

## CHARACTERISTICS OF A NEW ALL-VANADIUM REDOX FLOW BATTERY

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### Summary

The construction and performance of an all-vanadium redox flow system is described. The battery employs vanadyl sulphate in sulphuric acid solution as the electrolyte, carbon felt as the electrode material, and an ion-selective membrane as the separator. Working parameters, storage life, and a comparison of the characteristics with other battery systems are also presented. The cost of manufacture of a 1 kW battery of 5 kW h, 15 kW h, or 50 kW h capacity has been evaluated and the practical application of the system in large stationary installations and electric vehicles is also discussed.

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### Introduction

Energy storage systems based on the redox flow battery concept have been investigated and developed over the last 15 years [1 - 5]. The redox system possesses a number of advantages over conventional rechargeable batteries (*e.g.*, lead/acid, nickel/cadmium). By employing fully soluble redox couples and inert electrodes, undesirable electrode processes are eliminated and thus there are no fundamental cycle limitations. The system storage capacity is determined by the solution concentration and tank volume, while the system power is set by the arrangement of cells within the battery stack.

After screening many possible redox couples [3, 6] the iron/chromium system was initially selected by NASA [7, 8] and 1 kW units have been demonstrated both by this organization [9] and by the ETL group [10]. Because of the poor kinetics of the chromium redox reaction, however, a number of problems have still to be overcome. These include the development of special catalysts for the chromium electrode, and the need for a separate rebalance cell. To overcome these problems, we have advanced the concept of an all-vanadium redox flow system; the system is currently under development in our laboratories [11].

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Through the use of vanadium salt solutions in both half-cells, the problem of cross-contamination has been solved. Several vanadium compounds such as  $VCl_3$ ,  $V_2O_5$ ,  $VOSO_4$  have been investigated in different solutions (HCl, NaOH,  $H_2SO_4$ ) and at different concentrations. To avoid problems of chlorine generation,  $VCl_3$  and HCl have been eliminated. Slow solubility of  $V_2O_5$  in the acids has made the preparation of electrolytes difficult. Thus, vanadyl sulphate solution in sulphuric acid has been selected as the electrolyte for both half-cells.

### Battery performance

In initial laboratory experiments, graphite plates were employed as the electrodes and a sulphonated polyethylene anion-selective membrane as the separator. Lack of sufficient mixing, a high membrane resistance, and the large distance between electrodes (approx 60 mm) resulted in low voltage efficiencies at charge/discharge current densities of  $6 \text{ mA cm}^{-2}$ .

The new UNSW (University of New South Wales) vanadium redox cell uses carbon felt for the electrode materials (Le Carbone, Lorraine) and Selemion CMV cation-selective material for the membrane (Asahi Glass Co Ltd, Japan). Efficient electrolyte flow was ensured by the use of magnet pumps (Iwaki Co Ltd, Japan). Recent tests of the flow cell have shown a substantial improvement in the working parameters, as indicated in Table 1. Higher charge and discharge current densities and a decrease in the charging voltage have resulted in an increase in the voltage and power efficiencies.

The reaction kinetics of the vanadium redox couples are sufficiently high for no electrocatalysts to be required [11]. During charging of the cell up to a 90% state-of-charge, there is no hydrogen or oxygen evolution, so that high charging efficiencies (over 95%) have been obtained.

TABLE 1

General description of vanadium redox cell

Half-cell reactions	
Negative	$V(\text{III}) + e^- \xrightleftharpoons[\text{discharge}]{\text{charge}} V(\text{II})$
Positive	$V(\text{IV}) \xrightleftharpoons[\text{discharge}]{\text{charge}} V(\text{V}) + e^-$
Electrodes	Carbon felt, thickness 3 - 4 mm
Electrolyte	2 M $VOSO_4$ in 2 M $H_2SO_4$
Half-cell separator	Ion-selective or microporous membrane
Current collectors	Graphite plates
Working conditions	Open-circuit voltage 1.45 V
Average current density	Charging $80 \text{ mA cm}^{-2}$
	Discharging $50 \text{ mA cm}^{-2}$
Temperature	Ambient

High-performance storage batteries must have the ability to undergo a large number of deep charge/discharge cycles with high efficiency and without physical degradation. Charge/discharge cycling of the test battery has been carried out for over 1500 h with negligible decrease in performance. The only change observed during this period has been an increase in the membrane resistivity. Further work is required to determine which membrane (or separator) material has the best long-term stability.

On the basis of the results obtained to date, the projected parameters of a 1 kW (5 kW h) all-vanadium battery have been determined and are presented in Table 2.

Any increase in the energy storage capacity of the battery with the same power output will simply require an increase in the volume of electrolyte in the tanks. A range of membranes and electrode materials is currently being evaluated so that further improvements in performance and cycle life can be achieved.

TABLE 2

1 kW (5 kW h) vanadium redox battery

Number of cells	17
Open-circuit voltage	24.7 V
Current	
charging	up to 65 A
discharging	40.5 A
Approximate size (w × h × l)	30 × 33 × 20 cm
Volume of electrolyte	
in battery	6 dm <sup>3</sup> × 2
in tanks	74 dm <sup>3</sup> × 2

### Battery life

All conventional batteries undergo a process of self-discharge, which limits their shelf life. In a redox flow battery, the shelf-discharge rate is determined by the ion selectivity of the membrane or separator. Even with membranes of low selectivity, however, the degree of cross-mixing during storage is limited to the electrolyte that is contained within the battery, this being only a small fraction of the total electrolyte volume. Thus, in the case of a 1 kW–5 kW h system, 93% of the electrolyte would be contained in the separate storage tanks, and only 7% in the battery stack itself. Even after several weeks of storage, the open-circuit voltage of a cell employing a Selemon CMV membrane was still approximately 1.1 V, so that sufficient current could be obtained to start the pumping system. When a new portion of electrolyte was pumped to the cells, full power could be delivered within several seconds.

The stability of the charged electrolytes has been tested over the temperature range 5–60 °C, no noticeable change was detected over a period

of 12 months. Because of the sensitivity of the negative (reduced) V(II) solution to oxidation, however, and in order to prevent water evaporation, the electrolytes should be stored in air-tight tanks. Under these conditions, an unlimited shelf-life can be predicted for the electrolytes.

### Comparison with other battery systems

At present, the only commercial batteries with energy capacities greater than 100 W h are the lead/acid and alkaline nickel/cadmium systems. Utilization properties of the all-vanadium redox batteries compare favourably with these systems and are superior to many other systems currently under development.

The normal time taken to recharge the battery is only about 60% of the discharge period under full load. Another option, however, would be to refill the tanks with the new portions of charged electrolyte, the battery thus attaining its full power instantly. This possibility, which is specific to redox flow cells, would make such a system ideal for electric vehicle applications. From the stability of the electrolytes, it is possible to project a service life of 5 - 10 years.

In Table 3, the general properties and characteristics of the vanadium batteries are compared with other selected systems. The long service life, working parameters, range of capacity and power, and maintenance-free operation all serve to make the vanadium redox battery one of the most promising energy storage systems currently under development.

TABLE 3

Comparison of technical parameters of UNSW vanadium redox system with those of other batteries

Property	Vanadium redox	Iron/chromium redox	Lead/acid	Nickel/cadmium
Service life (years)	5 - 10	unknown	2 - 3	10+
Depth of discharge (%)	90	75	65	—
Self discharge (%)	< 10	< 10	90	20 - 90
Shelf life	unlimited	unknown	only dry cells	—
Open-circuit voltage (V)	1.5	0.9	2.0	1.3
Energy density (W h kg <sup>-1</sup> )	25+	~ 15	15 - 30	10 - 35
Recovery of active material (%)	100	not economical	possible	—
Maintenance	free	low	low	low

## Economical aspects

Little information could be obtained on component costs based on mass production. Many of the components used in the cost analysis were laboratory samples or hand-made elements. Calculated costs are thus probably overestimated, although some reduction in component prices was assumed for large-scale production. Reactant cost calculations are based on present prices of chemicals. For the last ten years, the price of vanadium, based on fused metallurgical grade vanadium pentoxide, has remained stable at US\$ 14 per kg. Using a factor of 1.5, the price of vanadium in vanadyl sulphate was estimated. Table 4 shows the quantities and approximate costs of chemicals for 1 dm<sup>3</sup> of electrolyte.

The components required for a 1 kW battery and their approximate costs are listed in Table 5.

Here it has been assumed that most of the components are purchased from outside manufacturers and assembled at the factory. By producing most of the elements on site, further reduction in cost can be expected. Depending on the energy storage capacity, the cost of electrolyte in the

TABLE 4

Composition and cost of 1 dm<sup>3</sup> of electrolyte

Component	Weight (g)	Price (US\$)
VOSO <sub>4</sub> ·H <sub>2</sub> O	362.0	2.10
H <sub>2</sub> SO <sub>4</sub> (98%)	187.6	0.40
H <sub>2</sub> O	750.4	0.05
<b>Total</b>	<b>1300.0</b>	<b>2.55</b>

TABLE 5

Components and estimated costs for 1 kW battery

Component	Quantity	Cost (US\$)
Electrolyte	4.13 dm <sup>3</sup> × 2	21.07
Electrodes (carbon felt)	810 cm <sup>2</sup> × 34	55.08
Bipolar plates	29 × 32 cm <sup>2</sup> × 16	48.00
Membrane	29 × 32 cm <sup>2</sup> × 17	47.33
Washers	4 × 17	6.80
Spacers	2 × 17	10.20
Box	1	5.00
Electrolyte pumps	2	80.00
<b>Total cost of materials</b>		<b>273.48</b>

separate reservoirs should be included Table 6 shows the total cost of materials and the approximate labour costs for a 1 kW system with a storage capacity of 5 kW h, 15 kW h, and 50 kW h

The significant drop in the cost per 1 kW h with increasing storage capacity of the system points to an additional economic advantage of the redox flow battery. The prices per 1 kW h shown in Table 6 compare favourably with the current retail prices of lead/acid batteries

TABLE 6

Factory costs for 1 kW vanadium redox system with different storage capacities

Component	Storage capacity (kW h)		
	5	15	50
<i>Materials</i>	\$	\$	\$
• 1 kW battery	273 48	273 48	273 48
• electrolyte in tanks	389 64	1209 72	4080 00
• tanks	15 00	20 00	40 00
Labour	40 00	50 00	60 00
Factory cost total	718 12	1553 20	4453 48
Cost per kW h (\$)	143 62	103 55	89 07

## Applications

Various possible applications of all-vanadium redox flow systems take advantage of one or more of its inherent characteristics. These applications can cover the range of power and energy requirements from small uninterruptable power supplies of several W h capacity, through stand-alone sites to electric utility control stations. Being superior to lead/acid batteries, the new vanadium redox system can replace these in many installations.

The following applications for the vanadium flow batteries can be considered

(i) Emergency uninterruptable power supply emergency lighting, hospital equipment, etc

(ii) Industrial batteries telecommunications, railroad signalling, relay stations, military installations.

(iii) Electric traction industrial trucks, delivery vehicles, passenger cars, submarines, military vehicles

(iv) Stand-alone applications. off-grid automatic low maintenance installations, power-supply systems for homesteads in remote areas.

(v) Electric load levelling night and day load levelling, peak shaving

Due to their very good deep-discharge characteristics, vanadium redox batteries are likely to be applied first as industrial batteries and in stand-

alone, off-grid installations. For such stationary applications, the size and energy density of the battery are not critical. For hybrid installations using photovoltaic panels or wind-driven generators together with a battery storage system, very high energy efficiencies are also not of great importance. Less selective membranes could thus be employed in the redox cell to reduce the price of the system.

In numerous countries in North and South America, Africa, and Australia there are many thousands of homesteads in remote rural areas not connected to the electricity supply network. Most of these could use a hybrid system with a wind or solar generator, a vanadium storage battery, and an inverter. Such installations, with negligible running costs, would certainly be competitive in price when the initial installation cost is averaged over 10 or more years.

Several other factors should also be considered in load-leveling applications of the vanadium redox system. One of the important factors is heat generation due to energy losses in the large batteries and the slow cooling of the electrolyte in the tanks. With inadequate cooling, the temperature of the electrolyte could increase by 20 - 40 °C. Proper design of the cooling system should solve this problem, although laboratory tests have shown that an increase in the cell working temperature has a beneficial effect on the kinetics of the electrochemical processes in the cells, and has no influence on the stability of the electrolytes.

The application of the vanadium battery to electric vehicles seems to be another attractive alternative. Unlike lead/acid batteries, the new system can be recharged at very high rates. However, by exchanging the electrolytes at specially equipped refuelling stations, the battery would be ready for use again after only a few minutes. The concept of a regenerative vanadium redox fuel is illustrated in Fig. 1.

Batteries for electric vehicles require high specific energy and high cycle efficiency. As can be seen in Table 3, the energy density of the vanadium

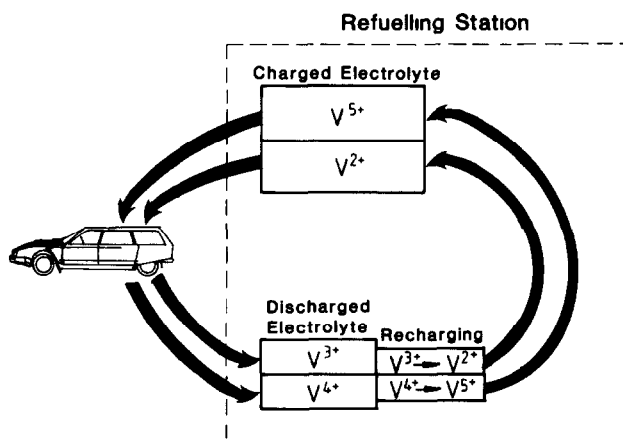


Fig 1 Application of vanadium redox fuel system to electric vehicles

battery is in the same range as those of the advanced lead/acid or nickel/cadmium batteries. Recent laboratory tests indicate that there is room for further improvement in the parameters of the vanadium redox system. Both power and energy density can be substantially increased. At present, a modern 2-person electric car assembled from commercially available elements and fitted with a 5 kW h vanadium battery, could cover a distance of approximately 150 km with a speed of up to 70 km h<sup>-1</sup>. Increasing both the battery size and the tank volumes will make it possible for the system to be employed in larger vehicles.

The use of vanadium redox batteries in non-nuclear submersibles can also be envisaged. Again, the possibility of a quick exchange of discharged electrolyte will be a great advantage. It would probably allow a reduction in the size of the engines used for charging the batteries.

The list of applications of the vanadium redox battery covered here is not complete. The unique characteristics of this system would make it suitable for many other special purposes.

## Conclusions

A vanadium redox flow system, employing vanadyl sulphate solution in sulphuric acid as electrolyte, and an ion-selective membrane as separator, has been shown to be fully competitive with other battery storage systems.

Based on current experimental results, an energy density of 25 W h kg<sup>-1</sup> has been predicted for a 1 kW, 5 kW h battery, this is similar to lead/acid and nickel/cadmium batteries and has good prospects of being improved further. The chemical stability of electrolyte is unlimited and there are no problems with cross-mixing. Up to 10 years service life of the battery can be predicted.

Several industrial applications for the vanadium storage system have been considered. Depending on the size of the battery and the volume of the electrolyte storage tanks, the system can be employed as an emergency power supply, in off-grid automatic low-maintenance installations, for electric traction, stand-alone hybrid systems, and in electric load-levelling installations. The application of the vanadium battery to electric vehicles benefits from the possibility of a rapid exchange of electrolyte. The discharged electrolyte can be regenerated and distributed at special refuelling stations. For countries with many remote homesteads and small settlements in rural areas, hybrid wind or solar generator/vanadium storage systems appear to be very attractive in comparison with current installations.

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## References

- 1 L H Thaller, *Proc 9th Inter-Soc Energy Conv Eng Conf*, American Society of Mechanical Engineers, 1974, p 924
- 2 L H Thaller, Electrically Rechargeable Redox Flow Cell, *US Pat 3,996,064*, Dec 1976
- 3 J Giner, L Swette and K Cahill, Screening of redox couples and electrode materials, *NASA CR-134705*, National Aeronautics and Space Administration, U S Dept of Energy, 1976
- 4 R F Gahn, N H Hagedorn and J A Johnson, Cyclic performance of the iron-chromium redox energy storage system, *NASA TM-87034*, National Aeronautics and Space Administration, U S Dept of Energy, 1985
- 5 N H Hagedorn, NASA Redox Storage System Development Project, Final Rep, *NASA TM-83677*, National Aeronautics and Space Administration, U S Dept of Energy, 1984
- 6 J Giner and K Cahill, Advanced screening of electrode couples, *NASA CR-159738*, National Aeronautics and Space Administration, U S Dept of Energy, 1980
- 7 N H Hagedorn and L H Thaller, Redox storage systems for solar applications, *NASA TM 81464*, National Aeronautics and Space Administration, U S Dept of Energy, 1980
- 8 F G Randall, H N Hagedorn and J S Ling, Single cell performance studied on the Fe/Cr redox energy storage system using mixed reactant solutions at elevated temperature, *NASA TM-83385*, National Aeronautics and Space Administration, U S Dept of Energy, 1983
- 9 D K Stalmaker and A Lieberman, Design and assembly considerations for redox cells and stacks, *NASA TM-82672*, National Aeronautics and Space Administration, U S Dept of Energy, 1981
- 10 K Nozaki, H Kaneko, A Negishi and T Ozawa, *Proc Symp Advances in Battery Materials*, Proceedings Vol 84-4, Electrochemical Society Inc, Princeton, NJ, 1984, p 143
- 11 M Skyllas-Kazacos, M Rychcik, R Robins, A Fane and M Green, *J Electrochem Soc*, 133 (1985) 1057
- 12 M Rychcik and M Skyllas-Kazacos, *J Power Sources*, 19 (1987) 45
- 13 M Skyllas-Kazacos, M Rychcik and R Robins, *Aust Patent Appl* 11 2 1986