Vanadium redox battery: Positive half-cell electrolyte studies

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ABSTRACT

The vanadium redox battery (VRB) employs two "electrolyte tanks" that store energy in the form of the two vanadium redox couples and a cell "stack" where the charge/discharge reactions occur. To date, 2 M vanadium electrolyte have been successfully used in large demonstration projects for stationary applications. For mobile applications however, higher vanadium concentrations are required to reduce the size and weight of the battery. The main limitation for the vanadium electrolyte concentration and subsequently its energy density in the VRB is the thermal precipitation of the V(V) ion at elevated temperatures. In this paper optimization study of vanadium V(V) supersaturated solutions in terms of concentrations, temperature, and precipitation behavior are reported along with properties such as density and viscosity. It appears that 3.0–3.5 M V(V) solutions in 6 M total sulfate are sufficiently stable at temperatures up to 30 °C, although 2 M solutions are still required for operation at higher temperatures of about 40 °C.

1. Introduction

Demand for new and large energy storage systems is increasing for applications such as remote area power systems, wind turbine generators, load leveling at electric power stations, as well as emergency back-up applications. The use of batteries as portable electrical power sources has increased dramatically and to some extent technology has not been able to keep pace with demands. Longer cycle life and higher volumetric energy densities are needed for electric vehicles while load-leveling applications are more sensitive to cost.

More recently the lithium and nickel metal hydride batteries have emerged as an excellent high energy density alternatives to the conventional lead-acid and nickel cadmium systems, however, their current high cost has to date limited their use to relatively small-scale portable equipment applications and hybrid electric vehicles. Amongst the new battery technologies currently under development around the world, the redox flow cell appears to offer great promise as a low cost, high efficiency system for large-scale energy storage [1–4]. The vanadium redox battery (G1 VRB), which was pioneered at The University of New South Wales (UNSW), Australia and employs vanadium redox couples in sulfuric acid in both half-cells, is now moving towards commercialization in a wide range of stationary applications [5–7].

Several demonstration batteries of various sizes have been evaluated in Australia, Thailand, USA and Japan. A 5-kW/13-kWh vanadium battery system was installed in a solar demonstration house Thailand in 1993 and its suitability for application in energy self-sufficient housing was evaluated. Another vanadium battery of size 4.1 kW peak power and 3.9 kWh capacity was evaluated at UNSW as a submarine back-up battery for the Australian Department of Defense, while a 5-kW vanadium battery was installed and field tested in an electric golf-cart at UNSW in the late 1990s [8,9]. In 1997, a 200-kW/800-kWh grid-connected vanadium battery was commissioned under license from the University of NSW, at the Kashima-Kita Electric Power station in Japan, where it was subjected to long-term testing as a load-leveling system. Sumitomo Electric and Kansai Electric Power Co., Inc. have been successfully testing the world's first 500 kW/1 MWh class vanadium redox battery since 1997 as a grid-connected, load-leveling unit at a power station in Japan, and has more recently installed a 4-MW/6-MWh VRB for the storage of wind energy storage in Hokkaido, Japan [10].

While the VRB technology is ready for commercialization in applications such as load leveling, uninterruptible power supply systems and renewable energy storage, its use in electric vehicles is currently restricted to vans and buses where a fixed driving range and the ability to mechanically refuel overcomes the limitations caused by the low energy density. In certain stationary applications it is also desirable to reduce the size and battery footprint, particularly in urban areas where land costs are high. It is therefore, desirable to increase the energy density of the VRB to allow future application in a wider range of both stationary and

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mobile applications. This can be achieved by increasing the concentration of the vanadium ions in solution above the present value of 2 M that has an equivalent electrolyte energy density of about 25 Wh kg^{-1}. Although higher vanadium concentrations have been recently achieved with the new Generation 2 vanadium bromide redox cell also invented at UNSW in 2001, further optimization of the original vanadium sulfate electrolyte may lead to an increased energy density.

In the VRB, the volume of the electrolyte determines the capacity of the battery depending upon the vanadium concentration. Increasing the concentration of vanadium in the electrolyte will increase the energy density of the battery, but any increases in vanadium ion concentration above 2 M in the sulfuric acid supporting electrolyte, leads to supersaturation of the solutions resulting in the precipitation of the electrolyte at low temperatures in the case of V(II)/V(III) or V(IV) solutions, or at elevated temperatures in the case of V(V) solution. To allow vanadium solutions of concentration greater than 2 M to be employed in the G1 VRB, therefore, an effort is being made to improve the stability of 3–4 M supersaturated vanadium solutions in sulfuric acid.

This study has thus focused on improving the stability of the V(V)/sulfuric acid positive half-cell solution in particular and the different factors that affect the precipitation of V(V) species such as state-of-charge (SOC), temperature, the V(V) concentration, supporting electrolyte (H$_2$SO$_4$) concentration. Properties such as density and viscosity of these highly concentrated V(V) solutions are also presented.

2. Vanadium redox battery features

The main features of the vanadium redox battery are shown in Fig. 1. The major components of the vanadium battery are: (i) the electrodes made up of carbon felt, (ii) the electrolyte (vanadium solution in sulfuric acid), and (iii) the selective ion-exchange membrane. The cell consists of two compartments (positive half-cell and negative half-cell) separated by a membrane, which prevents cross mixing of the electrolytes. Each side of the cell contains an inert electrode made of highly porous carbon felt. The electrolytes, the anolyte and catholyte, are stored in two external reservoirs. The electrolyte is prepared by dissolving vanadium oxide or sulfate in sulfuric acid solutions. The rechargeable electrolyte is pumped through the inert electrode where the electrochemical reactions occur. During charging and discharging of the G1 VRB, electrochemical reactions within the battery stack change the valence of the vanadium ions as follows:
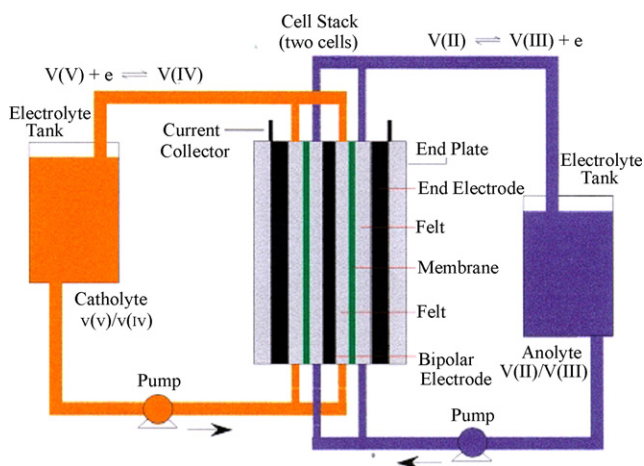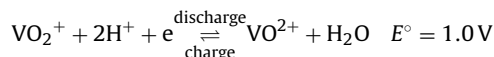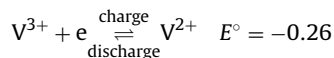
At the positive electrode:

$$VO_2{}^+ + 2H^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} VO^{2+} + H_2O \quad E^\circ = 1.0\,V$$

At the negative electrode:

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \quad E^\circ = -0.26$$

The standard cell potential is thus E° (cell) = 1.26 V at concentrations of 1 M and 25 °C. The concentration of vanadium ions in the electrolytes is determined by the solubilities of each of the V(II), V(III), V(IV) and V(V) ions, this being a function of temperature, sulfuric acid concentration and SOC. In the case of the V(II), V(III) and V(IV) oxidation states, the solubilities increase with increasing temperature and decreasing acid concentration. The reverse is true however, for the V(V) oxidation state which undergoes thermal precipitation at temperatures above 40 °C. During continuous operation of the VRB, higher operating temperatures are most likely to be experienced due to resistance losses which heat up the solutions. The stability of the positive half-cell electrolyte at elevated temperatures is thus the most critical parameter to be controlled if high vanadium concentrations are to be employed. In this study, the positive half-cell electrolyte composition has therefore been optimized to allow vanadium(V) electrolyte concentrations above 2 M to be employed for the G1 VRB system.

3. Experimental procedure

Supersaturated vanadium(V) solutions of various vanadium concentrations 2, 3, 4 and 5 M prepared in different sulfuric acid concentrations containing 5, 6 and 7 M total sulfate/bisulfate were used for studying the stability of vanadium(V) solutions. All of these vanadium(V) solutions were prepared by electrolytic oxidation of the corresponding VOSO$_4$ solutions.

From each vanadium(V) solution, 30 ml samples were taken in 40 ml sample glass bottles with teflon stoppers and placed in constant temperature water baths at 20, 30, 40 and 50 °C. A temperature controlled immersion circulator capable of controlling the temperature within ±0.5 °C was used to maintain the constant temperature.

The rate of precipitation was determined by monitoring the change in the V(V) concentration as a function of time by analyzing samples using atomic absorption spectrophotometry (Varian AA2 Plus). The sampling was done at different intervals for a period of 1000 h and the frequency of sampling was increased during initial precipitation after visual observation.

4. Results and discussion

The structure of a supersaturated solution is probably more complex than that of an unsaturated or saturated solution. As reported by Khamskii and Evgenii [11], a number of attempts have been made to find the distinguishing features of supersaturated solutions by investigating the dependences of various physical properties and electrochemical behavior on concentration, temperature, state-of-charge and so on. Some of these important properties of supersaturated vanadium(V) solutions are presented in the following paragraphs.

4.1. Effect of vanadium concentration

The main purpose of this study was to investigate the optimum conditions for stable vanadium(V)–sulfate/bisulfate system to achieve maximum energy density for the G1 VRB. A comprehensive stability evaluation program was undertaken by preparing 2, 3,
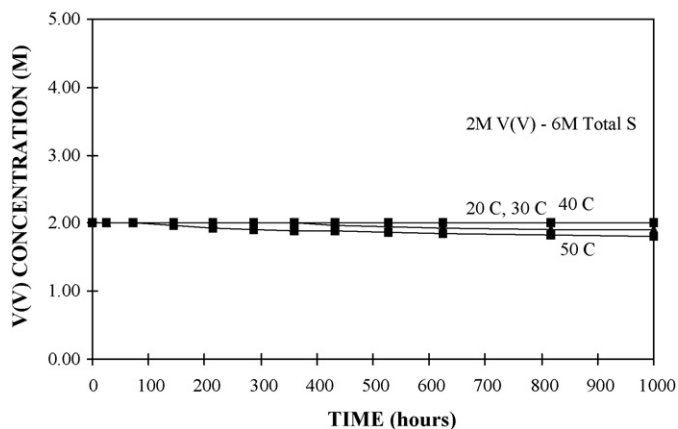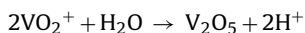

Fig. 1. Schematic of vanadium redox battery.

Fig. 2. Stability of 2 M V(V) solutions at different temperatures.

Fig. 4. Apparent equilibrium concentration of V(V) solutions in 6 M total sulfate at different temperatures after 1000 h.

4, and 5 M vanadium(V) solutions in H_2SO_4 supporting electrolyte containing 5, 6 and 7 M total sulfate/bisulfate. Each solution was evaluated at 20, 30, 40 and 50 °C to establish the stability region, determine the induction time and then study the kinetics of precipitation.

The variation in the vanadium(V) concentration with time for 2 and 3 M V(V) solution in 6 M total sulfate are shown in Figs. 2 and 3. Similar concentration profiles were generated for the other solutions to study their precipitation behavior. It can be observed from Figs. 2 and 3, that increasing vanadium concentration decreases the stability of the positive half-cell electrolyte at temperatures above 40 °C.

4.2. Effect of temperature

As mentioned above, V(V) suffers from thermal precipitation at higher temperatures. The concentration profiles shown in Figs. 2 and 3 illustrate the effect of temperature also on the stability of 2 and 3 M V(V) solutions at various temperatures. It is obvious that increasing temperature decreases the stability of V(V) solutions because of the endothermic nature of the precipitation reaction of the V(V) ions:

$$2VO_2^+ + H_2O \rightarrow V_2O_5 + 2H^+$$

It was noticed, however, that increasing the V(V) concentration over the range 2–4 M in 6 M total sulfate/bisulfate, appeared to increase the equilibrium vanadium concentration in solution at temperatures up to 40 °C. Thus as seen in Fig. 4, the 4-M V(V)
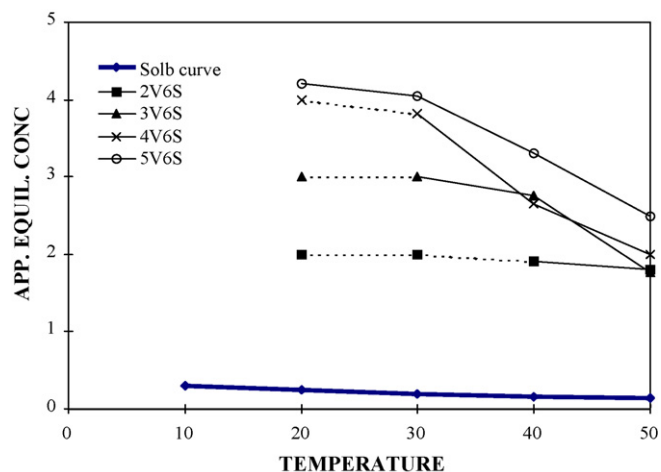
solutions in 6 M total sulfate/bisulfate at 30 °C dropped in concentration by only 5% after 1000 h and even the 5-M V(V) solution showed an "equilibrium" concentration of around 4 M after 1000 h at 30 °C. These results suggest that new, more stable vanadium species may be formed in solutions with very high initial V(V) concentration.

4.3. Effect of sulfuric acid concentration

Sulfuric acid concentration plays a very important role in stabilizing the supersaturated vanadium(V) solutions. Changes in the initial H_2SO_4 concentration basically change the concentrations of H^+, HSO_4^- and SO_4^{2-} ions which have direct interaction with the V(V) species in solution and the precipitation phenomena of V(V). Since the analysis of the samples was carried out by ICP which gives total sulfates and bisulfate, the results are discussed in terms of the total sulfate/bisulfate present in the system. The desupersaturation experiments were designed to study the effect of sulfuric acid concentrations of 5, 6 and 7 M total sulfate/bisulfate on the stability of V(V) solutions. Fig. 5 shows the effect of sulfuric acid concentration on the stability of V(V) solutions. The stability of V(V) solutions increased with increasing total sulfate/bisulfate concentration. It can be observed that, at 40 °C, the drop in concentration of 3 M V(V) solution in 5 M total sulfate/bisulfate after 1000 h was found
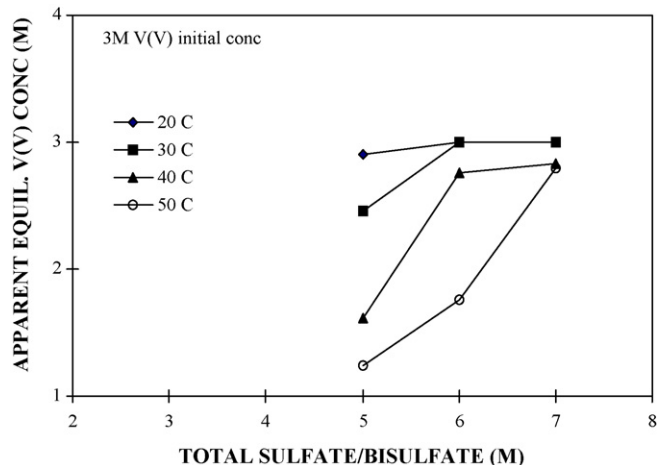

Fig. 3. Stability of 3 M V(V) solutions at different temperatures.

Fig. 5. Effect of total sulfate/bisulfate concentration on stability of 3 M V(V) solution after 1000 h at different temperatures.
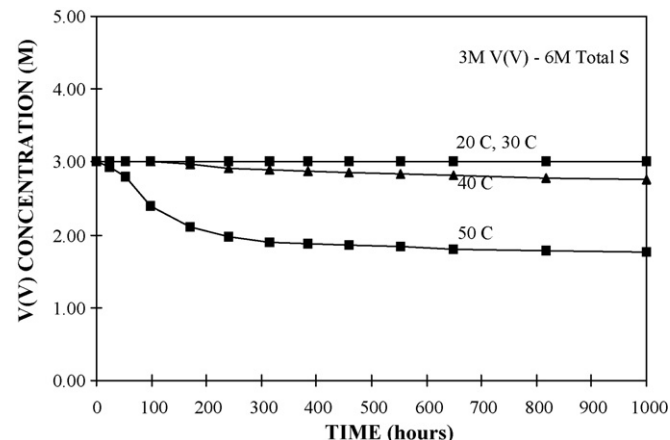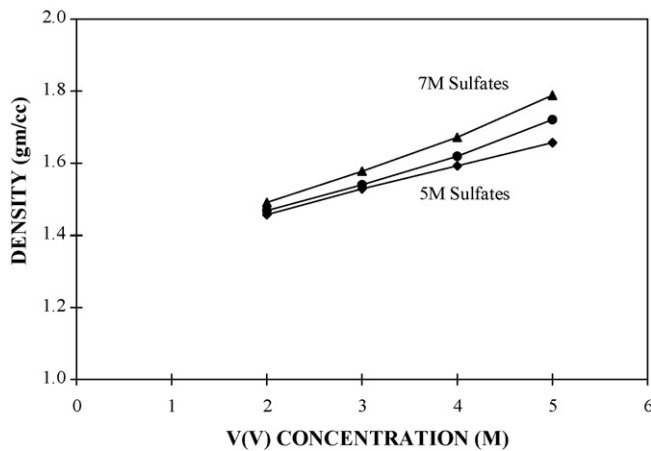
**Fig. 6.** Effect of vanadium concentration on density of the supersaturated V(V) solutions at 20 °C.

Fig. 7. Effect of total sulfate/bisulfate concentration on density of the supersaturated V(V) solutions at 20 °C.

to be 46% as compared to 8% in 6 M total sulfate/bisulfate and 5% in 7 M total sulfate/bisulfate.

The increased stability at higher H_2SO_4 concentration is due to the presence of more H^+ ions (increased ratio of H^+ ions to V(V) ions) which favors the following reaction in the forward direction [12,13].

$$V_2O_5(c) + 2H^+ \rightleftharpoons 2VO_2{}^+ + H_2O$$
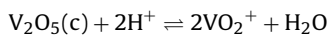
Although increasing sulfuric acid concentration increases the stability of V(V) solution, however, the limitation on sulfuric acid concentration arises from the stability of V(IV) species at lower temperatures. Since V(IV) ions precipitate as vanadyl sulfate in sulfuric acid solutions, the solubility of V(IV) sulfate decreases with increasing sulfuric acid concentration due to the common ion effect. Because of the reduced solubility of the V(IV) ions in the discharged positive half-cell electrolyte, it is not possible to increase the concentration of sulfuric acid above 6 M.

4.4. Density of vanadium(V) solutions

The density of different vanadium(V) solutions was measured using a 50-ml volumetric flask at 20 °C. The densities of all the 12 solutions under study are plotted in Fig. 6. It can be observed from Fig. 6 that the density of supersaturated vanadium(V) electrolytes increases linearly with increasing vanadium concentration. The effect of sulfate/bisulfate concentration on density is illustrated in Fig. 7. The densities of vanadium(V) solutions do not change significantly with changes in total sulfate/bisulfate concentration however, densities of solutions in 7 M total sulfate/bisulfate are distinctly higher than that in 5 and 6 M total sulfate/bisulfate. The effect of vanadium concentration on density appears to be more pronounced than that of the sulfate/bisulfate concentration.

4.5. Viscosity behavior of vanadium(V) solutions

One of the important properties of concentrated vanadium solutions is viscosity and is of considerable interest as it affects the conductivity and electrochemical behavior of V(V) solutions. Viscosity of supersaturated vanadium solutions was measured using a capillary viscometer of proper size to handle the relatively viscous vanadium(V) solutions. The viscosity of liquids generally decreases with increase in temperature. The molecules acquire more kinetic energy as the temperature increases and are able to move about more freely. This improves their ability to slide past each other and decreases the shear forces between layers and hence viscosity. Viscosity increases with increase in concentration of the electrolytes
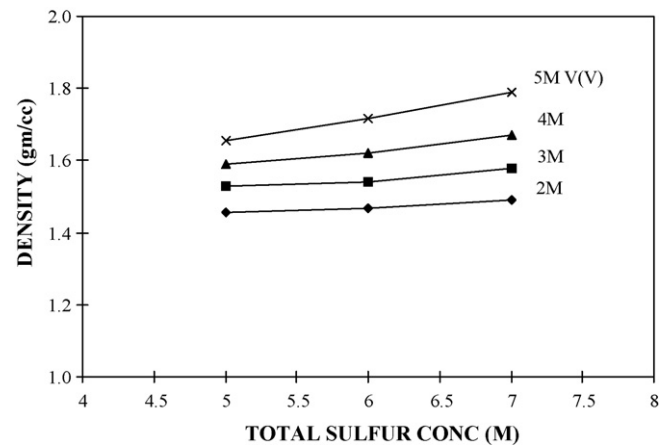
by increasing the intermolecular interactions and making the liquid more and more cohesive. In some types of electrolytes (KF, LiBr, etc.) when a certain concentration of solid phase is attained, the viscosity may reach such high values that the hydraulic type flow is replaced by plastic flow [14,15] as shown in Fig. 8. So, the maximum practical supersaturation is limited by the viscosity of the solution to be able to remain in the hydraulic flow region.

4.5.1. Effect of concentration on viscosity

The viscosity behavior of supersaturated vanadium(V) solutions was studied by measuring the viscosity of vanadium(V) solutions over the vanadium concentration range of 2–5 M in solutions containing 5–7 M total sulfate/bisulfate. The effect of total sulfate/bisulfate concentration on the viscosity of vanadium(V) solutions is more pronounced at higher vanadium concentration as shown in Fig. 9. The variation in viscosity of vanadium solutions with increasing vanadium concentration is presented in Fig. 10.

The viscosity increases linearly and gradually between 2 and 3.5 M vanadium(V) concentration and then increases rapidly on further increasing the vanadium concentration to 5 M. A concentration of about 3.5 M V(V) solution in 5–7 M total sulfate/bisulfate concentration appears to be the limiting concentration to be able
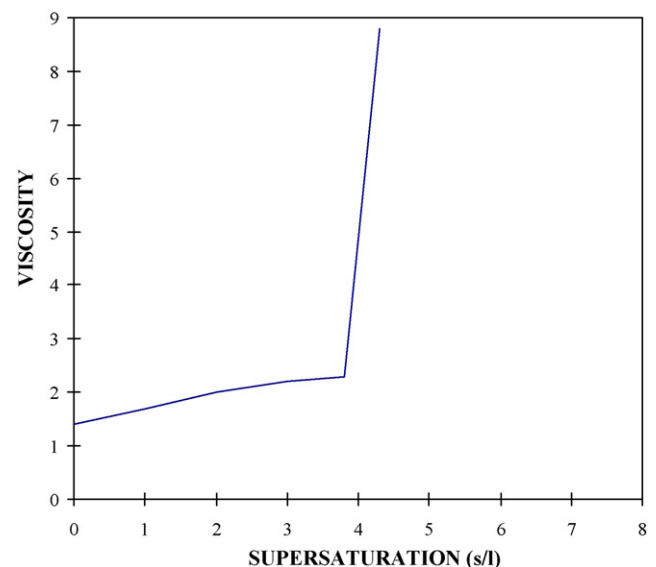
Fig. 8. Typical diagram showing effect of supersaturation on viscosity of concentrated solutions (Source: Nyvlt [14]).
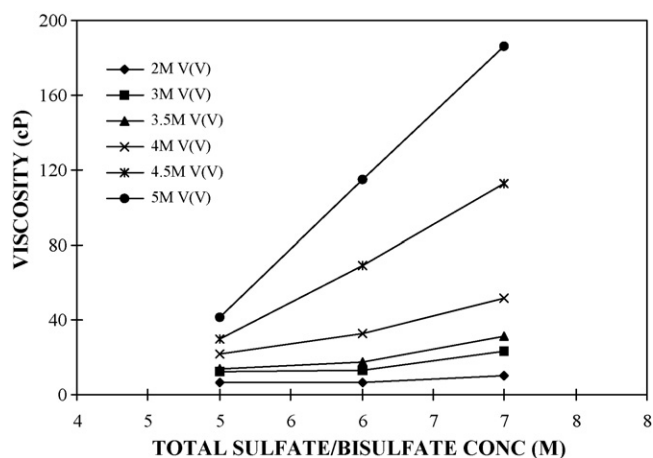
Fig. 9. Variation in viscosity of 5 M vanadium(V) solutions with total sulfate/bisulfate at 20 °C.

Fig. 11. Variation in viscosity of sucrose solutions with increase in concentration at 20 °C.

to remain in the hydraulic flow region and with further increase in V(V) concentration viscosity increases rapidly. This is probably due to the formation of extended chain polyvanadic molecules [16], subsequently increasing the viscosity more steeply. Also at such high supersaturations, ion distribution attains a degree of order resembling crystallinity and the influence of ion–ion interaction on viscosity increases significantly [17].

Another reason for the exponential increase in viscosity could be the start of dimerization of VO_2^+ ions to $V_2O_4^{2+}$ at sulfuric acid concentration of 7 M as suggested by Madic et al. [18]. They reported the mass action law constant for the dimerisation of VO_2^+ in 7, 8, 9 and 10 M H_2SO_4 as 0.26, 2.3, 19 and 83 respectively. Additional complexation with sulfate and bisulfate ions at increased sulfuric acid concentrations is also possibly occurring. This change in structure of VO_2^+ in higher vanadium as well as sulfuric acid concentrations is probably also contributing to the rapid increase in viscosities.

Similar behavior was reported by Stokes and Mills [19] in the case of sucrose solutions shown in Fig. 11, over the concentration range of 20–70%. Satoh and Hayashi [15] discussed the viscosity behavior of concentrated aqueous solutions of strong electrolytes from 0.5 to 5 mol l^{-1} at room temperature. They found that the plots of viscosity against concentration were of two types. In the first type (KF, LiCl, LiBr, NaBr, etc.), the viscosity rises almost linearly with concentration in the dilute range to a *critical concentration or deflection point*, above which the slope becomes increasingly positive. They explained that the normal water structure in concentrated solu-
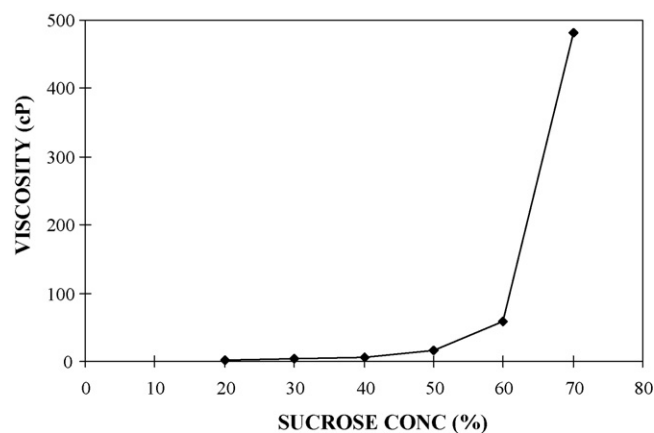
tions (>1 M) is considered to be broken down due to interaction between ionic hydration shells. The ions can then be pictured as embedded in a different solvent from that in the dilute range.

4.5.2. Effect of temperature on viscosity

The effect of temperature on the viscosity was studied using 4.5 M V(V) solution in 7 M total sulfate/bisulfate. It was found that the variation in temperature affects viscosity quite significantly which is shown in Fig. 12. The viscosity dropped very quickly with a slight increase in temperature, for example the viscosity decreased by about 24% when the temperature was raised from 20 to 25 °C. Hatschek [20] reported that at low temperatures the viscosity of sucrose solutions increases greatly with an increase in concentration, while at high concentration the decrease in viscosity with increasing temperature is extremely rapid.

4.5.3. Change in viscosity of V(V) solutions when exposed to atmosphere

When the 4.5-M V(V) solution in 7 M total sulfur was exposed to atmosphere for 45 days the viscosity decreased from 103 cP to 66 cP, a drop of about 35% as compared to about 10% drop when stored in closed container for 75 days.

The upper layer of the 4.5-M V(V) solution in 7 M total sulfur which was exposed to atmosphere appeared dark green when seen by tilting along the walls of the container. Small volumes of V(V) solution (about 5 ml) when placed in a beaker and kept open to
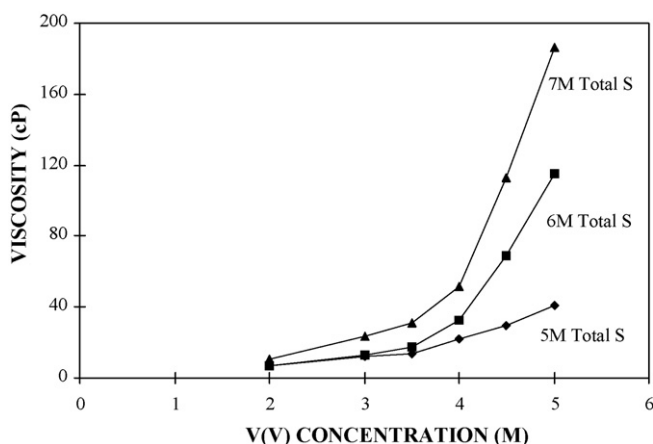

Fig. 10. Variation in viscosity of 2–5 M vanadium(V) solutions in 5–7 M total sulfate/bisulfate at 20 °C.

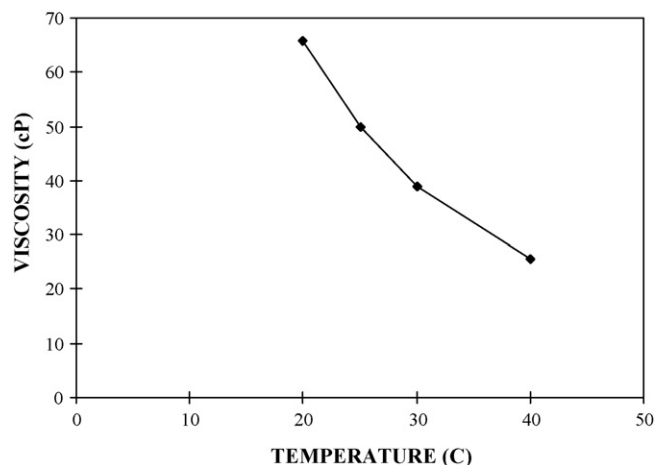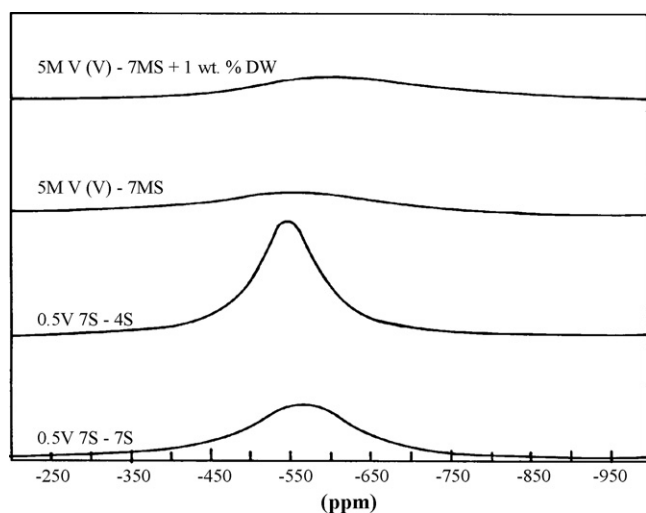**Fig. 12.** Effect of temperature on viscosity of 4.5 M V(V) solution in 7 M total sulfate/bisulfate.

Fig. 13. ^{51}V NMR spectra of various V(V) solutions in different supporting electrolyte concentrations.

atmosphere, the orange-red solution turned green after about 10 days. It was also observed that V(V) solution sticking to the walls of the beaker when left overnight becomes green. This green color is normally observed when water is added to V(V) solutions during titrations and cleaning of the glassware. On the basis of all the above observations it is believed that the solution is absorbing moisture present in the atmosphere because of the hygroscopic nature of sulfuric acid. Thus, this significant drop in viscosity of vanadium solutions when exposed to atmosphere is probably due to a slight dilution and disturbance of the polyvanadic structure of supersaturated V(V) solution by absorbing moisture from the atmosphere.

To develop a better understanding of the viscosity changes of the solutions when exposed to atmosphere, 1 vol./vol.% distilled water was added to the above mentioned 4.5 M V(V) solution, and after shaking it intermittently for about 2 h the viscosity was measured and it was found to be 93 cP a drop of about 18%. This result is most surprising as the 1-vol./vol.% water addition has a negligible effect on the vanadium or acid concentration. Again 1 vol./vol.% 7 M sulfuric acid was added to 5 M V(V) solution in 7 M total sulfur (5V7S), the viscosity dropped by about 9%. Although these observations are difficult to explain at this time, it is thought that the addition of water may be breaking the large size V(V) ions and sulfate/bisulfate complex species rendering more and more small size VO_2^+ ions or molecules thus decreasing the viscosity significantly whereas addition of same amount of acid would not disturb the V(V)–sulfate complex and therefore decreases viscosity only slightly. Good [21] from experiments confirms his earlier observations that ion–solvent interaction is the principal factor governing the fluid kinetics of electrolyte solutions.

4.5.4. ^{51}V NMR studies of vanadium(V) solutions

The 5V7S solution was analyzed by recording ^{51}V NMR spectra with a Bruker ACP 300 spectrometer to find out the effect of addition of water on the structure of V(V) solution and its speciation. The NMR spectra were obtained with a 10-mm broad-band probe tuned to observe ^{51}V at 78.94 Mhz. Because of very high viscosity due to the high vanadium(V) concentration of the sample, the NMR did not show any peak and both the solutions (5V7S and 5V7S-DW) gave almost a flat spectrum as shown in Fig. 13.

Further ^{51}V NMR investigations were carried out by analyzing two dilute solutions: (i) 2V7S solution diluted to 0.5 M V(V) using 7 M H_2SO_4 labeled as 0.5V7S-7S and (ii) 2V7S diluted to 0.5 M V(V) using 4 M H_2SO_4 labeled as 0.5V7S-4S in Fig. 13. The peaks obtained from these solutions are quite broad, again probably due to the

high viscosity of the solution which prevents a fast tumbling of the molecules. However, it can be observed from Fig. 13 that the second solution having more water (resulting in a 0.5-M V(V) in 4.8 M H_2SO_4) clearly indicates more free V(V) ions as compared with the first solution. Thus, it confirms that an increase in water content in the vanadium(V) solution breaks the large size vanadium-sulfate complex ions and generates small size free V(V) ions resulting in a significant drop in viscosity.

It was also noticed that the first solution (0.5V7S-7S) when diluted with 7 M H_2SO_4 did not change its color after dilution but the second solution became dark green after dilution with 4 M H_2SO_4. Both the solutions were analyzed by potentiometric titration to determine the presence of any V(IV) species in the solution which may contribute to the green coloration. It was found that both the solutions were at the same state-of-charge but the first solution (0.5V7S-7S) has slightly higher starting potential than the second solution (0.5V7S-4S). The green coloration is probably due to the formation of some hydrolyzed species at the slightly higher pH.

4.6. Effect of the state-of-charge

The stability of vanadium(V) solutions is also dependent on the SOC or oxidation state of the solution (i.e. V(V):V(IV) ratio). The effect of oxidation state was studied on 5 M vanadium solution in 6 M total sulfate/bisulfate. Two solutions were prepared having total vanadium [V(V) + V(IV)] concentration of 5 M, one with SOC of 85%[Solution A, 85% V(V) + 15% V(IV)] and the other with SOC of 95% [Solution B, 95% V(V) + 5% V(IV)]. The stability of these two solutions with different SOC was investigated at room temperature, and their concentration profiles with time are shown in Fig. 14. It was observed that the solution with total vanadium [V(V) + V(IV)] concentration of 5 M in 6.0 M H_2SO_4 with SOC of 95% [Solution B] decreased in concentration to 4.2 M total vanadium after 1000 h, a drop of 16%, while the one in 6.0 M H_2SO_4 with SOC of 85% [Solution A] did not decrease its concentration over the same period of time.

Slightly lower SOC [presence of low levels of V(IV) species] improves the stability of V(V) solutions greatly even at total vanadium concentrations as high as 5 M containing sulfate/bisulfate concentration of 6 M. Therefore, SOC is a very important parameter in designing the electrolyte composition and improving the stability of highly concentrated vanadium redox cell electrolytes for high energy density applications.

Before increasing the vanadium concentration in the VRB electrolyte above 2 M, however, the solubilities of the other vanadium oxidation states that occur during charge–discharge cycling of the
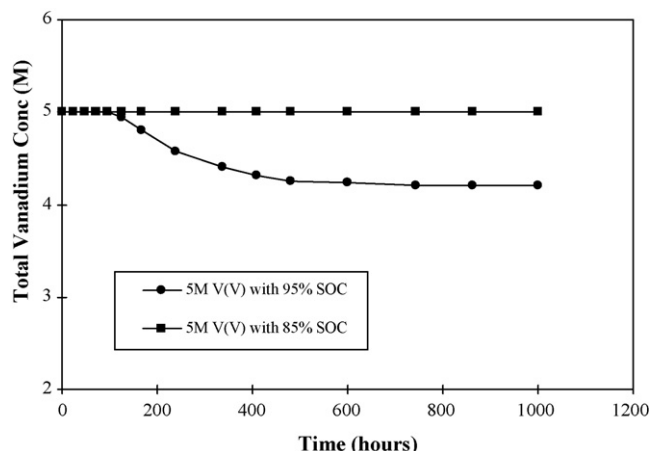
Fig. 14. Effect of SOC on stability of V(V) solution.

VRB need to be further studied over a wider range of temperatures, sulfuric acid concentrations and states-of-charge so as to optimize both the positive and negative half-cell electrolytes and thereby verify the feasibility of increasing the energy density VRB.

4.7. Conductivity behavior of vanadium(V) solutions

The electrical conductance of an aqueous solution can often be measured with high precision and thus affords a useful means of determining concentration. Robinson and Stokes [22] have given a detailed account of the methods in this area, but most of the published work is concerned with dilute systems. In concentrated solutions, Mullin [23] suggests that conductivity measurements are of limited use because of the poor reliability of measurement in near-saturated or supersaturated solutions. The temperature dependence of electrical conductivity usually demands a very high precision of temperature control. Conductivity measurements of supersaturated vanadium(V) solutions were thus made using Metrohm Model 660 conductometer at a constant temperature of $20\,^\circ C$. The conductivity was found to decrease with an increase in vanadium(V) concentration as shown in Fig. 15. This is due to the fact that at constant total sulfate/bisulfate concentration, increasing V(V) concentration will lower the free H_2SO_4 concentration and therefore decrease free H^+ ions in the solution resulting in a lowering of the conductivity.

Further experiments were carried out by measuring the conductivity of 5, 6 and 7 M sulfuric acid and it was found that the conductivity of sulfuric acid alone was also decreasing with increasing concentration in the range of 5–7 M.

4.8. Electrochemical behavior of vanadium electrolyte

The electrochemical behavior of supersaturated vanadium(V) solutions was studied using cyclic voltammetry as this is an effective electro-analytical technique for determining the variations in the positions of the V(V)/V(IV) redox couple peaks at different V(V) concentrations in various total sulfate/bisulfate levels. Information about reversibility of the V(V)/V(IV) system was obtained. The effect of various parameters such as V(V) concentration, total sulfate/bisulfate concentration, and elapsed time on the electrochemical activity of V(V) solutions was investigated.

This subsection deals with the study of the effect of increasing V(V) concentration on the electrochemical behavior of the V(V)/V(IV) redox couple. The CV of 2, 3, 3.5, 4 and 5 M V(V) solution in 6 M total sulfate/bisulfate obtained using a glassy carbon electrode at a scan rate of $0.02\,V\,s^{-1}$ is shown in Fig. 16. To discuss the effect of V(V) concentration, the anodic and cathodic peak currents
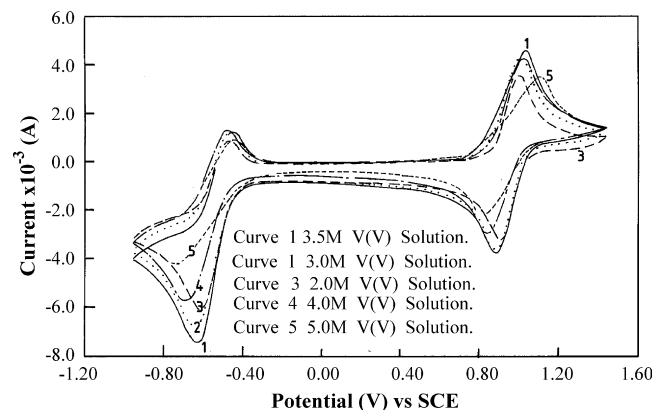

Fig. 16. Cyclic voltammogram of V(V) solution in 6 M total sulfate/bisulfate.

for the V(V)/V(IV) couple obtained from Fig. 16 were plotted as a function of V(V) concentration. It was found that the magnitude of peak current increases linearly as V(V) concentration was increased from 2 to 3.5 M, however, a further increase in V(V) concentration above 3.5 M decreases the peak heights. The decrease in peak currents with increasing V(V) concentration above 3.5 M may be due to the sharp increase in viscosity of the V(V) solution [24]. This sharp increase in viscosity results in a decrease in diffusion coefficient of the vanadium ions, which in turn leads to a decrease in peak currents. Furthermore, changes in the interfacial tension properties of the more concentrated solution may reduce the wettability of the glassy carbon electrode in the solution, thereby reducing the effective surface area and decreasing peak currents [25]. The optimum V(V) concentration to obtain highest peak current with a peak potential separation of about 0.15 V is therefore, about 3–3.5 M and the system may be considered as a quasi-reversible.

5. Conclusions

It was found that the stability of supersaturated V(V) solutions is a function of V(V) concentration, sulfuric acid concentration, temperature, density, viscosity, conductivity and the presence of V(IV) ions. A concentration of about 3.5 M V(V) solution in 5–6 M total sulfate/bisulfate concentration appears to be the limiting concentration to be able to remain in the hydraulic flow region and with further increase in V(V) concentration viscosity increases rapidly. From the overall evaluation of the desupersaturation experiments, density, viscosity and conductivity measurements, and electrochemical behavior of V(V) solutions, it was concluded that a 3-M V(V) solution in 6 M total sulfate/bisulfate may be suitable for the VRB up to a temperature of about $40\,^\circ C$. Increasing the vanadium concentration to 3 M will allow a 50% increase in the energy density compared with the 2-M solutions used to date.

References

[1] W. Kangro, H. Pieper, Zur Frage de Speicherung von Elektrischer Energie in Flussigkeiten Acta 7 (1962) 435.
[2] J. Boeke, Redox flow cell, United States Patent No. 3,540,933 (1970).
[3] L.H. Thaller, Electrically rechargeable redox flow cell, U.S. Patent No. 3,9996,064 (1976).
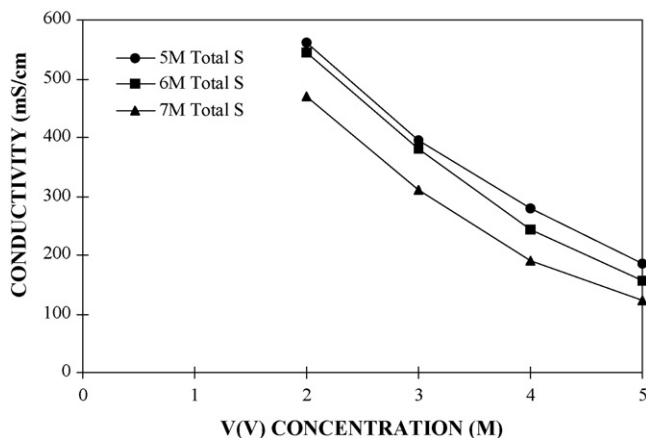[4] N.H. Hagedorn, L.H. Thaller, NASA TM-82686 (1982).

Fig. 15. Conductivity of vanadium(V) solutions in sulfuric acid at $20\,^\circ C$.

[5] M. Skyllas-Kazacos, R.G. Robbins, All vanadium redox battery, U.S. Patent No. 849,094 (1986).

[6] M. Skyllas-Kazacos, M. Rychcik, R.G. Robbins, A.G. Fane, M. Green, J. Electrochem. Soc. 113 (5) (1986) 1057.

[7] M. Skyllas-Kazacos, M. Kazacos, R. McDermott, Patent application PCT appl/AKU 88/000471 (1988).

[8] C. Menictas, D.R. Hong, Y.J. Wilson, M. Kazacos, M. S Skyllas-Kazacos, Electrical Engineering Congress, Sydney, Australia, November 24–30, 1994.

[9] Z. Takehara, in: A.R. Landgrebe, Z. Takehara (Eds.), Proceedings of the Symposium on Batteries and Fuel Cells for Stationary and Electric Vehicle Applications, vol. 93-8, The Electrochemical Society, Inc., NJ, 1994, pp. 12–25.

[10] J. McDowell, Proceedings First International Renewable Energy Storage Conference, IRES-2006, Gelsenkirchen, Germany, October 30–31, 2006.

[11] Khamskii, V. Evgenii, Crystallisation From Solutions, Consultants Bureau, New York, A division of Plenum Publishing Corporation, 1969.

[12] M. Kazacos, M. Cheng, M. Skyllas-Kazacos, J. Appl. Electrochem. 20 (1990) 463–467.

[13] C.F. Baes Jr., R.E. Mesmer, The Hydrolysis of Cations, Wiley, NY, 1976, pp. 197–210 (Chap. 10.2).

[14] J. Nyvlt, Industrial Crystallisation From Solutions, Butterworths, London, 1971.

[15] T. Satoh, K. Hayashi, Bull. Chem. Soc. Jpn. 34 (9) (1961), pp. 1260–1264 (CA56: 13566h).

[16] G.A. Pozarnsky, A.V. McCormick, Chem. Mater. 6 (1994) 380–385.

[17] W. Good, Electrochem. Acta 9 (2) (1964), pp. 759–765 (CA60: 8704c).

[18] C. Madic, G.M. Begun, R.L. Hahn, J.P. Launay, W.E. Thiessen, Inorg. Chem. 23 (1984) 469–476.

[19] R.H. Stokes, R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, 1965, p. 151.

[20] E. Hatschek, The Viscosity of Liquids, Bell and Sons, London, 1928.

[21] W. Good, Electrochem. Acta 11 (7) (1966), pp. 759–765 (CA65: 4717e).

[22] R.A. Robinson, R.H. Stokes (Eds.), Electrolyte Solutions, Butterworth, London, 1970.

[23] J.W. Mullin, Crystallisation, Butterworths, London, 1972.

[24] F. Rahman, Ph.D. Thesis, University of New South Wales, Sydney, 1998.

[25] M. Skyllas-Kazacos, C. Menictas, M. Kazacos, J. Electrochem. Soc. 143 (4) (1996) L86–L88.