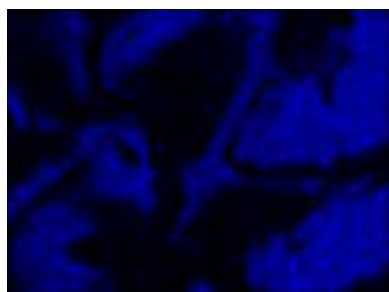
B)



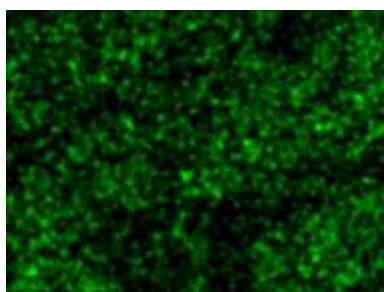
Supplementary Figure 6. (A) Scheme showing the assembly of the three-electrode cell utilized for HOR/HER experiments (discussed in the supplementary method 4). (B) Images of the experimental set-up.



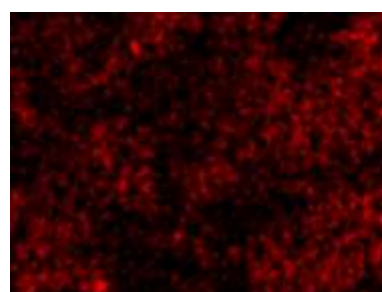
Pt



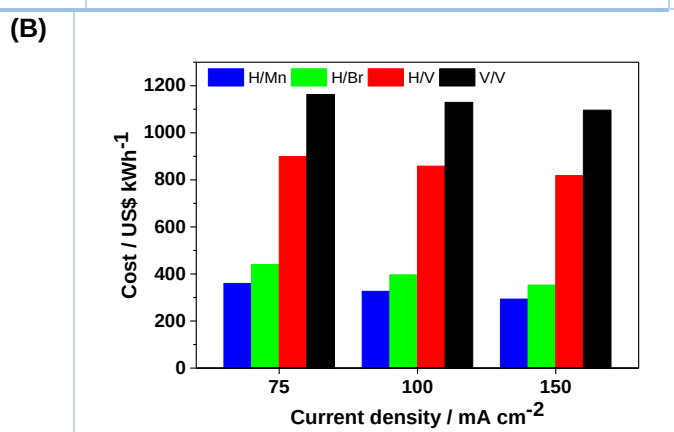
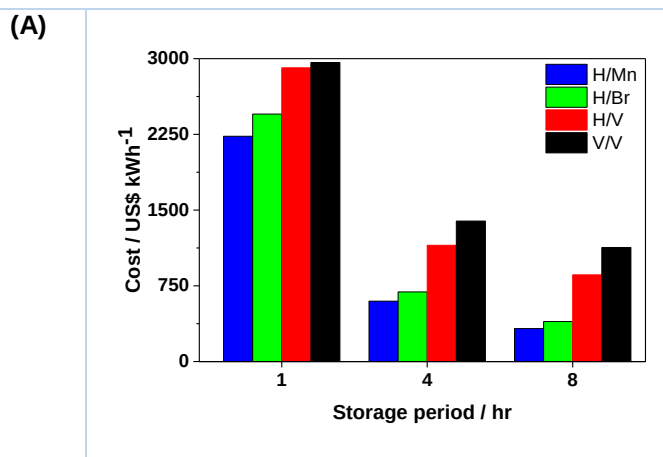
Mn



Ti



Supplementary Figure 7. Top: SEM image of the catalyst layer of the negative electrode after three-electrode cell HER studies. Bottom: EDX analyses for Pt (blue), Mn (green) and Ti (red).



Supplementary Figure 8. Cost analysis of hydrogen based hybrid redox systems with the all-vanadium flow battery. (A) As a function of storage duration, (B) As a function of current density. For assumptions and calculations please see Supplementary Note 6.

Supplementary Table 1

Table 1 Manganese and titanium concentration in liquid aliquots obtained upon electrolyte bulk electrolysis.

Time (h)	No additive (M)		Ti containing			
	Mn (M)	σ_{Mn}	Mn (M)	σ_{Mn}	Ti (M)	σ_{Ti}
0			1.054	0.004	1.247	0.008
1	0.145	0.004	1.012	0.003	1.245	0.002
4	0.029	0.002	1.016	0.005	1.189	0.003
17	0	0.002	1.027	0.004	1.231	0.006
25			1.058	0.006	1.246	0.003
29			1.069	0.002	1.262	0.004
33			1.033	0.004	1.254	0.002
48			1.072	0.002	1.247	0.005
72			1.085	0.003	1.257	0.001
96			1.006	0.004	1.199	0.009
120			0.894	0.006	1.271	0.005
2100			0.713	0.004	1.278	0.003

Supplementary Table 2

Table 2 List of samples examined at B18. Ti foil, Mn-acetonitrile, MnO₂ and Mn₃O₄ were used as standard samples.

Sample Number	Sample Contains	Sample active species
1	0.2M MnSO ₄ + 0.2M Ti(SO ₄) ₂ + 5M H ₂ SO ₄	Mn(II), Ti(IV)
2	0.2M MnSO ₄ + 5M H ₂ SO ₄ (Mn(II))	Mn(II)
3	0.2M MnSO ₄ + 5M H ₂ SO ₄	Mn(III)post-oxidation of sample 2
4	0.2M MnSO ₄ + 0.2M Ti(SO ₄) ₂ + 5M H ₂ SO ₄	Mn(III), Ti(IV) post-oxidation of sample 1
5	0.2M Ti(SO ₄) ₂ in 5M H ₂ SO ₄	Ti(IV)
6	0.2M Ti ₂ (SO ₄) ₃ in 5M H ₂ SO ₄	Ti(III)
7	0.1M TiOSO ₄ in 5M H ₂ SO ₄	Ti(IV) with oxo ligand
8	0.1M TiOSO ₄ + 0.1M MnSO ₄ + 5M H ₂ SO ₄	Mn(III), Ti(IV) with oxo ligand

Supplementary Table 3

Table 3 – Linear combination fit results for Mn and Ti K-edge XANES spectra

<i>Mn XANES</i> ^a						
Sample	Mn ₃ O ₄	MnO ₂	Sample 1	Sample 9	R factor ^b	red χ^2 ^c
	%					
3	55.2	45.0			0.00135	0.00034
4	41.8	23.4	24.2	12.5	0.00151	0.00031
<i>Ti XANES</i> ^d						
Sample	Sample 1	Sample 8	Sample 9		R factor	red χ^2
	%					
4	74.9		25.2		0.00027	0.00005
	76.4	23.7			0.00033	0.00007
5 ^e	86.6		13.4		0.00052	0.00010
	85.8	14.2			0.00052	0.00010

^a Mn K-edge XANES spectra were analyzed by LCF in the range: 6530 – 6590 eV. Fittings were not constrained to sum 100 %.

^b Normalized sum of the squared residuals of the fit [$R \text{ factor} = \sum(\text{data-fit})^2 / \sum \text{data}^2$]

^c Goodness-of-fit between different fittings was assessed by the chi-squared (χ^2) parameter [$= N_{\text{idp}}/N_{\text{pts}} \sum((\text{data-fit})/\varepsilon)^2$]; where , N_{idp} is the number of independent points in the model fit, N_{pts} is the number of data points and ε is the measurement uncertainty.

^d Ti K-edge XANES spectra were analyzed by LCF in the range: 4960 – 5020 eV. Fittings were not constrained to sum 100 %.

^e Sample 5 was used as standard for the LCF of sample 4, and subsequently analyzed as independent sample.

Supplementary Note 1:

In terms of system architecture, a liquid-liquid RFB configuration presents some drawbacks associated with the transport of the active species across the membrane. Electrolyte crossover leads to a gradual performance and capacity decay that may be irreversible unless the same active species are employed on both sides of the RFB, as in the case of all-vanadium RFBs. However, even in the latter case, vanadium crossover leads to electrolyte concentration imbalance which necessitates the implementation of periodic maintenance protocols based on remixing and conditioning of the electrolyte to sustain battery performance.¹ In contrast, crossover issues are mitigated when the liquid anolyte is replaced by a gas (such as hydrogen) which cannot be “contaminated” by the liquid catholyte, allowing simple and efficient rebalancing of the electrolyte. In the gas-liquid RFB it is easy to separate any small amount of liquid that crosses from the liquid to gas side. This is achieved by collecting the catholyte and pumping it back to the cathode side. In a large scale system hydrogen can be lost during long term operation leading to electrolyte imbalance (i.e. all the liquid electrolyte is not fully consumed). Measuring hydrogen imbalance is easily achieved by simply measuring the pressure of the hydrogen in the storage tank at the beginning and end of a discharge cycle. Any imbalance can be easily solved as hydrogen can be topped up from a cylinder or utilising an external electrolyser. The easy separation of the two different reactants allows the use of thinner membranes thus reducing internal resistance of the cell and decreasing the cost of the stack; allowing fast RFB charge and discharge due to the kinetically facile hydrogen reaction; minimization of detrimental side-reactions; and good charge reversibility.

Supplementary Note 2:

Determination of the manganese and titanium concentration in the liquid phase: metal content determination in the liquid phase of the electrolyte was conducted with a Perkin Elmer inductively coupled plasma (ICP) atomic emission spectrometer (Optima 2000) equipped with an AS-90PLUS Autosampler. Detector calibration was carried out before measurements utilizing standard solutions for each metal. ICP cannot distinguish different oxidation states for a given element which is critical in the case of Mn(III) determination. The disproportionation reaction involves the degradation of two Mn(III) atoms into one Mn(II) atom (equation 1) remaining in solution and one solid MnO_2 which precipitates. Hence the soluble Mn is detected during ICP experiments along with any remaining Mn(III). As a result, each Mn(III) measurement was compared to the initial metal content and the decrease in concentration was multiplied by two in order to account for the Mn(II) in solution. Results shown in Figure 1A and supplementary table 1 reflect these corrected measurements which are assumed to only reflect Mn(III) concentration in solution.

Supplementary Note 3:

Mn K-edge XANES spectra interpretation: Linear combination fits (LCF) of Mn K-edge XANES spectra indicated the prevalence of the manganese (II) di-manganese (III) oxide (Mn_3O_4) for all electrochemically treated samples (supplementary table 2). Sample 3 presented a mixture of Mn_3O_4 and MnO_2 (55% and 45%, respectively) suggesting the oxidation of Mn(II) to Mn(III) with a subsequently disproportionation over time to Mn(II) + Mn(IV). When analyzing sample 4 by LCF, an important decrease in the content of Mn(IV) was obtained (23.9% of MnO_2) pointing out the performance of titanium in inhibiting the disproportionation. The magnitude of Mn_3O_4 decreased as well, while contributions of acidified aqueous phases appeared: Sample 1 ($\approx 20\text{-}24\%$) and sample 8 ($\approx 12\%$).

Supplementary Note 4:

Ti K-edge XANES spectra interpretation: As expected, sample 1 was the main component of the two analyzed samples by LCF with contributions between 74.9 and 86.6% in all cases. Similar proportions of samples 7 and 8 were found (23-25% sample 4) as primary and secondary fitting options (supplementary Table 3 and supplementary Figure 2).

Supplementary Note 5:

Mn(III) stabilization mechanism discussion based on supplementary figure 3, supplementary table 3 and supplementary notes 3 and 4: The significant contribution of sample 8 ($\text{MnSO}_4 + \text{Ti(IV)}$ with oxo-ligand in acidic conditions) to the linear combination fits of Mn XANES ($\approx 12\%$, supplementary table 3) for sample 4 suggests the importance of the Ti(IV) with oxo-ligand in the Mn(III) stabilization during the electrochemical processes. The complementary contribution of sample 7 (Ti(IV) with oxo-ligand in acidic conditions) and sample 8 ($\text{MnSO}_4 + \text{Ti(IV)}$ with oxo-ligand in acidic conditions) as primary and secondary linear combination fits of Ti XANES (supplementary table 3), together with the absence of sample 5 (Ti(IV) in acidic conditions) or sample 6 (Ti(III) in acidic conditions) in those fittings, may suggest the occurrence of a weak interaction between Mn(III) and Ti(IV) through oxo-bridge ligands as a plausible mechanism to promote enhanced Mn(III) stability in acid electrochemical processes. Unfortunately, we were unable to confirm the Mn(III) stabilization mechanism by extended X-ray absorption fine structure spectroscopy (EXAFS) due to the poor quality of the acquired spectra (data not shown). Further EXAFS analyses will be important in order to fully understand the Ti(IV) oxo-ligand role in the Mn(III) stabilization mechanism.

Supplementary Note 6:

Economic analysis compared to competing technologies: The cost analysis has been carried out using the data presented in a previously reported study² that includes the tabulated cost of all the balance-of-plant and stack components, pipes and tubing, electrolyte, additives, hydrogen storage and others. The calculation considers the total power input as well as current density-voltage characteristics of the single RFB cell and projects the total cost associated with the total area of the stack components which is defined by the power of the system. The total charge of the redox system was estimated as the ratio between total stored energy and theoretical Nernst potential for each considered chemistry and then used to calculate the weight and the volume (at a given concentration) of the electrolyte. Thereafter, the total volume of the electrolyte was used to calculate the cost of electrolyte tanks, piping and pumps. Total electrolyte (and hydrogen) volume flow was estimated from Faraday's law. For hydrogen based systems, a maximum pressure of 10 atm and a hydrogen stoichiometric ratio of 1.2 was used in all the calculations. The cost of vanadium pentoxide, manganese sulphate and titanium dioxide used in the analysis was 76 \$/kg, 0.885 \$/kg and 1.5 \$ /kg respectively based on the data from <http://www.molbase.com/>. The cost of vanadium and titanium electrolyte preparation was included in the calculations. In this context, the manganese-titanium electrolyte (1:1 ratio) cost calculation relies on a synthesis of the $\text{Ti}(\text{SO}_4)_2$ additive from the treatment of TiO_2 with concentrated H_2SO_4 . The cost of additives in the case of the H_2 -Br system to avoid the formation of toxic vapors (using N-ethyl-N-methyl pyrrolidinium bromide) was estimated based on the weight of bromine. The calculations did not take into account any losses related to balance-of-plant, nor any mass transport limitations associated with low state of charge as this is assumed to be fairly similar in all systems studied.

Supplementary Figure 7A shows the device comparison as a function of storage capacity for a system operating at 100 mA cm^{-2} . This estimation reflects an increasing contribution of the electrolyte cost as storage time is increased from 1 to 8 hours. Moderate capital cost

reduction is observed by the replacement of the negative liquid electrolyte in an all-vanadium RFB (V/V, black) by a gas phase redox couple (H/V, red). This variation is more significant for large system capacity and reaches a 25% drop in cost for 8 hours of storage. However, the critical variable that determines the capital cost of the device appears to be the cost of the redox couple. Based on the experimentally obtained cell performance, the implementation of the manganese redox couple (H/Mn, blue) leads to a 70% cost reduction compared to the all-vanadium RFB for 8 hour storage periods. In addition, the hydrogen/manganese chemistry is between 10% (1 hour capacity) and 20% (8 hour capacity) cheaper than bromine-based chemistry (H/Br, green) concurrently offering a safer non-toxic electrolyte. The substitution of bromine by manganese also promotes better HER/HOR catalyst durability as no signs of Pt corrosion were detected for the hydrogen/manganese hybrid RFB (an issue in the H/Br system). The impact of increasing the operating current density from 75 to 150 mA cm⁻² on the capital cost was investigated for 8 hours capacity, Supplementary Figure 7(B). The calculation reflects the value of decreasing the size of the stack (therefore its cost in \$/kWh) for optimized energy efficiency and electrolyte utilization. Compared to an all-vanadium RFB, the hydrogen/manganese hybrid RFB enables a 74% cost reduction when operated at 150 A cm⁻².

References

- 1 Rudolph, S., Schroder, U. & Bayanov, I. M. On-line controlled state of charge rebalancing in vanadium redox flow battery. *Journal of Electroanalytical Chemistry* **703**, 29-37 (2013).
- 2 Singh, N. & McFarland, E. W. Levelized cost of energy and sensitivity analysis for the hydrogen-bromine flow battery. *Journal of Power Sources* **288**, 187-198 (2015).