In this paper, a high energy density vanadium redox battery employing a 3 M vanadium electrolyte is reported. To stabilise the highly supersaturated vanadium solutions, several additives were evaluated as possible stabilizing agents for the thermal precipitation of supersaturated V(V) solutions at elevated temperatures. The Blank 3 M V(V) solution in a sulfuric acid supporting electrolyte containing 5 M total sulfates, showed thermal precipitation after 3 days, while the solution containing 1 wt% H₃PO₄ additive increased the induction time for precipitation to over 47 days at 30°C. After 32 days, 3 M V(V) solutions containing 1 wt% sodium pentapolyphosphate, 1 wt% K₃PO₄ and 2 wt% (NH₄)₂SO₄ + 1 wt% H₃PO₄ showed final V(V) concentrations of 2.7, 2.7 and 2.6 M respectively, compared to 2.4 M V(V) in the Blank solution. From the screening tests, selected additives were used in vanadium redox flow cell cycling studies employing a 3 M vanadium electrolyte. The cell was subjected to 90 charge-discharge cycles and no precipitation or capacity loss was observed in the presence of 1 wt% H₃PO₄ + 2 wt% ammonium sulfate. These results demonstrate that a significant enhancement in the energy density of the VRB can be achieved in the presence of additives that act as precipitation inhibitors for the vanadium ions.

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The UNSW All-vanadium redox flow battery (VRB) has been attracting considerable commercial interest in recent years, with several companies currently manufacturing VRB systems in Japan, USA, Austria and China. Although its energy density is relatively low compared to Li-ion batteries, the VRB offers excellent cycle life, energy efficiency and reasonable costs for storage capacities greater than 4 hours, making it ideal for large-scale energy storage in a range of stationary applications. Efforts to increase the energy density of the vanadium redox flow battery have included the use of a mixed halide electrolyte in the cell of the vanadium bromide redox battery developed by Skyllas-Kazacos and co-workers in Australia and a mixed HCl-H₂SO₄ supporting electrolyte as proposed by researchers at the Pacific Northwest National Laboratories in the USA. In both cases however, the use of HCl and/or HBr in the electrolytes introduces the risk of acid, chlorine or bromine vapors at elevated temperatures or during overcharge, and therefore restricts the operating state-of-charge range of the batteries, while also presenting a potential safety hazard.

In contrast to both the VBr and mixed acid vanadium chemistries, the original UNSW All-Vanadium Redox Flow Battery employs sulfuric acid as the supporting electrolyte, so any overcharge reactions produce oxygen gas at the positive electrode, making it a much safer system. Current VRB systems employ solutions of between 1.6 and 2 M vanadium ions in sulfuric acid with total sulfate concentrations ranging between 4 and 5 M and utilise the V(II)/V(III) and V(IV)/V(V) couples in the negative and positive half-cell electrolytes respectively. Increasing the vanadium ion concentration above 2 M will increase the energy density, however, this is limited by the solubilities of the different vanadium ions in the temperature range of 10 to 40°C. The V(II), V(III), and V(IV) ions precipitate as sulfates, so their solubility increases with increasing temperature but decreases with increasing sulfuric acid concentration because of the common ion effect of the sulfate ion. On the other hand, the V(V) ions in the positive half-cell electrolyte can undergo thermal precipitation to form V₂O₅ at elevated temperatures according to the endothermic reaction:

\[ 2\text{VO}_4^2^- + 2\text{H}_2\text{O} \rightleftharpoons \text{V}_2\text{O}_5(s) + 2\text{H}^+ \]  \[ 1 \]

The effect of this reaction on the stability of the positive half-cell electrolyte in the VRB was described by Skyllas-Kazacos and co-workers in 1990. The stability of the positive electrolyte of the vanadium redox cell was studied at various temperatures and at different solution compositions and solution states-of-charge (SOC). The authors found that at elevated temperatures for extended periods, V(V) can slowly precipitate from solution, the extent and rate of which being dependent on temperature, vanadium and sulfuric acid concentration as well as the SOC of the electrolyte. In contrast to the V(V) ions, V(II), V(III) and V(IV) ions will precipitate at temperatures below 10°C at concentrations above 1.6 M in solutions with total sulfate concentration of 5 M.

Practical VRB systems thus operate with vanadium electrolyte concentrations between 1.6 and 1.8 M and usually also employ electrolyte cooling and heating systems to maintain the temperature between 15 and 40°C. This limits the energy density of the VRB to levels that are still acceptable for most stationary energy storage applications, however, a higher energy density flow battery electrolyte will allow a wider range of applications to be exploited.

In an effort to enhance the energy density of the VRB, Skyllas-Kazacos and co-workers evaluated the use of precipitation inhibitors to stabilise supersaturated vanadium solutions in the early 1990s and filed a series of provisional and international patents on the high energy density VRB. Of the stabilizing agents tested, most carboxylic acids were found to slowly oxidize in the V(V) solutions, producing CO₂. When used at low levels, ammonium oxalate was found to oxidize only very slowly, while EDTA and malic acid oxidized quite rapidly, even at low concentrations. Reduction of V(V) to V(IV) was observed with relatively high levels of glycine but at low concentrations, the rate of glycine oxidation was considerably reduced. From their observations, they suggested that polyhydric secondary and tertiary alcohols, either ring or chain compounds would be expected to be the best stabilizing agents to use for the vanadium redox cell as these would offer the greatest resistance to oxidation by V(V). For example, inositol was suggested as a suitable additive due to its ring structure that offered improved stability to the oxidizing V(V) solutions. Organic compounds with 2 or more secondary or tertiary –SH or –NH₂ groups were also suggested as suitable stabilizing agents for highly concentrated vanadium solutions.

When a low level of a suitable stabilizing agent was added to the electrolyte solution during the vanadium oxide powder dissolution
step, Skyllas-Kazacos and co-workers found that stable supersaturated solutions of vanadium ions could be prepared. Different stabilising agents were found to stabilise the vanadium electrolyte solutions to different degrees of supersaturation. For example, 3.6 M solutions could be produced in the presence of 1 wt% glycine plus 2 wt% ammonium sulfate. They proposed that the different extent of stabilisation was related to the absorption of these additives on the surface of the nuclei, giving rise to electrostatic repulsion which inhibits precipitation by retarding crystal growth. Long-term stability tests showed however, that most organic additives were eventually fully oxidised by the V(V) ions in the positive half-cell electrolyte, so that any stabilisation would only be temporary. Inorganic additives were thus proposed, including ammonium compounds, phosphates and polyphosphates. Other inorganic compounds which were suggested to have the same properties included sulfimide, imidodsulfonylamine, as well as ammonium derivatives of phosphorous acids, as well as thiphosphoric acid derivatives.10

Skyllas Kazacos and co-workers also studied and screened a number of additives to be used as precipitation inhibitors for supersaturated V(IV) solutions to prevent precipitation at low temperatures. Supernatated 4 M vanadyl sulfate solutions were prepared and additives like sodium hexametaphosphate (SHMP), K2SO4, Li2SO4 and urea were evaluated. Among these, K2SO4, SHMP and urea were found to reduce the precipitation rate of supersaturated V(IV) solutions.11

Since then, very little further work was reported on stabilizing additives for the VRB until Huang and co-workers12 reported results using some of the original organic compounds originally proposed by Skyllas-Kazacos. They studied the effect of additives such fructose, mannitol, glucose, d-sorbitol in the vanadium electrolyte and reported that d-sorbitol exhibits the best electrochemical performance (energy efficiency 81.8%) in the VRB, proposing that the electrochemical activity of the electrolyte is improved by increasing (-OH) groups that provide active sites for electron transfer. They also proposed that VO2+ ions form a complex with the d-sorbitol which improves the solubility of V(V) in the electrolyte. Unfortunately however, the long-term stability of these additives was not investigated.

In a subsequent study by Wu et al.,13 inositol and phytic acid were evaluated as organic additives for the positive electrolyte for the VRB to improve its stability and electrochemical reversibility. Inositol had been previously reported as a good V(V) stabilizing agent by Skyllas-Kazacos et al.10 and this was confirmed by Wu et al. who found that the thermal stability of the V(V) electrolyte could be improved by both inositol and phytic acid additives. The long-term stability of these organic compounds in V(V) was not confirmed however.

1-glutamic acid was also studied as an additive for the positive electrolyte of all-vanadium redox flow battery by Liang et al.14 who reported that the addition of L-glutamic can significantly alleviate the precipitation of V2O5 from the positive electrolyte. A high coulombic efficiency of over 95% and energy efficiency of 74% are obtained, while XPS spectra were used to illustrate that L-glutamic can react with the surface of the carbon felt electrode and introduce more oxygen-containing and nitrogen-containing groups, which should be responsible for the improvement of electrochemical performance.

Since most organic compounds are likely to exhibit some degree of oxidation and degradation by the highly oxidizing V(V) ions in the charged positive half-cell electrolyte of the VRB, inorganic additives would be preferred. In this study, the early work of Skyllas-Kazacos and co-workers was extended to further investigate the effect of a number of inorganic additives on the stability of supersaturated V(V) solutions against thermal precipitation in the VRB. The results of the additive screening tests were then applied to vanadium redox flow cell charge-discharge cycling using a 3 M vanadium solution and the results are presented here.

**Experimental**

Electrolyte preparation and additive screening.—Equimolar amounts of vanadium trioxide and pentoxide powders were initially added to a sulfuric acid solution and heated to generate a 3 M V(IV)

| Additive                        | Concentration additive in V(V) solution (M) |
|---------------------------------|--------------------------------------------|
| 1 wt% Sodium pentapolyphosphate - | 0.041                                      |
| Na2P2O7 (SPPP)                  | 0.073                                      |
| 1 wt% K2PO4                     | 0.16                                       |
| 1 wt% (NH4)2SO4                 | 0.12                                       |
| 2 wt% (NH4)2SO4 + 1 wt% SPPPP   | 0.23 + 0.041                               |
| 2 wt% (NH4)2SO4 + 1 wt% H2PO4   | 0.23 + 0.16                                |

solution by electrochemical dissolution. When V2O5 is added to a suspension of V2O5 powder, the V(III) ions in solution electrochemically leach the V2O5 powder, causing it to reduce to the more soluble tetralevate state that dissolves in solution according to:

\[
\frac{1}{2} V_2O_5 + V^{3+} + H^+ \to 2VO^{2+} + \frac{1}{2} H_2O
\]

The V(IV) solution thus prepared was electrolyzed to V(V) in the positive half-cell of a 2-compartment electrolysis cell. The final V(V) and total sulfate concentration of the solution was determined by Inductively Coupled Plasma (ICP) analysis. To avoid precipitation, the V(V) solution was stored at 0°C until use. Three levels of addition were used in the initial additive screening studies: 1, 2 and 3 weight percent of the additive dissolved in 10 mL of the V(V) electrolyte. A Blank containing the same vanadium and total sulfate concentration but with no additive was also observed for comparison.

Precipitation rate studies.—The precipitation rate study was carried out by measuring of the change in V(V) concentration as a function of time for solutions with and without additive. The solutions were placed in a water bath set at either 30°C or 50°C and samples were periodically removed and analyzed by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AAS) analysis to determine the concentration of V(V) in solution as a function of time.

Additive preparation.—The concentration adjustment for the vanadium solutions in sulfuric acid was performed at the same time as the additive was added to the solution. The required amount of each solid additive was weighed into glass tubes to give 1, 2 and 3 weight percent solutions in water or acid and using the measured density of the 3 M V solution (1.53 g/mL at 20°C), the appropriate volume of the additive solution was mixed with the V(V) solution to give the required final concentration.

The molar concentration of the additive present in each solution was also calculated and the values are presented in Table I.

**Cell cycling tests.—** The design parameters of the vanadium test cell used for evaluating the 3 M vanadium electrolyte are detailed in Table II.

**Table I. Concentration of additives in V(V) solutions.**

| Additive                        | Concentration additive in V(V) solution (M) |
|---------------------------------|--------------------------------------------|
| 1 wt% Sodium pentapolyphosphate - | 0.041                                      |
| Na2P2O7 (SPPP)                  | 0.073                                      |
| 1 wt% K2PO4                     | 0.16                                       |
| 1 wt% (NH4)2SO4                 | 0.12                                       |
| 2 wt% (NH4)2SO4 + 1 wt% SPPPP   | 0.23 + 0.041                               |
| 2 wt% (NH4)2SO4 + 1 wt% H2PO4   | 0.23 + 0.16                                |

**Table II. Test Cell Specifications.**

| Electrode collector: | Glassy carbon. |
|----------------------|---------------|
| Graphite Felt:       | 5.5 mm Sigri  |
| Electrode Area:      | 4.5 cm x 5 cm = 22.5 cm² |
| Membrane:            | Selenion Type III, Asahi Glass, Japan |
| Flowframe:           | 2 x 2 mm PVC flow-frames |
| Half-Cell Cavity:    | 2 mm flow-frame + 2 x 1 mm gaskets with resulting thickness after cell assembly = 3.5 mm |
| Electrolyte:         | 3 M Vanadium in 5 M or 5.5 M sulfate/H2SO4 |
Results and Discussion

The results from the initial additive screening in solutions of 3 M V(V) in 5 M sulfates at 30 °C are presented in Table III for each of the additives at a range of concentrations. The table shows the induction time and the amount of precipitate present at 22 days as a percentage of the total solution volume. The Blank solution showed precipitate after 3 days. In contrast, 1 wt% H2PO4 increased the induction time for precipitation to over 47 days at 30 °C, while SPPP and K2PO4 increase induction time to 14 and 18 days respectively.

The action of the phosphates on V(V) precipitation inhibition may be associated with the formation of binuclear V(V) complexes with phosphate ions.15 These workers evidenced the complex formation between the V(V) ion (VO2+) and H2PO4 by a bridging HPO42− ligand. Since the molar concentration of phosphate ions used in the present study was considerably lower than the concentration of vanadium ions in solution however, this mechanism would not fully explain the stabilization effects observed here, so other processes must also be contributing to the precipitation inhibition.

The addition of H2PO4 will also increase the H+ concentration in solution that may shift the thermal precipitation equilibrium of V(V) to the left so as to favor the V2O5 dissolution reaction as shown below:

\[
2\mathrm{VO}_2^+ + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{V}_2\mathrm{O}_5 + 2\mathrm{H}^+ \tag{[2]}
\]

The concentration of H2PO4 in solution at 1 wt% is 0.16 M, and given the high H+ concentrations in these solutions, it can be assumed that the only the first acid dissociation will occur, leading to an extra 0.16 M H+ in solution. By comparison, K2PO4 at 3 wt% also lengthened the induction time significantly from 3 days to 18 days, but in this case there are no extra H+ ions introduced by the additive, which may account for the difference between the stabilizing power of H2PO4 and K2PO4.

Polyporphosphates function as threshold treatments because they are effective at dosages much less than those stoichiometrically required to react with the cations. The mechanism of V(V) precipitation retardation in the case of sodium pentapolyphosphate would thus likely be working on the principles of complex formation with VO2+ to form (VO2)2PO4, together with adsorption on the V2O5 nuclei to retard crystal growth.16

From these results, it is apparent that the inhibition of V(V) precipitation must be due to the presence of the phosphate species in solution that act by forming V(V)- phosphate complexes15 and by adsorbing onto the surface of the nuclei, inhibiting crystal growth.10,16 The additional H+ ions introduced by the H2PO4 additive provides additional stabilization of the V(V) ions by shifting the equilibrium reaction 1 to the left.

In the case of K2PO4, only traces of precipitate were observed at the induction time and after 22 days at all concentration levels, so the large difference in induction time recorded for 3% addition, may simply be an artefact of the experiment. On the other hand, addition of ammonium sulfate gave induction times similar to those observed for the Blank solution. The amount of precipitate at 22 days for the 1 wt% addition was also similar to that in the Blank solution, but was significantly higher for the 2 and 3 wt% addition. The reasons for this are not fully understood and require further in-depth evaluation.

**Performance of additives in V(V) solutions at 50 °C.** — The stability of the 3 M vanadium solutions was further evaluated at 50 °C. Based on the results of the preliminary screening studies, 3 M V(V) solutions containing the following additives were prepared as described previously (abbreviations used are shown in square brackets): Blank solution with no additive [Blank] Sodium pentapolyphosphate [SPPP] 1 wt% Potassium phosphate [KP] 1 wt% H2PO4 [HP] 1 wt% Ammonium sulfate [AS] 1 wt% Ammonium sulfate 2 wt% + Sodium pentapolyphosphate 1 wt% [AS+SPPP] Ammonium sulfate 2 wt% + H2PO4 1 wt% [AS+HP]

Figure 1 shows the desupersaturation curves for the V(V) solutions, obtained by plotting concentration as a function of time. The desupersaturation curve for the Blank solution shows a large initial drop in concentration, before reaching an equilibrium concentration of 1.1 M vanadium after 32 days.

In the case of the additive containing solutions, a small lag is observed before the rapid desupersaturation of the solutions containing 1 wt% SPPP, 1 wt% H2PO4 and 2 wt% AS + 1 wt% H2PO4. Significantly however, the V(V) concentration in the Blank solution dropped to 1.6 M after 1 day, while in the case of the H2PO4, SPPP, AS and AS + H2PO4 additives, the V(V) concentration remained above 2.5 M within the same time frame. The slower rate of decline in the V(V) concentration over the first 4 days in each of these solutions at 50 °C, suggest that these additives could be potential stabilizing agents for the highly supersaturated V(V) solutions, decreasing the rate of precipitation of the charged positive half-cell electrolyte at elevated temperatures.

From these accelerated precipitation studies, the additive formulation using 2 wt% ammonium sulfate + 1 wt% H2PO4 appears to provide the best stabilization against high temperature precipitation of 3 M V(V) solutions. This additive formulation was also found to be effective for stabilization of supersaturated V(II) solutions in the negative half-cell of the VRB.17 It was therefore selected for further evaluation in a vanadium redox flow cell employing a 3 M vanadium electrolyte at 30 °C. Based on earlier screening studies reported by Skylas-Kazacos,8 glycerine and ammonium oxalate were shown to stabilise supersaturated V(II) solutions. These additives were therefore incorporated in different mixed additive formulations for further assessment and the results are presented below.

**Charge-Discharge Cycling of 3 M Vanadium Solution in Vanadium Redox Flow Cell**

Since the additive combination of 1% (w/w) glycerol and 2% (w/w) ammonium oxalate had previously been reported as been effective in stabilizing both the negative and positive half-cell electrolytes of the
VRB, it was decided to evaluate this additive formulation in the vanadium redox cell employing a 3 M vanadium solution in 5.0 M H₂SO₄. The cell was initially charged at a current density of 50 mA.cm⁻², but as the cell was being charged, gassing became evident in the positive solution as the system approached 50% SOC. This gassing is known to be due to the oxidation of glycerol and oxalate ions by V(V), producing CO₂ gas in solution. The gassing was so significant that the positive half-cell pump kept cavitating, stopping electrolyte flow. The cell was left to stand overnight at 50% SOC to allow all gassing to subside. The pumps were then re-primed and the cell was charged at 80 mA.cm⁻² to an upper limit of 1.8 V and discharged at 50 mA.cm⁻² to a lower limit of 0.8 V. From the cell voltage vs time

Figure 1. Concentration vs Time Curves for Precipitation from 3 M V(V) Solutions in 5 M Total Sulfates at 50°C.
plots, the coulombic, voltage and energy efficiencies were calculate and the values obtained are plotted in Figure 2. The cell capacity was also calculated for each discharge cycle and this is plotted vs cycle number in Figure 3. Significant capacity fluctuations can be observed throughout the experiment that can be attributed to on-going gassing and electrolyte flow problems that also led to excessive transfer of electrolyte from the positive half-cell into the negative half-cell. This was periodically adjusted by manually transferring solution back to the positive half-cell reservoir before resuming charge-discharge cycling.

The decreasing trend in capacity as a function of cycle number observed in Figure 3 is associated with a number of factors:

1. Transfer of vanadium ions from one half-cell to the other, caused by the different rates of diffusion of (VII), V(III), V(IV) and V(V) ions across the membrane, leading to a buildup of vanadium ions in one half-cell and a dilution in the other.

2. The transfer of electrolyte across the membrane from one half-cell to the other during charge-discharge cycling that leads to unequal volumes of electrolyte in the two half-cells.

3. Reduction in the oxidation state of the positive half-cell electrolyte due to the reaction between V(V) and the glycerine and oxalate additives that generates CO₂ gas and gives rise to an imbalance between the two half-cell solutions.

The generation of bubbles in the positive half-cell also restricts electrolyte flow and gives rise to a pressure buildup that has been observed to push solution across the membrane and a further loss of capacity. Capacity loss caused by processes (1) and (2) above can be readily restored by simply remixing the two half-cell solutions and returning half of the total volume to each reservoir. On the other hand, capacity loss caused by process (3) leads to an imbalance in the state-of-charge of the two half-cell electrolytes that cannot be restored by electrolyte remixing.

Figure 3 shows that full remixing of the solutions allowed the capacity to increase to 2.83 Ah, which is slightly less than the original capacity of 3.23 Ah. This suggests that the capacity loss observed in Figure 3 is associated with all 3 processes described above. The observation of gas bubbles in the positive half-cell solution as the cell approached 50% SOC that continue to form even when charging ceases, indicates the reaction between V(V) and glycerine and ammonium oxalate to produce V(IV) and CO₂ bubbles. The oxidation state of the positive half-cell solution is thereby reduced so that its state-of-charge is no longer the same as that of the negative half-cell. This imbalance cannot be restored by remixing, but requires a chemical or electrochemical rebalancing process that involves a partial oxidation of the V²⁺ ions in the negative half-cell to equalise the SOC’s of the two half-cell solutions. One simple method to achieve a chemical rebalance would be to bubble oxygen through the negative half-cell to partially oxidise the V²⁺ ions until the V(II):V(III) ratio matches the V(V):V(IV) ratio in the positive half-cell electrolyte.

The use of glycerine and ammonium oxalate as precipitation inhibitors is therefore confirmed as unsuitable for long-term use in the high energy density VRB because of the oxidation of the organic species by V(V) ions that leads to gassing and loss of stabilizing agent over time.

Inorganic precipitation inhibitors would therefore be preferred stabilizing agents for the high energy density VRB since they would not be susceptible to oxidation by V(V). Similar tests were thus performed with a 3 M V electrolyte in 5 M total sulfate solution containing 1 wt% H₃PO₄ + 2 wt% ammonium sulfate under the same conditions. The reservoirs were filled with 65 m of the 3 M V⁺ solution and the cell was cycled at charging and discharging current densities of 80 and 50 mA.cm⁻² respectively. Cell efficiencies were calculated for every 10th cycle and the results are presented in Figure 4. In comparison to the previous cell employing glycerine and ammonium oxalate, a higher voltage and energy efficiency is observed for this
cell, while the efficiencies remain stable over the 90 charge-discharge cycles.

The cell capacity was also calculated for each discharge cycle and this is plotted in Figure 5. Comparing the cell capacity with the theoretical value calculated from Faraday’s Law shows that the active material utilization in these experiments was only 62% for the set upper and lower voltage limits set for the charge-discharge cycling experiments. Extending the voltage limits will allow a wider SOC range to be achieved with a greater active material utilization being possible. Further cell materials and design optimization can also reduce some of the ohmic resistances in the cell, allowing higher energy efficiencies and a wider SOC range for the same voltage limits. Future improvements can include the use of new low resistance membranes that are currently being investigated by our group and will be the subject of future publications.

In Figure 5, the cell capacity is seen to decrease only slightly during the experiment as a result of a slight transfer of vanadium ions across the membrane. In contrast to the previous experiment, only a small electrolyte volume transfer was observed from the positive into the negative half-cell electrolyte. In this case, no electrolyte remixing was required to restore capacity over the 90 charge-discharge cycles. During the course of these experiments, no precipitation was observed in either half-cell electrolyte, nor was the electrolyte flow-rate restricted at any time (as occurs when precipitate is formed inside the felt). The use of 1 wt% H3PO4 + 2 wt% ammonium sulfate as precipitation inhibitors is thus seen as effective additives to stabilise a 3 M vanadium electrolyte for use in a high energy density VRB.

The results of this study therefore provide evidence for the viability of the 3 M V electrolyte that allows a 60–90% increase in the volumetric energy density compared with the regular 1.6–1.8 M V electrolytes currently employed in commercial VRB systems. The 3 M solution also represents a 20% increase in volumetric energy density compared with the 2.5 M V solution used in the mixed H2SO4/HCl electrolyte cell, without the risk of hazardous chlorine evolution during overcharge.

Conclusions

In this study, precipitation inhibitors were used to stabilise a 3 M vanadium electrolyte for use in a high energy density vanadium redox flow battery. The induction time and precipitation rate of 3 M V(V) solutions were first investigated in the presence of a number of additives to explore their stabilization potential against thermal precipitation during operation of the VRB. After 32 days, 3.2 M V(V) solutions containing 1 wt% SPPP, 1 wt% K3PO4, and 2 wt% AS + 1 wt% H3PO4 showed final V(V) concentrations of 2.7, 2.7 and 2.6 M respectively, compared to 2.4 M V(V) in the Blank solution. After 1 day at 50 °C, the V(V) concentration in the Blank solution dropped to 1.6 M, while in the case of the H3PO4, SPPP, AS and AS+ H3PO4 additives, the V(V) concentration remained above 2.5 M within the same time frame. The additives 1 wt% H3PO4 + 2 wt% ammonium sulfate were thus selected for evaluation in a high energy density VRB employing a 3 M V electrolyte and stable cell efficiencies and capacity were observed over 90 charge-discharge cycles. In contrast, a vanadium redox cell employing 3 M V in the presence of glycine + ammonium oxalate, showed significant gassing during charging and a loss in capacity and efficiency over a smaller time-frame. This was a result of oxidation of the glycine and oxalate specied by V(V), producing CO2 gas and a decrease in the oxidation state of the positive electrolyte.

Inorganic additives are thus seen to be effective stabilising agents for supersaturated vanadium solutions for use in a high energy density VRB. Although 3 M V(V) solutions at 100% state-of-charge (SOC) can only be stabilised for a few days at 50 °C in the presence of additive, this should not be a problem since V(V) solutions at less than 100% state-of-charge are known to be stabilised by the presence of only 5% V(V) as shown by Rahman. Since the VRB is typically operated between 10–20% and 80–90% SOC therefore, stable operation should still be possible even if the temperature goes above or below 30 °C. If the cell is allowed to stand for extended periods of time, however, temperature control would be recommended to maintain a relatively constant temperature. Periodic charge-discharge cycling should however be schedule to ensure that the induction time for precipitation of the vanadium ions is not exceeded.

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