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Hydrogen/manganese hybrid redox flow battery

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Abstract

Electrochemical energy storage is a key enabling technology for further integration of renewables sources. Redox flow batteries (RFBs) are promising candidates for such applications as a result of their durability, efficiency and fast response. However, deployment of existing RFBs is hindered by the relatively high cost of the (typically vanadium-based) electrolyte. Manganese is an earth-abundant and inexpensive element that is widely used in disposable alkaline batteries. However it has hitherto been little explored for RFBs due to the instability of Mn(III) leading to precipitation of MnO2 via a disproportionation reaction. Here we show that by combining the facile hydrogen negative electrode reaction with electrolytes that suppress Mn(III) disproportionation, it is possible to construct a hydrogen/manganese hybrid RFB with high round trip energy efficiency (82%), and high power and energy density (1410 mW cm−2, 33 Wh l−1), at an estimated 70% cost reduction compared to vanadium redox flow batteries.

1. Introduction

Photovoltaic and wind generation are fluctuating and intermittent energy sources. This poses serious difficulties for the management of electricity grids in terms of frequency and power quality. To avoid these issues, further penetration of clean energy sources into the energy mix require the implementation of highly efficient, short response time and low cost energy storage technologies. Among the potential candidates, Redox Flow Batteries (RFBs) are a promising solution for medium to large scale energy storage applications due to their easy scalability, superior longevity, fast response and low maintenance cost[1]. In these systems, energy is stored within a fluid contained in reservoirs (gas or liquid) and pumped towards the electrodes where redox reactions occur, generating power. Such an architecture allows independent scaling of power and energy capacity, enabling flexibility in engineering systems and reducing the manufacturing cost of the device for given applications.

Different redox chemistries have been used, and new ones are still being developed, with the vanadium redox couple being the most successful to date[2, 3]. Vanadium RFBs provide an extremely large cycle-life (above 10 000 cycles in deep discharge) with low capacity decay over deep charge and discharge cycles. However, the wide deployment of vanadium RFBs is constrained by the high capital cost of the vanadium electrolyte which represents more than 54% of system cost for a 10 h storage system[4]. Volatile vanadium pricing and future resource limitations (the known vanadium worldwide reserves are 14 million tonnes) are likely to limit the ability of vanadium RFBs to store no more than a small percentage of global daily energy consumption in a future world[5]. More recently, significant efforts have been devoted to the exploration of lower cost actives species such as metal-free redox couples. Fast and reversible redox couples including quinones[6, 7], oxazolines[8, 9] or redox active polymers[10] have shown some promise in RFB applications and are not resource constrained. However, most current metal-free RFBs utilize toxic (e.g. bromine)[11] or carcinogenic (e.g. [12]...
viologen derivatives \[12\] species to achieve acceptable cell voltages which may constrain their applicability. Moreover, the longevity of these systems is yet to be explored.

In this context, manganese is the 12th most abundant element in the Earth’s crust (worldwide known reserves of several billion tonnes \[3\]) and is available without significant geographic restrictions. It is already used in the ubiquitous disposable alkaline battery, composing about 1/3 the weight of a typical alkaline zinc battery. The Mn(III)/Mn(II) redox couple offers a high standard redox potential \(E^\circ = 1.51 \text{ V}\), low cost and high solubility which encourages the development of Mn-based energy storage technologies for large scale applications. Very few studies dealing with soluble aqueous manganese formulations for RFB applications have been reported to date \[13–15\]. During battery charging, Mn(III) is produced and in an aqueous environment this species quickly undergoes a disproportionation reaction to yield soluble Mn(II) and MnO\(_2\) as a precipitate (equation 1) \[16\].

\[
2\text{Mn}^{3+} + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{Mn}^{2+} + 4\text{H}^+.
\] (1)

The formation of solid, insoluble MnO\(_2\) particles in a RFB would lead to a larger flow pressure drop and reduced mass transport due to electrode and flow field blocking. Moreover, MnO\(_2\) formation will decrease the concentration of the active species in solution and cause an irreversible decay in RFB capacity and power.

Such a process also occurs in vanadium RFBs under certain conditions of pH, temperature, concentration and oxidation state \[17\]. The implementation of additives such as polymers \[18\], halides \[19\] or phosphates \[20\] have been found to inhibit this undesired reaction in vanadium RFBs. In the case of manganese, examples of limited kinetic stabilization of Mn(III) in water using ligands including fluoride \[21\] or pyrophosphate \[22\] have been reported.

Use of metal additives \[14, 23\] has shown some promise as well. This paper demonstrates the benefits of merging a hybrid RFB architecture (which utilizes H\(_2\) as negative electrode reactant) and the use of earth-abundant redox couples (stable Mn(III) complexes in acidic conditions). A hybrid design, in which liquid and gas are easily separated, significantly mitigates issues associated with the crossover of redox species in the cell during operation. For a liquid–liquid RFB configuration, the crossover of active species leads to either: irreversible degradation of the system; or to the necessity of frequent electrolyte rebalancing which increases operation costs. The rebalancing of the electrolyte in a hydrogen/manganese RFB would be as simple as pumping the liquid back to the gas side and/or H\(_2\) top up from a cylinder, which has an obvious advantage over current RFBs. Moreover, the use of manganese liquid electrolytes, allows us to preserve the activity of the metal catalyst at the gas side which is an advancement when compared to previous hydrogen/bromine hybrid systems. The combination of excellent system longevity, impressive power output and high round-trip efficiency, confirms the hydrogen/manganese hybrid RFB here reported as a relatively inexpensive technology especially well suited large scale energy storage applications.

2. Methods

2.1. Electrolyte preparation
The electrolyte is an equimolar solution of manganese (II) and titanium (IV) in 3 M sulphuric acid solution. To achieve such a composition, sulphuric acid is first added to a Ti(SO\(_4\))\(_2\) solution (15 wt%, Fisher Scientific). Then the solution is heated to boiling to promote water evaporation and increase the metal concentration. Once the desired concentration is achieved the solution is cooled to room temperature and MnCO\(_3\) (99.99%, Sigma-Aldrich) is slowly added (with consequent formation of CO\(_2\) bubbles).

2.2. Electrochemical testing
A Nafion® 212 membrane (nominal thickness 52 μm) was placed on top of the catalyst layer of a Hydrogen electrode (Fuel Cell Store, 0.4 mg, cm\(^{-2}\) loading on carbon paper, 0.22 mm thick). The membrane side was directly exposed to the electrolyte solution while the back of the electrode was electrically contacted with a Pt ring/wire current collector. As shown in supplementary figure 6 which is available online at stacks.iop.org/JPENERGY/1/015006/mmmedia, the working electrode faces a Luggin capillary which was equipped with a leak-free Ag/AgCl (sat) reference electrode (Harvard Instruments, UK). The Hydrogen oxygen reaction (HOR) and hydrogen evolution reaction (HER) at 100 mA cm\(^{-2}\) were studied using a SIGRACET graphite felt counter electrode (SGL, Germany) using a potentiostat (Autolab, model PGSTAT20).

2.3. RFB operation
The RFB fixture was purchased from Scribner Associates. The cell consisted of two POCO graphite bipolar plates with a machined flow field in contact with gold-plated copper current collectors that are held together utilizing anodized aluminium end plates. Active area of the electrodes was 5 cm\(^2\). Commercially available 0.32 mm thick
untreated carbon paper (SGL group, Germany, Sigracet SGL 10AA, typically 3 layers) or 4.6 mm thick untreated graphite felt (SGL group, Germany, Sigracell GFD4,6 EA) was used as the positive electrode. The Hydrogen negative electrode was obtained from Fuel Cell Store, 0.4 mg/cm² loading on Carbon paper or 0.03 mg/cm² loading on Carbon Cloth. The membrane was Nafion 212 (nominal thickness 52 μm). A peristaltic pump (Masterflex easy-load, Cole-Palmer) and Masterflex platinum-cured silicone tubing (L/S 14, 25 ft) were used to pump the manganese electrolyte through the cell at a flow rate of 25–100 ml min⁻¹. Hydrogen was provided by a fuel cell test station (850e, Scribner Associates), passing through the negative side at a flow rate of 35–150 ml min⁻¹. Due to the current range, polarization curves were recorded using a fuel cell test station (850e, Scribner Associates) whereas galvanostatic charge and charge experiments were conducted with a Gamry Reference 3000 potentiostat.

Discharge at different SoC was achieved by taking a fully charged electrolyte and then running the cell a defined time to achieve 75% or 50% SOC. This assumes a CE which has been shown for this system, figure 3(A).

The polarization curves at different SoC were measured using the Scribner 850e Fuel cell test station with 20 mA cm⁻² steps which were held for 20 s. The electrolyte was 300 ml of 1 M MnSO₄, 1 M Ti(SO₄)₂ in 3 M H₂SO₄ with a liquid flow rate of 50 ml min⁻¹. For the gas side, a H₂ flow rate of 100 ml min⁻¹ was used.

2.4. XANES experiments and analyses

Manganese and titanium K-edge X-ray absorption spectroscopy spectra were recorded at the B18 beamline at Diamond Lightsource (Daresbury, United Kingdom) (3 GeV, 300 mA, Si(111) monochromator crystals) at room temperature (RT) using a 9-element Ge solid state detector. The beam energy was calibrated by setting the first inflection point in the K absorption edge of a metallic Mn foil to 6.539 keV or a metallic Ti foil to 4.9664 keV. The sample spectra were acquired in fluorescence mode, starting at 6350 eV (Mn) or 4800 eV (Ti).

The pre-edge step size was set to 5 eV, and the edge step size along the edge was set to 0.5 eV.

For a summary of the composition of the measured samples please see supplementary table 3.

**Manganese:** Mn(acac)₃, Mn₃O₄ and MnO₂ were measured as powders. In addition, measurements were performed on liquid samples of similar composition to those used within the experiments and labelled as sample 1 (0.2 M MnSO₄ + 0.2 M Ti(SO₄)₂ + 3 M H₂SO₄) sample 2 (0.2 M MnSO₄ + 3 M H₂SO₄) and sample 8 (0.1 M MnSO₄ + 0.1 M TiOSO₄ + 3 M H₂SO₄). These samples were used as standards for samples electrochemically treated (3 and 4).

**Titanium:** the electrochemically treated sample 4 was compared with sample 1 (0.2 M MnSO₄ + 0.2 M Ti(SO₄)₂ + 3 M H₂SO₄), sample 5 (0.2 M Ti(SO₄)₂), sample 6 (0.2 M Ti₂(SO₄)₃ in 3 M H₂SO₄), sample 7 (0.1 M TiOSO₄ in 3 M H₂SO₄) and sample 8 (0.1 M MnSO₄ + 0.1 M TiOSO₄ + 3 M H₂SO₄). Sample 5 was additionally analyzed as an electrochemically treated sample to examine the oxidation of Ti₂(SO₄)₃ to Ti(SO₄)₂.

All reference and standards (six spectra for Mn, five spectra for Ti) were screened to determine combinations of reference spectra that best matched the data. Subsequently, samples were analysed by linear least-squares combination fittings over the range 0 to 100 and + 40 eV for both elements using the software code Athena [24]. The E₀ was fixed at 6530 eV for Mn and 4980 eV for Ti. The background was subtracted using a linear fit through the pre-edge region and the Autobk routine in Athena for the spline fit through the XANES region (Rbkg = 1, k-weight = 3, spline k-range = 0.5–10.5 Å⁻¹).

Starting from the best fit with one component, the number of components n was increased as long as the normalized sum of the squared residuals (NSSR = Σ[(dataᵢ - fitᵢ)²/Σ(dataᵢ)²] of best n + 1-component fit was at least 10% lower than the NSSR of the best n-component fit and if no component account for less than 5% of total. Linear combination fittings were not constrained to sum 100% (figure 1(B), supplementary figure 3 and supplementary table 2).

3. Results and discussion

Solutions of MnSO₄ in H₂SO₄ in the absence and presence of aluminium or titanium metal salt additives were prepared and electrochemically oxidized within a bulk electrolysis cell (*in situ* formation of Mn(III) complexes). In the absence of additives, a brown precipitate identified as MnO₂ was clearly seen after less than 10 min of electrochemical oxidation. In the solutions containing metal additives Mn(III) was stabilised and no solid precipitates were seen, even after one hour of polarisation. Visual observation of the stability of electrochemically generated Mn⁴⁺ in the presence of different metal ion species showed increasing stability in the order Al³⁺ < TiO₂²⁺ < Ti⁴⁺. These results are well aligned with recent development of electrolytes for liquid–liquid RFB architectures [14, 15]. Electrochemical measurement of voltammetry of solutions of MnSO₄ in H₂SO₄ in the presence and absence of Ti(SO₄)₂ showed increased electrochemical reversibility and the
absence of a ‘nucleation loop’ indicative of nucleation and growth of a solid phase [25]) when the titanium species was present in solution (see supplementary figure 2).

We subsequently focussed our attention on investigating the stability of an electrolyte consisting of 1 M MnSO₄ and 3 M H₂SO₄ with or without 1 M Ti(SO₄)₂. Manganese and titanium content was monitored using Inductively Coupled Plasma Spectrometry (ICP) from aliquots periodically taken from the liquid phase after bulk electrolysis. The evolution of the Mn(III) concentration with time is shown in figure 1(A). The disproportionation reaction involves the degradation of two Mn(III) atoms with one Mn(II) atom remaining in solution (equation (1), see supplementary note 2 for calculation method).

Figure 1(A) shows the evolution of Mn(III) concentration in a charged electrolyte over time. Error values associated with concentration determination are provided in supplementary table 1, and are smaller than the symbols used in the diagram. Without the Ti additive the electrolyte becomes turbid over the course of the electrolysis process due to the simultaneous occurrence of the disproportionation reaction (see supplementary figure 1(A)). Once the cell reaches the cut off voltage (1.7 V), a brown precipitate is observable at the bottom of the vial and the liquid phase showed an Mn(III) content of only 0.15 M (figure 1(A), blue). Over a short period of time the solution keeps evolving as the precipitation reaction progresses and the Mn(III) concentration drops to 0.03 M after one hour and reaches a negligible value after 20 h. In contrast, significantly enhanced stability is obtained with a 1:1 (Mn:Ti) solution. The electrolyte remains transparent (although optically dense) during the whole electrolytic process and no turbidity was observed (see supplementary figure 1(B)). The concentration of Mn(III) remains constant for more than 72 h, figure 1(A) (black). Little formation of solid is observed after 100 h and even after 120 h only a decrease of manganese concentration to 0.9 M is seen. After five months the solution maintains a Mn(III) concentration of 0.84 M. Hence it can be concluded that the addition of Ti⁴⁺ has a noticeable role in suppressing the disproportionation reaction. Suppression of MnO₂ formation has an important impact in utilising Mn(II)/Mn(III) in RFBs under real conditions.

We carried out x-ray absorption near edge structure (XANES) analyses at the Ti and Mn K-edges as an attempt to investigate the nature of the Mn(III)-stabilization mechanism. Figure 1(B) shows a comparison of freshly produced Mn(III) electrolytes with and without Ti⁴⁺ additive compared with standard samples selected to investigate the metal signature as a function of oxidation states. A linear combination fit of the XANES spectra leads to the red dashed lines in figure 1(B) and revealed a decrease of Mn(IV) contribution to the experimental result in the presence of titanium (see supplementary note 3). Moreover, Ti K-edge XANES data analysis of samples containing TiOSO₄ instead of Ti(SO₄)₂ showed similar curve fitting in the presence of Mn(III). This could be attributed to Ti⁴⁺ coordination with oxo-ligands, which would lead to a metal environment closer to TiO²⁻ (see supplementary note 4&5 and supplementary figure 3). A full paper analysing the factors affecting the stability of the electrolyte and speciation of the reacting species tracked using x-ray and electrochemical methods is currently being developed.

Huber et al observed an enhancement of Mn(III) stability upon oxidation of Mn(II) by Cr(VI) in the presence of oxalate ligands. It was hypothesised that the ligands promoted a change in the spatial arrangement of the metallic centre [23]. A change in Mn(III) conformation modifies the energy levels of the molecular orbitals (Jahn-Teller effect) which may enable the stabilization of the metallic complex. Based on these early reports and
on the results here discussed, we hypothesize 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 (see Methods and supplementary table 3). However, further analysis will be necessary to fully understand the stabilization mechanism.

Encouraged by the stability of an electrolyte formulation containing 1 M MnSO₄ and 1 M Ti(SO₄)₂ in 3 M H₂SO₄, we decided to investigate the performance of a hybrid H₂-Mn RFB cell in which the cell reactions are

\[
\text{charge} \quad \text{Mn}^{2+} + e^- \rightarrow \text{Mn}^{3+}
\]

\[
\text{discharge} \quad \text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}
\]

with simultaneous H⁺ transport across the membrane and HER at the negative electrode.

\[
\text{charge} \quad 2H^+ + 2e^- \rightarrow H_2
\]

\[
\text{discharge} \quad H_2 \rightarrow 2H^+ + 2e^-
\]

The opposite processes occur during cell discharge with oxidation of H₂ to H⁺ and reduction of Mn(III) to Mn(II). Utilising hydrogen as the negative electrode reaction has a number of benefits (see supplementary note 1 for advantages and discussion).

Several liquid electrolytes have been previously studied in a hybrid RFB configuration [26–28] but the use of Br₂-based catholytes has received more attention owing to advantages in terms of cost, efficiency, power output [29] and resource availability [5]. However, HBr and Br₂ are highly corrosive and toxic compounds and the storage of the electrolyte can be considered a major safety issue [30]. Moreover, liquid crossover to the gas side leads to irreversible degradation of the HER/HOR catalyst and substantially reduces the durability of the system due to corrosion and poisoning reactions. The replacement of bromine by an environmentally friendly and low cost manganese electrolyte could therefore offer significant advantages in terms of RFB cost, longevity and safety. Manganese is an essential element for mammals, required for bone growth and present in a number of metallo-enzymes and only an exposure to very significant concentrations can lead to toxic effects [31], leading to acceptance of manganese in the home in the form of alkaline zinc batteries. This emphasizes the interest of manganese electrolytes as a safer alternative for large scale energy storage applications in case of unintentional spillage of liquid.

Testing of the RFB utilising the system is described in the methods section. During battery testing there was no observable formation of solids in the electrolyte or electrodes suggesting the absence of direct oxidation of Mn(II) to Mn(IV) as a side reaction. Figure 2(A) shows charge and discharge performance obtained at different current densities (75, 100 and 150 mA cm⁻²). Discharge capacity values as high as 432 (80% theoretical), 498 (93% theoretical) and 534 mAh (100% theoretical) at 150, 100 and 75 mA cm⁻² were obtained. This represents an outstanding electrolyte utilization with values close to theoretical (536 mAh) and exemplifies a highly desirable RFB feature. Figure 2(A) (inset) shows the average Coulombic Efficiency (CE, ratio of the discharge capacity over the charge capacity), Voltage Efficiency (VE, ratio between the average voltage for charging and discharging) and energy efficiency (EE, product of CE and VE) after 5 cycles. Remarkably high CE values are obtained even when

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (A) Galvanostatic charge and discharge at different current densities: 75, 100 and 150 mA cm⁻². Electrolyte 1 M MnSO₄, 1 M Ti(SO₄)₂ and 3 M H₂SO₄. Hydrogen 100 ml min⁻¹ and liquid flow rate: 50 ml min⁻¹. (B) HOR and HER galvanostatic experiments using a three-electrode cell configuration with Ag/AgCl (sat) as reference electrode, graphite felt as counter electrode and a anode/Nafion membrane assembly as working electrode. Electrolyte 1M MnSO₄, 1M Ti(SO₄)₂ and 3 M H₂SO₄. See supplementary figure 6 for configuration.
operating at 150 mA cm$^{-2}$ (98.5%) which strongly suggests that there is little side reaction. A small contribution from the oxygen evolution/oxygen reduction reaction (OER/ORR) catalysed by manganese oxide species cannot be entirely discounted. However, the extent to which this reaction occurs must be very small due to the highly irreversible nature of these reactions and the limited solubility of oxygen in the electrolyte during the ORR (ca. 0.5 mM). Furthermore, if the reaction does occur, it clearly does not hinder the performance and still allows the system to achieve very high coulombic efficiency (>98.5%). The formation of MnO$_2$ would lead to a significant reduction in CE and a gradual decrease in the electrochemical surface area of the electrodes and increased reaction overpotentials. Indeed, such a process occurs without metal additives as turbid solutions and precipitates were rapidly obtained. Degradation of the electrolyte in the absence of added Ti$^{4+}$ induces a rapid rise of cell voltage during charge to values above the cut-off limit during the first cycle, and the irreversible degradation of the RFB after the second cycle (see supplementary figure 4). In contrast, the use of Ti(SO$_4$)$_2$ as an additive allowed low overpotential and high VE for the studied current density range, 75 (82.1%), 100 (79.7%) and 150 (69.7%) mA cm$^{-2}$ respectively. This performance was translated into an EE of 81%, 79% and 69% respectively showing low inter-cycle variability (<1%). This performance is comparable to commercially available all-vanadium RFBs which normally operate below 120 mA cm$^{-2}$ (commonly 80 mA cm$^{-2}$) to ensure high energy efficiency (>85%) and good electrolyte utilization (>75%) [32].

Surprisingly, the time-dependent cell potential shows an interesting feature during both RFB charge and discharge experiments (figure 2(A)) being more prominent as higher current densities were utilized. At the beginning of the charging process, the reaction requires a high overpotential which gradually decreases after around 10% state of charge (SoC) is reached. Likewise, two different discharge voltage plateaus are observable during discharge for instance at 1.38 V and 1.25 V respectively at 100 mA cm$^{-2}$. These voltage variations may be attributed to unidentified chemical reactions. However, the same behaviour was found in a hydrogen-vanadium RFB configuration (see supplementary figure 5) which decouples these voltage anomalies from the chemistry of the liquid redox couple.

A three-electrode cell was constructed to independently explore the electrochemistry of the negative electrode systems used in the above RFB (see supplementary figure 6). In this case HOR/HER experiments were conducted under galvanostatic conditions on the same electrode/electrolyte system as used in the RFB. We find a close analogy between the RFB performance and the three electrode electrochemical cell result. Using this set-up, we mimicked RFB charging (i.e. HER) by applying $–100$ mA cm$^{-2}$, figure 2(B) (blue) which revealed a high initial and a progressive shift of voltage towards more positive values. After one hour of HER, energy-dispersive X-ray spectroscopy analysis was carried on the catalyst layer and manganese and titanium were detected, and this is assumed to have occurred due to electrolyte crossover (see supplementary figure 7). Assuming an RFB charge behaviour dominated by processes taking place at the negative electrode, the HER experiment completely replicates the experimental full cell results. Consequently, the initial high overpotential during charging seen in figure 2(B) could be associated with metallic species passing through the membrane from the liquid to the gas side. In the same cell we mimicked the RFB discharging process at 100 mA cm$^{-2}$ (HOR), figure 2(B) black trace. A high initial overpotential with a gradual decrease is observed, however a constant voltage value is reached after approximately 900 s. This could be attributed to the transport of Mn/Ti compounds back to the liquid reservoir by electroosmotic drag, removing adsorbed metal ions from the catalyst surface and progressively facilitating the access of H$_2$ to the more reactive Pt sites.

The timeframe for the stabilization of HOR voltage is congruent with the position of the RFB discharge voltage transition which is found after 700–1000 s. The depletion of active species at the liquid side leads to mass transport limitations which, in conjunction with the stable potential at the negative electrode, can promote a cell voltage transition towards a lower discharge plateau. Analogous voltage anomalies such as the ones here observed are commonly reported for soluble lead RFBs [33]. They are described as the result of the formation of insoluble species at the electrode that subsequently dissolve. This leads to an initial high overpotential that progressively decreases. This mechanism is known as charge and discharge coup de fouet and could be occurring in the hybrid RFB, although in this case it is the HOR/HER which is affected.

To put in perspective the future of the hydrogen/manganese hybrid RFB for practical applications, we investigated the efficiency and capacity retention of the system over many cycles utilising a current density of 100 mA cm$^{-2}$. It is worth mentioning that full charge and discharge cycles were conducted to better understand potential degradation issues and/or undesired reactions, rather than the partial charge/discharge cycles often used to obtain an large (but somewhat artificial) number of cycles. Figure 3(A) shows the capacity retention and efficiency of the battery over 160 cycles using 0.2 M of MnSO$_4$ and 0.2 M Ti(SO$_4$)$_2$ in 3 M H$_2$SO$_4$ electrolyte. CE values were > 99% which suggest very little side reaction. In contrast, some variability in the VE, EE, and capacity retention was observed as a result of water evaporation and manganese crossover. However, these issues were easily mitigated by establishing an electrolyte rebalancing strategy every 5–7 cycles. An average EE value of 72.3% ± 1.6% with excellent electrolyte utilization (>81%) and good capacity retention was therefore ensured. No significant decay between the initial and final cycle was seen, which suggests a promising longevity.

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**Figure 2:** The efficiency of the battery over 160 cycles using 0.2 M of MnSO$_4$ and 0.2 M Ti(SO$_4$)$_2$ in 3 M H$_2$SO$_4$ electrolyte. CE values were > 99% which suggest very little side reaction. In contrast, some variability in the VE, EE, and capacity retention was observed as a result of water evaporation and manganese crossover. However, these issues were easily mitigated by establishing an electrolyte rebalancing strategy every 5–7 cycles. An average EE value of 72.3% ± 1.6% with excellent electrolyte utilization (>81%) and good capacity retention was therefore ensured. No significant decay between the initial and final cycle was seen, which suggests a promising longevity.
High manganese concentration within the liquid electrolyte would increase the energy density of the hybrid RFB. However, this could simultaneously lead to the formation of MnO₂ during battery operation which would result in cell degradation. We studied operation with higher manganese concentration utilizing a 1 M MnSO₄ and 1 M Ti(SO₄)₂ in 3 M H₂SO₄ electrolyte and conducting more than 35 full charge and discharge cycles using the same cell configuration, figure 3(B). Lower VE and EE oscillation was observed for each cycle in this case, which is most likely due to the minor impact of Mn crossing to the gas side on the liquid electrolyte composition. An average EE as high as 75% was obtained with no sign of cell degradation, as supported by the high CE value (>99%). An impressive energy density of 33.4 Wh l⁻¹ liquid electrolyte is achieved (i.e. if the volume of gas produced during charge is not considered). Assuming gas formation occurring at 10 bar, which is well within the ability of electrochemical hydrogen compression occurring within the cell, the obtained average energy density across both the liquid and gas phase is 15.0 Wh l⁻¹ liquid + gas whereas, operating at 30 bar hydrogen storage pressure the average energy density increases to 24.4 Wh l⁻¹ liquid + gas. These values compare favourably with current vanadium RFBs which show typical values of 10–15 Wh l⁻¹ and illustrates the versatility of a gas–liquid RFB configuration in terms of compact character and lower volume footprint.

Polarization and power curves were recorded to estimate the maximum power delivery of the hybrid RFB and highlight a further benefit of the system, figure 4. The curves were iR-corrected in order to account for the ohmic losses using the high frequency resistance (hfr) values recorded at each current density (hfr shown as an inset in the figure; see Methods for discussion of how curves were collected). Figure 4(A) shows curves obtained at different SoC using 3 layer of SGL carbon paper as the positive electrode. At 100% SoC, a peak power density of 590 mW cm⁻² is obtained at 0.85 V. As the SoC decreases, peak power density decreases to 510 mW cm⁻² (75% SoC) and 420 mW cm⁻² (50% SoC). The use of a graphite felt positive electrode instead of carbon paper leads to an impressive increase in peak power density; above 1410 mW cm⁻² at 1 V (100% SoC), figure 4(B).
is most likely the consequence of larger electrochemical surface area at the cathode and represents a value that largely surpasses previous hybrid RFBs chemistries including iron [28], vanadium [27] or cerium [26, 34] while being comparable to hydrogen-bromine systems [35]. Moreover, when compared to bromine-based systems, the use of non-toxic active species such as manganese and titanium is an obvious advantage. Importantly, no signs of Pt corrosion or cell degradation as a result of liquid crossover to the gas side were observed, even after more than one hundred full cycles. As previously mentioned, catalyst degradation is a widely known issue in the case of hydrogen-halogen systems [36].

A capital cost estimation considering the construction of 1 MW/8 MWh systems was conducted to put in perspective the advantages of a manganese-based hybrid RFB in terms of scalability for medium to large scale energy storage applications (see supplementary figure 8 and note 6 for more information). Our methodology was implemented based on previous literature on the subject [37, 38] and shows a 70% cost reduction compared to the all-vanadium RFB for 8 h storage periods using Mn:Ti electrolyte in a hybrid RFB configuration. It also shows economic benefits when compared to other hybrid RFB chemistries based on bromine and vanadium. Further improvements in performance and cost reduction can be achieved via optimisation of single cell components (bipolar plates, membranes and others). In this context, Pt loading at the negative electrode is a critical component of the stack in terms of cost. We explored the effect of Pt loading on the hybrid RFB performance by decreasing the noble metal content from 0.4 mgPt cm\(^{-2}\) to 0.03 mgPt cm\(^{-2}\), figure 4(B). Even with more than one order of magnitude lower metal content, very high peak power density (1000 mW cm\(^{-2}\) at 1 V) is obtained at 100% SoC. This result reinforces the benefits of a gas–liquid hybrid RFB configuration utilising the kinetically fast hydrogen reaction. This also points towards a system with minimized cost for large scale energy storage applications.

4. Conclusions

By controlling the Mn\(^{3+}\) disproportionation reaction and by using the facile and highly kinetically reversible hydrogen reaction, it is possible to produce a RFB with low cost, high energy density and high power. A techno-economic evaluation of that system suggests that at large scale, this system would be appreciably cheaper to buy and operate than a similar energy store comprised of lithium ion batteries. The stabilisation of the electrolyte appears to be associated with the coordination of titanium with the manganese in solution. Further work is ongoing to identify the precise structure of this compound and also to assess the long term viability of the RFB.

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