

Evaluation of an NH_4VO_3 -derived electrolyte for the vanadium-redox flow battery

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Abstract

The electrolyte used in the vanadium-redox flow battery provides an energy storage system that produces no waste products. Initially, the electrolyte was derived from VOSO_4 and significant cost reductions were obtained by using an electrolyte derived from V_2O_5 . The use of NH_4VO_3 as the starting material for electrolyte production offers further possible cost reductions. A coulombic efficiency of 98%, a voltage efficiency of 94%, and an overall energy efficiency of 91.8% are obtained at a constant charging and discharging current density of 14.5 mA cm^{-2} for a test vanadium-redox flow cell that employs an electrolyte derived from NH_4VO_3 . The electrolyte has been further treated to examine the possibility of ammonium removal. Cell-resistance measurements and cyclic voltammetry studies are reported for the treated and untreated NH_4VO_3 electrolyte.

Introduction

The vanadium-redox flow battery, which is being developed at the University of New South Wales [1], is one of the most efficient of energy storage systems. Energy efficiencies of up to 90% have been achieved [2] in 1–3 kW prototype stacks. The applications and advantages of this battery have been reported previously [2, 3]. At present, further development and improvements are continuing with a view to early commercialization of the system.

Currently, the electrolyte for the vanadium-redox battery is prepared by the electrolytic reduction of vanadium pentoxide (V_2O_5) in sulfuric acid to produce a vanadium sulfate solution. This is used in both half-cells. The use of V_2O_5 for the preparation of the electrolyte has allowed considerable cost reduction to be achieved compared with VOSO_4 that was used previously [4, 5]. Estimates have shown [2] that the vanadium-redox battery is cost-competitive with other types of storage system.

In the preparation of V_2O_5 , ammonium metavanadate is first produced and then ignited according to:



The direct use of NH_4VO_3 for the production of vanadium electrolyte would further lower the cost of the vanadium battery since it could lead to the elimination of a number of steps in the preparation of V_2O_5 powder.

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Like V_2O_5 , NH_4VO_3 is sparingly soluble in water and its solubility in acid is also very low. It is thus impossible to use it directly as a solute in the preparation of electrolyte for the vanadium-redox cell, where high concentrations of vanadium are required. This leads to the possibility of using electrolytic dissolution of NH_4VO_3 for the production of vanadium solutions of any oxidation state. Accordingly, the electrolysis of NH_4VO_3 in H_2SO_4 -supporting electrolyte, the treatment of the NH_4VO_3 electrolysis solution to remove NH_4^+ ions and the electrochemical characteristics of the electrolyte produced are investigated in the present study.

Experimental

Sufficient NH_4VO_3 powder to produce either 1.5 or 2.5 M NH_4VO_3 in 5 M H_2SO_4 was placed into the negative compartment of an electrolytic cell. A constant current density of 20 mA cm^{-2} was applied with the powder suspended by a flow of nitrogen. The procedure for the electrolysis of NH_4VO_3 was very similar to that used for V_2O_5 powder electrolysis [5]. The electrolysis was continued until sufficient charge had been provided to convert the NH_4VO_3 to a 50:50 mixture of V(III) and V(IV). The vanadium electrolytes were prepared using the membrane cell shown in Fig. 1.

The test cell used to conduct the evaluation of the treated and untreated electrolytes prepared from NH_4VO_3 was a single flow cell with an electrode area of 138 cm^2 . The electrodes were made of graphite felt that was heat-bonded to a conducting plastic substrate with a copper foil backing [6]. Details of the cell design are given in Table 1.

The electrolyte produced by the electrolytic dissolution of NH_4VO_3 was also treated to remove NH_4^+ ions so that higher vanadium ion concentrations could be achieved. The treatment process involved the use of $Ca(OH)_2$ powder to adjust the pH so that NH_3 could be boiled off. The powder was dissolved in distilled water to produce a solution of $Ca(OH)_2$. This solution was then added to the NH_4VO_3 electrolysis solution to adjust the pH to over 7. After the solution became basic, it was heated to boiling and stirred until the colour of wet pH paper above the solution did not change. This indicated that all of the NH_3 had been evolved. The precipitated $CaSO_4$

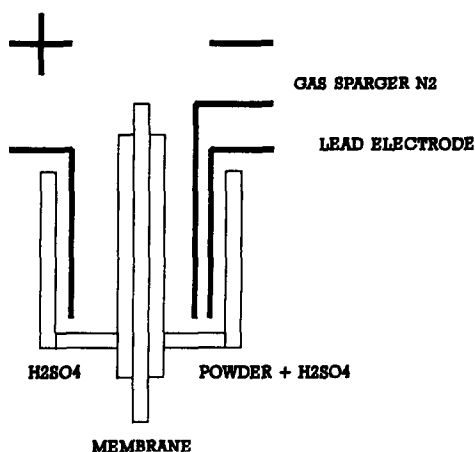


Fig. 1. Membrane cell used for preparation of vanadium electrolytes by electrolytic dissolution of NH_4VO_3 powder.

TABLE 1
Specifications of test cell

Electrode area	138 cm ²
Membrane	Selemion CMV (Asahi Glass, Japan)
Half-cell cavity thickness	4.7 mm
Current collectors	copper sheet (thickness 1 mm)
Electrode material	
Felt	6 mm (nominal)
Conducting plastic	graphite-impregnated polyethylene sheet (0.3 mm)
Electrolyte volume	150 ml (per half-cell)

was then vacuum filtered from the solution and finally the filtered basic solution was adjusted back to its original acidity and volume and analysed by inductively-coupled plasma (ICP) to determine the concentration of vanadium and calcium.

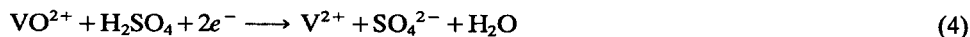
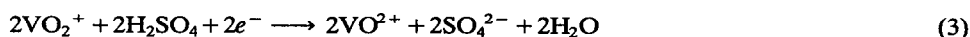
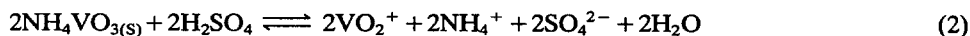
Cyclic voltammetry was used to evaluate any effect of residual NH_4^+ and Ca^{2+} ions on the reversibility of the vanadium-redox couples. In the cyclic voltammetry experiments, 100 cm³ of solution was used. Graphite or glassy carbon was employed as the working electrode and graphite as the counter. A mercury/mercurous sulfate reference electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4$) was used in conjunction with the graphite working electrode and a saturated calomel electrode (SCE) with the glassy-carbon version. Before use, the graphite working electrode (area 31 mm²) was first polished with P1200 silicon-carbide paper, and the glassy-carbon electrode (area 7 mm²) with the same paper followed by 2/0 emery paper. Ammonium ions and calcium ions were introduced into the solution by the addition of ammonium sulfate or calcium hydroxide, respectively.

During cyclic voltammetry, the electrode was continually cycled until steady state was reached at room temperature, unless stated otherwise. The peak potential separation for the redox couples was used to compare the reversibility in the different electrolytes. X-ray diffraction (XRD) and ICP analysis were performed using a Rigaku, Model 2351B1 X-ray diffractometer and a Labtest, Model Plasmalab ICP spectrometer/monochromator, respectively.

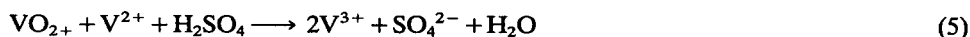
Results and discussion

NH₄VO₃ electrolytic dissolution

During electrolysis of the NH_4VO_3 powder, the following reactions occur:

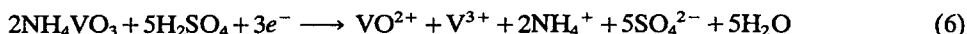


followed by:



The reduction of VO^{2+} to V^{3+} has been found to be kinetically slow and does not proceed [7]. VO^{2+} is thus reduced directly to V^{2+} at the electrode surface and this reacts with the VO^{2+} in solution to produce V^{3+} according to reaction (5).

The overall reaction for the preparation of 1 M V(III)+1 M V(IV) (i.e., $V^{3.5+}$) solution which is the mixed electrolyte used in both half-cells of the vanadium-redox battery can thus be described as follows:



At the beginning of the electrolysis, it was observed that the white NH_4VO_3 powder tended to agglomerate as it contacted the H_2SO_4 solution and, thereby, formed large red lumps. When the lumps were broken down to finer particles, the NH_4VO_3 could be gradually dissolved and reduced. After 40 h of electrolysis, all the NH_4VO_3 powder dissolved to produce a blue-green solution that consisted of 1 M V(III)+1 M V(IV) in 2.5 M H_2SO_4 +2 M NH_4^+ . Before employing this solution in the vanadium-redox cell, cyclic voltammetric studies were performed to compare the electrochemical reversibility of the vanadium redox couples in this electrolyte with that observed in the V_2O_5 -derived electrolyte. In Fig. 2, a typical cyclic voltammogram obtained at a graphite working electrode in the NH_4VO_3 electrolysis solution, and consisting of 0.1 M V(IV)+0.1 M NH_4^+ in 1 M H_2SO_4 , is given in curve (a), while that obtained in the solution prepared from the V_2O_5 electrolysis solution, and consisting of 0.1 M V(IV) in 1 M H_2SO_4 , is represented by curve (b). A comparison of the peak current and peak potential separation values shows that the electrochemical activity of the vanadium-redox couples is the same in the two electrolytes.

Vanadium-redox cell performance using NH_4VO_3 electrolyte

Equal volumes of NH_4VO_3 -derived solution were placed in each side of a vanadium-redox cell and fully charged to produce V(II) and V(V) on the negative and positive sides, respectively. After the initial charging steps, the charge/discharge reactions can be described as:

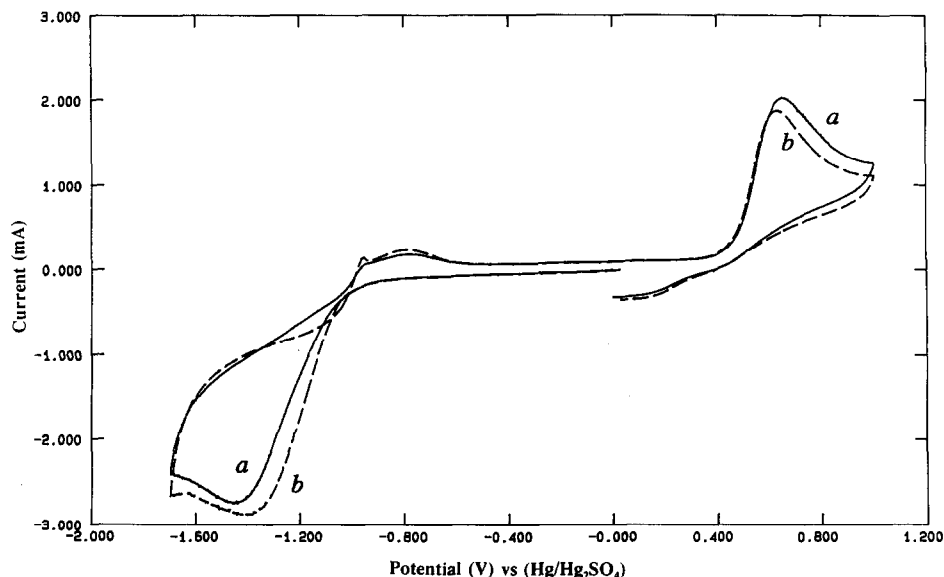


Fig. 2. Typical cyclic voltammograms obtained in: (a) 0.1 M V(IV)+0.1 M NH_4^+ in 1.0 M H_2SO_4 solution prepared from electrolysis of NH_4VO_3 , and (b) 0.1 M V(IV) in 1.0 M H_2SO_4 prepared from electrolysis of V_2O_5 . Voltammograms are for the 1st cycle at a graphite working electrode, scan rate of 20 mV s⁻¹.

positive side:



negative side:



During the subsequent discharge of the vanadium-redox cell, however, a precipitate was observed to form in both half-cells. The precipitate in each half-cell was filtered to obtain the saturated solutions. The latter were analysed using ICP and the equilibrium V(II) concentration for the negative half-cell solution and the equilibrium V(V) concentration for the positive half-cell solution were both found to be 1.75 M.

A 1.5 M vanadium solution was prepared from NH_4VO_3 in 3 M H_2SO_4 (referred to the V(IV) state-of-charge (SOC)). The solution was charged and discharged in the redox-flow test cell. Figure 3 shows a typical charge/discharge voltage profile for a constant charging and discharging current density of 14.5 mA cm^{-2} between the upper and lower voltage limits of 1.8 and 1.0 V, respectively. From the curves, the coulombic efficiency was calculated as 98%, voltage efficiency as 94%, and the overall energy efficiency as 91.8%. These results are similar, if not slightly higher, than those previously observed [3, 6] for V_2O_5 -derived electrolytes under otherwise identical conditions. The values of efficiency, calculated over a range of constant charge/discharge current densities, are shown in Table 2 and plotted in Fig. 4. The results show that the coulombic efficiency remains relatively constant but that the voltage efficiency, as expected, decreases with increasing current density due to increased IR losses. The maximum efficiency of 91.8% is thus observed at 14.5 mA cm^{-2} .

The cell was also charged at a constant current density of 36.2 mA cm^{-2} and discharged at various rates that ranged from 14.5 to 72.5 mA cm^{-2} . The discharge curves are presented in Fig. 5 and the calculated values of energy efficiency are listed

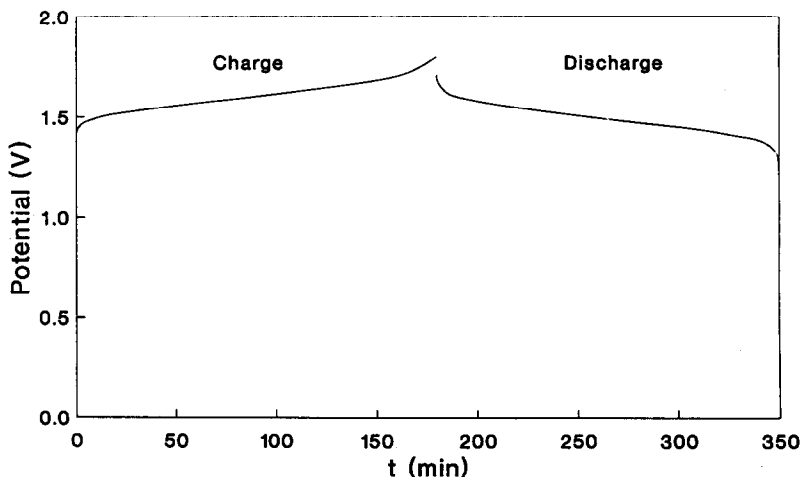


Fig. 3. Typical charge/discharge voltage profile for vanadium-redox cell employing NH_4VO_3 -derived electrolyte.

TABLE 2

Efficiencies for vanadium electrolyte prepared from electrolytic reduction of NH_4VO_3 in H_2SO_4

Current density (mA cm^{-2})	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
14.5	97.5	94.2	91.8
21.7	98.7	91.4	90.2
29.0	100.0	86.1	86.1
36.2	98.5	84.2	83.0

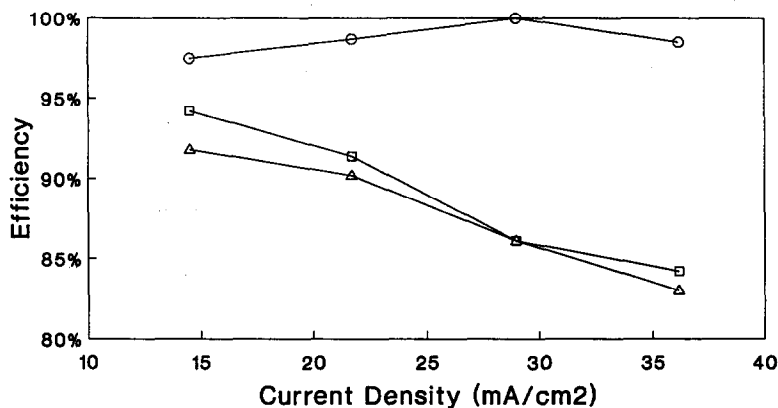


Fig. 4. Efficiencies for various constant charging/discharging current densities: (—○—) current; (—□—) potential, and (—△—) energy.

in Table 3, together with the capacity at each discharge rate. The results show that the capacity of the cell remains relatively constant even at discharge rates as high as 72.5 mA cm^{-2} .

The internal resistance of the cell was determined by measuring the voltage at various current densities for both charging and discharging at a constant SOC.

From the slope of the plot of the potential versus current density at an SOC of 50%, illustrated in Fig. 6, the cell resistance was calculated to be $3.6 \Omega \text{ cm}^2$.

The above results show that, apart from reducing the solubility of the V(II) and V(V) ions to approximately 1.7 M, the use of NH_4VO_3 instead of V_2O_5 in the preparation of the electrolyte has no adverse effects on the performance of the vanadium-redox cell. If higher vanadium concentrations are required, however, it would be necessary to treat the solution to remove the NH_4^+ ions.

Treatment of NH_4VO_3 electrolyte to remove NH_4^+ ions

According to the chemical properties of ammonia, it is known that the evolution of NH_3 from solution by heating can only occur under basic conditions. The acidic NH_4VO_3 electrolysis solution must therefore be adjusted to a basic solution, and it must be further ensured that no additional undesirable cations are introduced that would affect the vanadium solubility in the final solution. For these reasons, calcium hydroxide, $\text{Ca}(\text{OH})_2$, was chosen to adjust the solution pH.

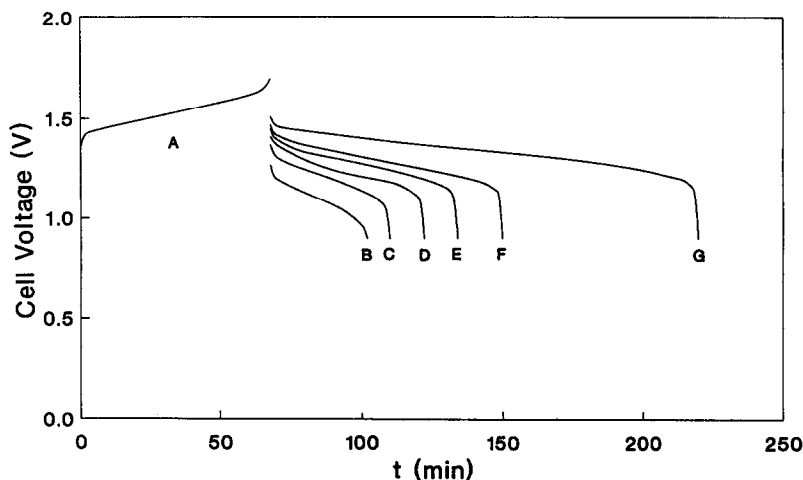


Fig. 5. Voltage profile for: (A) a constant charging current density of 36.2 mA cm^{-2} ; various discharging current densities of (B) 72.5 mA cm^{-2} , (C) 58.0 mA cm^{-2} , (D) 43.5 mA cm^{-2} , (E) 36.2 mA cm^{-2} , (F) 29.0 mA cm^{-2} , and (G) 14.5 mA cm^{-2} .

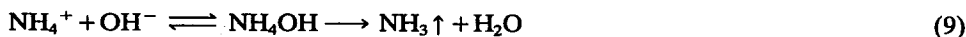
TABLE 3

Discharge capacities for various discharge current densities

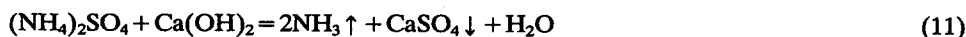
Charge current density 36 mA cm^{-2}				
Discharge current density (mA cm^{-2})	Coulombic efficiency (%)	Potential efficiency (%)	Energy efficiency (%)	Capacity ^a (Ah)
14.5	96.4	89.3	86.1	5.1
29.0	97.7	87.2	85.2	5.5
36.2	97.8	84.2	82.4	5.6
43.5	97.9	83.2	81.4	5.6
58.0	99.0	80.5	79.7	5.5
72.5	100	74.1	74.1	5.7

^aTheoretical capacity = 6 Ah.

During treatment, the following reactions will occur:



The overall reaction is described as:



$\text{Ca}(\text{OH})_2$ is thus used to make the vanadium solution basic so that the NH_3 can be boiled off, while precipitation of CaSO_4 ensures that the Ca^{2+} ions do not remain and contaminate the final solution. The procedure of this treatment was described earlier. The results of ICP analysis showed that, after treatment, a concentration of

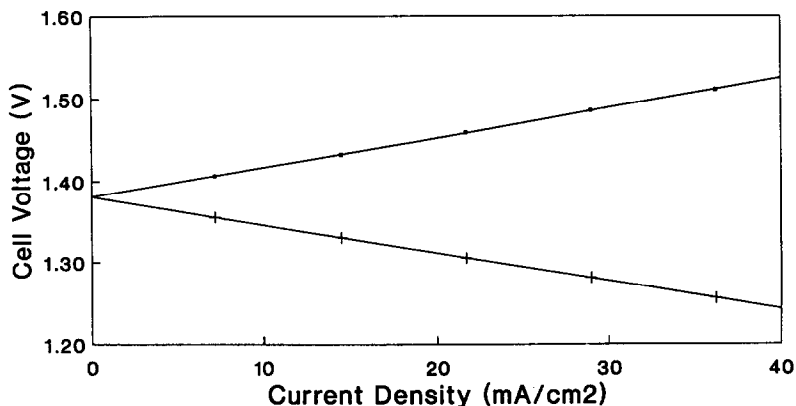


Fig. 6. Polarization curves for vanadium redox cell at 50% state-of-charge: (●) charging, and (+) discharging.

up to 2.48 M vanadium ion could be achieved and that only 0.9% of the vanadium was lost during treatment. For ICP analysis, it was also found that the quantity of Ca^{2+} that remained in the final treated solution was only about 7.51×10^{-4} M.

In order to confirm the composition of the precipitate obtained during treatment, the precipitate was washed with distilled water, dried in an oven at ~ 100 °C and finally analysed by XRD spectroscopy. The result is shown in Fig. 7(a). From comparison with the XRD pattern for pure CaSO_4 , shown in Fig. 7(b), it is clear that the precipitate is indeed CaSO_4 .

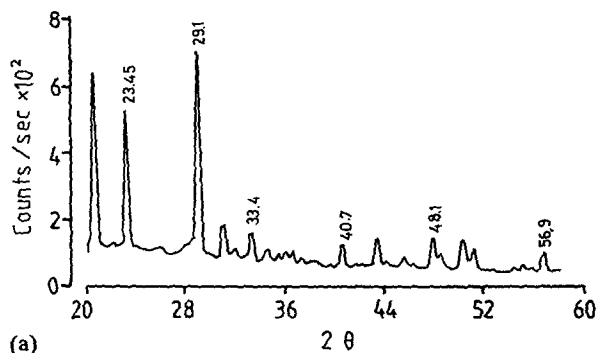
Cyclic voltammetry

Before employing the treated NH_4VO_3 -derived electrolyte in the vanadium-redox cell, the effects of any trace NH_4^+ ions and Ca^{2+} ions (from the treatment) on the reversibility of the V(II)/V(III) and V(IV)/V(V) reactions was first investigated using cyclic voltammetry. This was to ensure that these ions do not affect adversely the vanadium reactions.

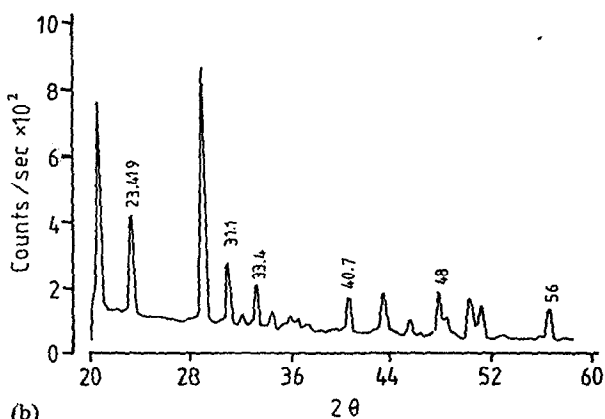
Various amounts of CaSO_4 were added to 2 M $\text{V}^{3.5+}$ in 2.5 M H_2SO_4 solution produced by V_2O_5 powder electrolysis. These mixed solutions were then studied by cyclic voltammetry. The peak potential separations, ΔE_p , for both vanadium-redox couples are seen to increase slightly with increased addition of Ca^{2+} , as shown in Table 4.

By contrast, when different amounts of $(\text{NH}_4)_2\text{SO}_4$ were added to 2 M $\text{V}^{3.5+}$ in 2.5 M H_2SO_4 solution, the resulting cyclic voltammograms displayed no adverse effect on the peak potential separation values, as seen in Table 5. Thus, it can be concluded that small additions of ammonium ions (NH_4^+) should not produce any adverse effects on the reversibility of the vanadium-redox reactions.

Similar cyclic voltammograms were obtained for the treated NH_4VO_3 electrolysis solution and the V_2O_5 electrolysis solution. Values of ΔE_p for V(V)/V(IV) and V(III)/V(II) redox couples in this electrolyte are listed in Table 6. Slightly lower values of ΔE_p are observed for each of the vanadium-redox couples in the treated NH_4VO_3 electrolysis solution compared with those obtained in the V_2O_5 -derived electrolyte. This variation may, however, be within experimental error.



(a)



(b)

Fig. 7. XRD of (a) precipitate produced by addition of 4 M $\text{Ca}(\text{OH})_2$ to NH_4VO_3 electrolysis solution, and (b) XRD pattern for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

TABLE 4

Variation of peak potential separations of vanadium-redox couples in V_2O_5 electrolysis solution with addition of CaSO_4 at glassy carbon

$\text{Ca}^{2+}/\text{VO}^{2+}$ (mol%)	Peak potential separation (V)	
	V(II)/V(III)	V(IV)/V(V)
0.00	0.70	0.57
0.05	0.73	0.58
0.10	0.75	0.60
0.40	0.82	0.67
1.00	0.86	0.72

Vanadium-redox cell performance using treated NH_4VO_3 electrolyte

An evaluation was made of the treated NH_4VO_3 electrolysis solution as the electrolyte in the vanadium-redox cell. Solutions corresponding to 50% SOC positive and negative electrolytes were prepared from this solution and placed in the corresponding half-cells of the redox cell. The cell was charged at a constant current density in the

TABLE 5

Variation of peak potential separations of vanadium-redox couples in V_2O_5 electrolysis solution with addition of $(NH_4)_2SO_4$ at glassy carbon

NH_4^+/VO^{2+} (mol%)	Peak potential separation (V)	
	V(II)/V(III)	V(IV)/V(V)
0.00	0.70	0.58
0.07	0.69	0.57
0.10	0.65	0.52
0.14	0.60	0.50
0.40	0.63	0.52
0.70	0.65	0.53
1.37	0.69	0.55

TABLE 6

Peak separations of vanadium redox couples in V_2O_5 and treated NH_4VO_3 electrolysis solution from cyclic voltammograms at glassy carbon

Electrolyte	Peak potential separation (V)	
	V(II)/V(III)	V(IV)/V(V)
V_2O_5	0.70	0.47
Treated NH_4VO_3	0.50	0.35

range 25 to 75 mA cm^{-2} for 1 min; after a few seconds, discharge of the cell was performed under the same conditions.

During the test, the resultant voltage response was recorded and the results were plotted as a function of the applied current to obtain the polarization curves shown in Fig. 8. The latter also gives the polarization curve for a cell containing the V_2O_5 -derived electrolysis solution. The cell-resistance values calculated from these plots are summarized in Table 7. Within experimental error, the cell-resistance values obtained with treated NH_4VO_3 electrolysis solution are similar to those obtained with the V_2O_5 electrolysis solution for both charging and discharging of the vanadium redox cell.

The treated NH_4VO_3 electrolysis solution was also subjected to further charge/discharge tests and the results are presented in Table 8. It can be seen that the coulombic efficiency is the same for both electrolytes, but that the cell-voltage efficiency with a treated NH_4VO_3 electrolysis solution is slightly higher than that with V_2O_5 electrolysis solution; this is consistent with the lower ΔE_p values observed with cyclic voltammetry.

Conclusions

The vanadium electrolyte prepared from NH_4VO_3 in H_2SO_4 has been shown to be suitable for use in the vanadium-redox battery. In an laboratory-test cell, an overall energy efficiency of 92% is obtained with this solution. The presence of excess NH_4^+

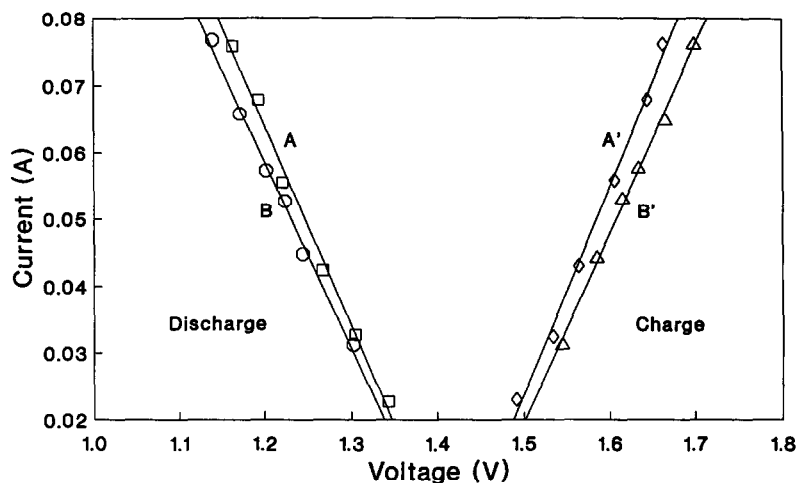


Fig. 8. Polarization curves for treated NH_4VO_3 (curves A and A') and V_2O_5 (curves B and B') electrolysis solution.

TABLE 7

Cell resistance for treated NH_4VO_3 and V_2O_5 electrolysis solutions

Electrolyte	Cell resistance on charge ($\Omega \text{ cm}^2$)	Cell resistance on discharge ($\Omega \text{ cm}^2$)
V_2O_5	3.41	3.62
Treated NH_4VO_3	3.20	3.34

TABLE 8

Cell efficiency for treated NH_4VO_3 and V_2O_5 electrolysis solutions

Electrolyte	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
V_2O_5	95.4	86.8	82.8
Treated NH_4VO_3	96.5	91.9	88.7

is seen, however, to reduce the solubility of the V(II) and V(V) species. Treatment of this solution to remove NH_4^+ ions can, however, be successfully achieved by using $\text{Ca}(\text{OH})_2$ to increase the pH so that NH_3 can be boiled off. Precipitation of CaSO_4 ensures that Ca^{2+} ions do not contaminate the solution.

A slightly higher cell energy efficiency obtained with treated NH_4VO_3 -derived electrolyte compared with V_2O_5 -derived electrolyte is consistent with cyclic voltammetric results. The latter show an improved electrochemical reversibility of the vanadium-redox couples in the presence of small amounts of NH_4^+ ions. Although these results are only preliminary, it is indicated that the NH_4^+ ions may somehow enhance the

electrochemical reversibility of the vanadium reactions at the carbon electrodes. Since the price of NH_4VO_3 is also potentially lower than V_2O_5 , its use should further reduce the cost of the vanadium-redox flow battery and thus give this device further benefits over other storage systems.

Acknowledgements

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