JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 463–467

Vanadium redox cell electrolyte optimization studies

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Received 21 March 1989; revised 14 August 1989

The stability of the positive electrolyte of the vanadium redox cell has been studied at various temperatures and at different solution compositions and solution state-of-charge (SOC). It has been 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 sulphuric acid concentration as well as the SOC of the electrolyte. A H_2SO_4 concentration of 3–4 M has been found to be more suitable than 2 M, not only from the point of view of increased stability, but also because of the higher electrolyte conductivity which leads to increased voltage efficiencies during battery cycling.

1. Introduction

The vanadium redox cell presently under development at the University of New South Wales is showing great promise as an efficient new energy storage for a wide range of applications [1–4]. By employing the same metal in both half-cell electrolytes, problems of cross-contamination inherent in other types of redox cells, such as the Fe/Cr system, are eliminated in the vanadium systems. The cell employs the V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes, respectively, with H_2SO_4 as the supporting electrolyte. Energy efficiencies of between 83 and 86% have been obtained in the temperature range 5–45° C using graphite felt electrodes bonded to carbon plastic current collectors [5].

The higher open circuit voltage (1.35 V at 50% state-of-charge (SOC)) compared with the Fe/Cr system (1.1 V at 50% SOC) and the higher reactant concentration (up to 2 M vanadium sulphate) are additional advantages of the system which allow improved energy densities to be achieved.

Early tests on the electrolyte stability showed that the charged electrolytes are stable at temperatures between − 5 and 20° C for periods of up to 12 months. Shorter-term tests conducted at temperatures up to 60° C also revealed no signs of electrolyte decomposition, and with continuous charge–discharge cycling the electrolytes showed excellent stability for several months. More recent tests on the fully charged positive electrolyte (2 M V(V) in 2–3 M H_2SO_4), however, have shown that problems can arise if the positive electrolyte is stored for extended periods at elevated temperatures in the fully charged state. Under such conditions crystals of a V(V) compound slowly precipitate from solution, the rate and extent of which being dependent on the temperature and H_2SO_4 concentration. The solubility of V_2O_5 in a number of strong acids has been reported in [6] in HCl, H_2SO_4 and $HClO_4$, in [7] in H_2SO_4 and in [8] in HCl, H_2SO_4 and $HClO_4$. Discrepancies appear among those authors on the equilibrium solubility under similar conditions of temperature and acid concentration. The problems arose from two factors: the allowance of insufficient times to approach a true equilibrium with the solid phase and the possible existence of impurities of lower vanadium oxides which are more soluble than V_2O_5. A more detailed study of the V(V) precipitation phenomenon was therefore undertaken to determine the optimum electrolyte composition for the vanadium redox battery.

2. Experimental details

Solutions of various vanadium sulphate and H_2SO_4 concentrations were prepared by electrolytic dissolution of the appropriate weight of V_2O_5 in the H_2SO_4 supporting electrolyte [9]. The resultant solution was then placed in the vanadium redox cell and charged at constant current until a bright yellow solution of V(V) and a bright violet solution of V(II) were produced in the positive and negative half-cells, respectively. The required volumes of each solution were removed from the cell and the remaining electrolytes were discharged in the cell to produce a blue solution of V(IV) and a green solution of V(III) in the positive and negative half-cells, respectively.

The V(V) and V(IV) solutions thus obtained were then mixed in various ratios to simulate the positive half-cell electrolyte at various states-of-charge. These solutions were placed in sealed glass jars in water baths set at 40 and 50° C for 18 days. Each solution was examined visually every day and the time taken for a slight precipitate of V_2O_5 to appear was recorded. At the end of the 18-day test period the solutions were filtered and the 'equilibrium' vanadium ion concentration determined by ICP (inductively coupled plasma) analysis.

The electrolyte stability was also tested under temperature cycling conditions to simulate the tempera-

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0021-891X/90 $03.00 + .12

Table 1. Stability of V(V) in H_2SO_4 at 40° C*

Concentration of V(V)	*Concentration of H_2SO_4*			
	3.6 M	3.0 M	2.0 M	1.0 M
0.5 M	No ppt	–	> 30	–
1.0 M	No ppt	> 30	> 30	1
1.5 M	No ppt	–	4	1
1.8 M	12	–	–	–
1.9 M		7	–	–
2.0 M	–	2	1	1

*Stability refers to time taken (in days) for a slight precipitate to appear in solution.

ture fluctuations that are more likely to be experienced in the field. This was achieved by using an electronic timer set to turn on at 08.00 h each morning, heating the water bath to 40° C. The heater was switched off at 1600 h every afternoon, allowing the solutions to cool to room temperature (20–25° C) overnight.

Conductivity measurements were also carried out on the electrolytes for various vanadium and sulphuric acid concentrations. A Radiometer conductivity meter was employed at a temperature of 22° C.

3. Results and discussion

Solutions (10 mls) of various concentrations of V(V) and H_2SO_4 were initially allowed to stand for 35 days at a constant temperature of 40° C and the time taken for a slight precipitate to appear was recorded. The results are summarized in Table 1.

Further tests were performed on the V(V) solutions using simulated daytime to night-time temperature fluctuations as described in Section 2. These results are presented in Table 2 and show that under these less severe conditions a longer time is required before a slight precipitate appears in the solution. As previously, the solutions were observed for 35 days.

The precipitation of V_2O_5 from the charged positive electrolyte of the vanadium redox cell could thus be a problem in certain applications where high temperatures are experienced and where the system is likely to remain fully charged for extended periods. As mentioned above, no problem arises if the electrolytes undergo continuous charge–discharge cycling at high rates since the V_2O_5 does not have sufficient time to nucleate before being converted to V(IV) on discharge.

Table 2. Stability of V(V) solutions under conditions of temperature cycling between 20 and 40° C*

Concentration of V(V)	*Concentration of H_2SO_4*	
	3 M	2 M
0.5 M	No ppt	No ppt
1.0 M	No ppt	No ppt
1.5 M	No ppt	21
2.0 M	4	3

*Stability refers to time taken (in days) for a slight precipitate to appear in solution.

From the results of Tables 1 and 2, however, it seems clear that for 2 M V(V) a 3 M H_2SO_4 supporting electrolyte is more suitable than the previously used 2 M H_2SO_4 solutions. The higher H_2SO_4 concentration is also beneficial for redox cell applications, because of the higher conductivity of both positive and negative electrolytes. Conductivity values of 279 and 370 mS cm^{-1} were obtained at 20° C for the fully charged positive electrolytes containing 2 M vanadium sulphate in 2 M H_2SO_4 and 3 M H_2SO_4, respectively. Similarly, for the fully charged negative electrolyte the conductivity increased from 142 to 300 mS cm^{-1} at 20° C in the 2 M and 3 M H_2SO_4 electrolytes, respectively. The higher H_2SO_4 concentration thus gives rise to improved voltage efficiencies in the vanadium redox cell system [5]. This solution was therefore tested further to determine the maximum 'safe' SOC to be employed at various temperatures. Solutions of various ratios of V(IV)/V(V), corresponding to different SOCs, were placed in water baths set at 30, 40 and 50° C. The solutions were examined visually daily, and the time taken for a slight precipitate to appear was recorded. After 18 days of exposure the filtered solutions were analysed by ICP to determine the equilibrium concentration of vanadium in the 3 M H_2SO_4 supporting electrolyte.

The solution employed in the temperature stability tests was 2 M V in 3 M H_2SO_4 and was prepared by electrolytic dissolution of V_2O_5 powder [9]. Table 3 summarizes the results obtained with regard to the time taken for precipitate to appear in each of the solutions tested.

These results were obtained after continuous exposure to the temperature shown and again can be considered as an extreme condition. Under normal circumstances the solution temperature would be affected by environmental temperature fluctuations as shown above. Thus, the solution stability should be extended significantly under such conditions.

Even at the constant temperature of 40° C, however, a 90% charged solution showed no signs of precipitation even after 18 days. At 50° C constant temperature no precipitate appeared after 18 days in the 60% SOC solution, whereas the 80% SOC solution shows signs of precipitation after 9 days.

Table 4 shows values of total dissolved vanadium concentration obtained by ICP analysis of each of the solutions after 18 days exposed to the constant temperature. From these values a plot of 'equilibrium' vanadium concentration against temperature was prepared and is shown in Fig. 1. A fully charged 2 M V + 3 M H_2SO_4 solution is stable at 25° C for several months, and this condition is incorporated with the ICP results to obtain the 'thermal stability diagram' of Fig. 1. This diagram can thus be employed to design a vanadium redox cell for a range of applications and operating conditions.

For example, if the environmental temperature is not expected to exceed 30° C, a 2 M solution could be

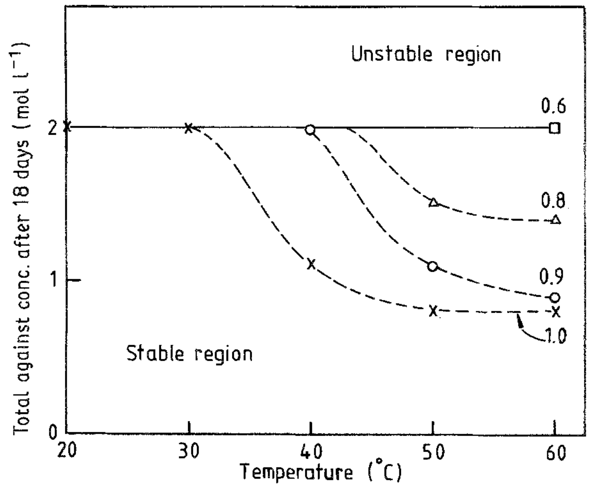

Fig. 1. Stability diagram of V(IV)/(V) sulphate system in 3 M H_2SO_4. Initial total vanadium concentration 2 M. The numbers on the curves represent the solution 'state-of-charge'.

stored in a fully charged state for extended periods. However, if the temperature periodically reaches 40° C, the system should be maintained between 90 and 80% SOC, depending on the duration of the exposure to the elevated temperature or the particular application.

The equilibrium V(V) concentration at each temperature (after 18 days) was also calculated and is shown in Table 4. These results show that the increased stability of the lower SOC solutions is not simply a function of the V(V) concentration, but that interactions between the V(IV) and V(V) ions are involved.

The chemistry of V(V) is very complex, with 12 species being known to exist in aqueous solutions of moderate concentrations. However, in very acidic solutions (pH < 1), as employed in this study, the VO_2^+ species predominates as illustrated in Figs 10.6 and 10.7 of [10].

The solubility of V_2O_5 has been given as [10]

$$\tfrac{1}{2}V_2O_{5(c)} + H^+ \rightleftharpoons VO_2^+ + \tfrac{1}{2}H_2O \quad (1)$$

$$\log K_s = -0.66 \pm 0.06 \quad (2)$$

In 3 M H_2SO_4, if we assume only the first dissociation, and using the above value of K_s, an equilibrium VO_2^+ concentration of 0.539 M would be therefore expected.

In acid solutions in the presence of sulphate, however, Ivakin [11] reported that VO_2^+ ion forms complexes with the sulphate ion by the following reactions:

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+ \quad (3)$$

$$VO_2^+ + SO_4^= \rightleftharpoons VO_2SO_4^- \quad (4)$$

$$VO_2^+ + VO_2SO_4^- \rightleftharpoons (VO_2)_2SO_4 \quad (5)$$

The complex $(VO_2)_2SO_4$, however, is found not to be formed to an appreciable extent. Equilibrium constants of 9.32 ± 0.43 and 0.73 ± 0.14 were determined for Reactions 3 and 4, respectively. The higher equilibrium constant for Reaction 3 indicates that this reaction would predominate, the formation of the complex $VO_2SO_4^-$, thus shifting Reaction 1 to the right and increasing the solubility of V_2O_5. Higher V_2O_5 solubilities than predicted from Equation 2 are thus possible in acidic sulphate media due to the ion-pairing reactions of VO_2^+. Assuming that Equilibrium 3 predominates therefore, for a concentration of H_2SO_4 of 3 M, the total equilibrium concentration of VO_2^+ was calculated as 2.91 M, whereas for 4 M H_2SO_4 the total equilibrium VO_2^+ concentration was 3.88 M. These values are much higher than those observed experimentally, suggesting that the equilibria may be more complex than is assumed above.

Concentrations of up to 2 M VO_2^+, prepared by the oxidation of VO_2^+ solutions, are stable for several months at room temperature in 3 M and 4 M H_2SO_4. However, the fact that V_2O_5 precipitates from these solutions at higher temperatures suggests that the backward rate constant for Reaction 1 must be very small. Increasing the temperature, as expected, increases the rate of precipitation of V(V), so that the 'true' equilibrium VO_2^+ concentration is reached more rapidly.

Reaction 1 also illustrates the importance of the H^+ concentration in the solubility of V_2O_5. As confirmed in the present study, the higher the H^+ concentration is, the higher the V_2O_5 solubility. However, if the H_2SO_4 concentration is increased too much (> 5 M), the solubility appears to decrease again.

Warm sulphuric acid has also been reported to cause reduction of V(V) with evolution of oxygen [12]. The evolution of gas has not been observed at the temperatures employed in the present study, and from

Table 3. Stability of positive vanadium electrolyte at various states-of-charge

Solution	*SOC (%)*	*Precipitation time (days)*		
		30° C	40° C	50° C
100% V(V) in 3 M H_2SO_4	100	No ppt after 18 days	7	2
90% V(V) + 10% V(IV)	90	No ppt after 18 days	No ppt after 18 days	3
80% V(IV) V(V) + 20% V(IV)	80	No ppt after 18 days	No ppt after 18 days	9
60% V(V) + 40% V(IV)	60	No ppt after 18 days	No ppt after 18 days	No ppt after 18 days

Table 4. Vanadium concentration as a function of temperature and state-of-charge (after 18 days)

SOC (%)	*Temperature (° C)*							
	30		40		50		60	
	Total [V]	*V(V) conc.*	*Total [V]*	*V(V) conc.*	*Total [V]*	*V(V) conc.*	*Total [V]*	*V(V) conc.*
100	2.0	2.0	1.1	1.1	0.8	0.8	0.8	0.8
90	2.0	1.8	2.0	1.8	1.1	1.0	0.9	0.8
80	2.0	1.6	2.0	1.6	1.5	1.2	1.4	1.1
60	2.0	1.2	2.0	1.2	2.0	1.2	2.0	1.2

the colours of the precipitate and the solution (orange-brown), this reaction does not appear to be very significant.

The results presented in Table 4 also suggest that the total V(V) equilibrium concentration in H_2SO_4 is influenced by the presence of V(IV) in solution. This can be explained by the existence in aqueous sulphate solutions of complex V(IV) ions containing both SO_4^{2-} and HSO_4^- ions [13, 14]. The presence of these complexes in the positive vanadium electrolyte will thus lead to several equilibria in addition to those given in Equations 1–5, making the V(V) solubility even more complex.

The nature of the thermal precipitate of V(V) was also investigated using X-ray diffraction spectroscopy and it was found not to be V_2O_5, but some complex vanadium compound probably involving sulphate species. This compound has not yet been identified, but further analyses are being undertaken in an attempt to establish its composition.

A number of experiments were also conducted on the precipitated solutions to determine if the V(V) precipitate could be readily redissolved. The original 10 ml V(V)/V(IV) solutions containing 2.0 M total V in 3 M H_2SO_5 which had precipitated at various temperatures within 18 days were allowed to cool to room temperature and 2 M V(II) solution was added slowly until the precipitate had dissolved totally. The volume of V(II) solution required and the solution temperature after mixing were recorded.

In each case the precipitate was found to dissolve completely on addition of between 4 and 6 ml V(II) solution, and the final temperature of the mixture varied from 40 to 45° C. These results thus show that if precipitation of V(V) does not occur, then the precipitate can quite readily be redissolved by simply mixing the negative and positive electrolytes of the battery together to obtain a 50 : 50 mixture of V(III) + V(IV) on each side of the battery. This solution can then be recharged with 1.5 equiv mol^{-1} of vanadium to obtain the fully charged battery electrolytes, ready for further cycling. Actual battery tests have also shown that by simply discharging the electrolytes in the cell, any V(V) precipitate in the positive electrolyte tank will readily redissolve. Precipitation of V(V) is not therefore an irreversible problem if it were to occur in practice. In areas and applications where high temperatures and irregular cycling are likely to occur, however, a microprocessor control system could be employed to ensure that precipitation does not occur.

The actual solution temperature will obviously be affected by the surrounding air temperature, but will also be a function of the system design and operating conditions. A mathematical model which could be used to predict the solution temperature for a particular location and operation would thus be invaluable in system design. Thermal modelling of the vanadium redox cell system has been undertaken and is presented in a separate paper [15].

4. Conclusions

The results of the present study have shown that the positive eletrolyte of the vanadium redox cell could be vulnerable to precipitation of V(V) if the fully charged solutions are maintained at elevated temperatures for extended periods without cycling. Concentrations of 2 M V(V) in 3–4 M H_2SO_4 could be safely employed in applications where the battery undergoes continuous cycling and if high temperatures are not experienced over long periods. In applications where high temperatures and/or infrequent cycling would be expected, however, a more suitable electrolyte composition would be 1.5 M V in 3–4 M H_2SO_4. Alternatively, if a higher vanadium concentration were employed, the SOC should be limited to 60–80%, depending on the electrolyte temperature. If any precipitation of V(V) does occur, however, the precipitate can be readily redissolved either by mixing with the negative electrolyte or by simply discharging in the cell. A simple mathematical model has been developed to predict the electrolyte temperature that is likely to be experienced under various climatic conditions and for different system designs. This is presented separately [15] and, together with the solubility data presented here, it would be possible to design a battery system which would be suitable for the particular application.

Acknowledgements

This project was funded by grants from the Australian National Energy Research Development and Demonstration Council and Agnew Clough Ltd.

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