Conclusion

Cell performance tests with the graphite felt/EPR modified carbon-polypropylene composites electrode have shown that these electrodes are promising for vanadium battery applications. An overall voltage efficiency of up to 80% can be achieved with these electrodes in cell testing at a voltage efficiency of up to 80% can be achieved with these electrodes in cell testing at a charge/discharge current density of 20 $mA.cm^{-2}$. Long-term cycling tests have been conducted over more than 100 cycles and the EPR modified carbon-PP composite electrode was shown to be stable during normal cell operation and is thus a reliable electrode matrix material for the vanadium redox battery.

Results obtained from the 100th cycle performed at various temperatures showed that increasing the temperature increases the voltage efficiency and decreases coulombic efficiency. The combined effect of coulombic and voltage efficiencies trends produced a maximum overall energy efficiency of 88.3% at 23^0 C.

Table (3) Cell Efficiency of Vanadium Redox Cell Employing Untreated Sigri Graphite Felt/Carbon-PP Composite Electrode (i=20 $mA.cm^{-2}$).

Cycle Number	Efficiency		
	Voltage η_V	Coulombic η_C	Energy η_E
1	88.5	92.5	81.9
100	87.5	92.0	80.5

References

[1] Sun, B., "The Studies in Electrode Activation for Vanadium Redox Flow Battery Application" *PhD Thesis, University of New South Wales, Australia* (1991).

[2] Haddadi-Asl, V., Kazacos, M., and Skyllas-Kazacos, M., *J. Applied Polymer Science,* 57 (1995) 1455.

[3] Haddadi-Asl, V., Kazacos, M., and Skyllas-Kazacos, M., *J. Applied Electrochemistry,* 25 (1995) 29.

[4] Mohammadi, F., "Activation of Carbon-Plastic Composite Electrodes for Vanadium Redox Flow Battery", *MSc. Thesis, University of New South Wales, Australia* (1993).

[5] Zhong, S., "Carbon-Plastic Composite Electrode for Vanadium Redox Flow Battery Application", *PhD Thesis, University of New South Wales,* Australia (1992).

[6] Kazacos, M., and Skyllas-Kazacos, M., *J. Electrochem. Soc.,* 138 (1989) 2759.

In order to evaluate the applicability of the composite electrodes in the vanadium rebox battery, two end-electrodes were fabricated to fit into a cell which had a working surface of 138 cm^2. the electrodes comprised EPR modified PP composite substrates with Sigri graphite felt active layer heat bonded on both sides (as an active layer in one side and a current collect collector on the other side with working surface areas of 115×12 cm^2 and 17.5×21.5 cm^2 respectively). The electrical resistance of each electrode was 0.51 Ω.cm^2.

The working conditions of the cell were as follows:

Positive half-cell electrolyte: 2MV(IV)/3M H$_2$SO$_4$;
Negative half-cell electrolyte: 2MV(III)/2M H$_2$SO$_4$;
Membrane: Nafion 112 (Asahi Glass, Japan);
Charging/discharging current density: 20 mAcm^{-2} (constant);
Electrolyte volume per half-cell: 250 ml:
Temperature: 25^{0}C.

The role of sculptures acid is as a supporting electrolyte to increase the conductivity of the electrolyte as well as to enhance vanadium ion solubility. From the comparison of the cell internal resistance using 2M vanandium (IV) sulphate in 2M H$_2$SO$_4$ with that using 2M vanadium (IV) sulphate in 3M H$_2$SO$_4$ it was observed that the higher concentration of sulphuric acid yields a much lower cell internal resistance due to the higher conductivity of the latter electrolyte. The higher H$_2$SO$_4$ concentration thus gives rise to higher overall electrolyte conductivities which lead to reduced IR losses during battery cycling and thus produce the lower cell resistance values observed by Kazacos and Skyllas-Kazacos [6].

Since higher efficiency is the most desirable performance criteria, the cell with these electrodes at conditions described above was run for up to 100 cycles, a typical charge-discharge curve being presented in Figure 15. Table 3 shows the voltage, coulombic and energy efficiencies of the first and 100th cycles. As seen in Table 3' voltage efficiencies (calculated from the ratio of the average voltage during charging) of 88.5% and 87.5% were achieved for the first and hundredth cycles respectively in the cell charge/discharge testing at a current density of 20 mA.cm^{-2} at room temperature. These values indicate that the composite electrode has good electrical conductivity and electrochemical activity, although even better performance could be achieved if the electroactive surface area could be enhanced.
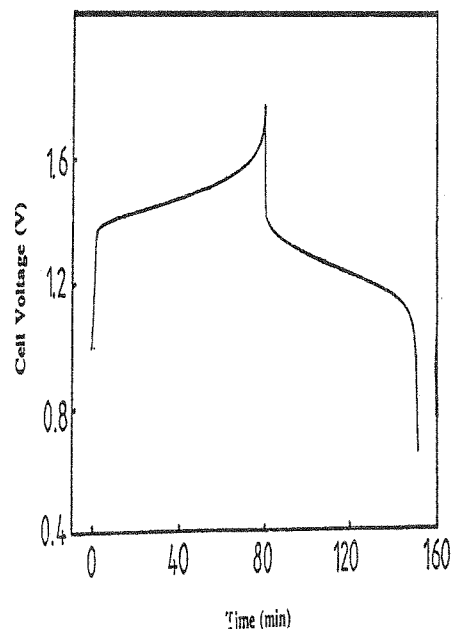

Figure (15) Charge/discharge curve of vanadium redox cell employming graphite felt/EPR modified carbon-PP composite electrode (i = 20 mA.cm^{-2}, cell voltage upper limit = 1.8 V, lower limit = 0.8 V).
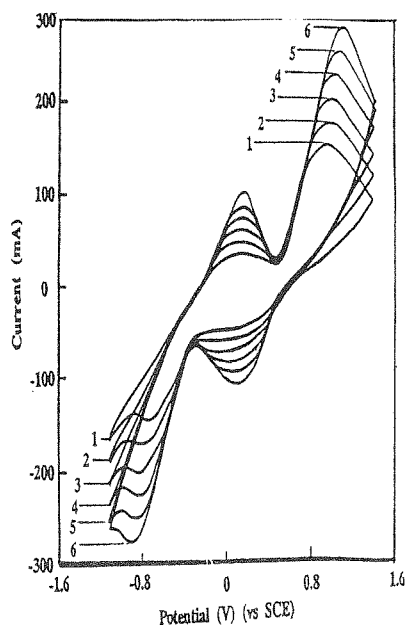
Figure (13) Cyclic voltammograms of graphite felt/composite electrode with sweep rates from 1 to 6 V.min^{-1} (numbers on the curves represent scan rate).
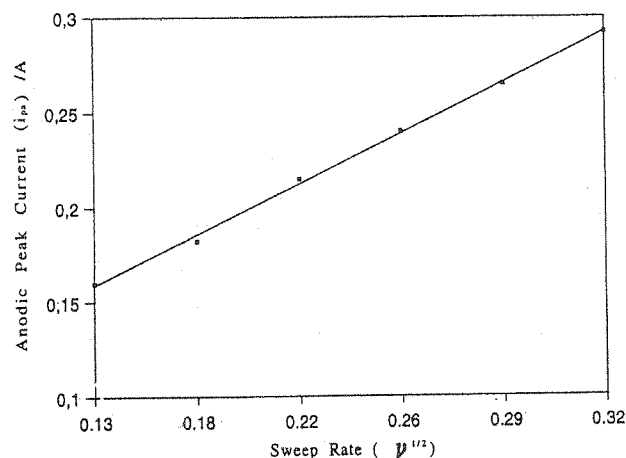
Figure (14) Plot of anodic peak currents (i_{pc}) versus sweep rates ($v^{1/2}$) for graphite felt/composite electrode.

Table (1) Cyclic Voltammetry Data for V(IV) + e-V(V) Reaction on the Graphite Rod and Graphite Felt/Composite Electrodes.

V (V.min^{-1})	$v^{1/2}$ (V.sec^{-1})$^{1/2}$	Graphite Rod Electrode		Graphite Felt/Composite Electrode	
		i_{pa} (A)	E_{pa} (V)	i_{pa} (A)	E_{pa} (V)
1	0.1290	0.018	1.07	0.160	0.92
2	0.1826	0.023	1.10	0.182	0.95
3	0.2236	0.026	1.11	0.215	0.97
4	0.2582	0.030	1.12	0.240	1.00
5	0.2887	0.034	1.13	0.265	1.04
6	0.3162	0.036	1.16	0.292	1.06

Table (2) Surface Area Comparison of the Cyclic Voltammetry and Mercury Intrusion Methods for Sigri Graphite Felt.

Cyclic Voltammetry		Mercury Intrusion	
Active Area (cm^2)	Surface Area (m^2.g^{-1})	Specific Surface Area for Main Pores (m^2.g^{-1})	Specific Surface Area for Total Measured Pores (m^2.g^{-1})
2.06	0.04	0.390	266.86

Cell Performance of Composite Electrodes

For an electrode to be suitable for use in the vanadium redox battery, high voltage and energy efficiencies with associated low cell resistance values are necessary. A series of charge-Discharge tests as well as cell resistance measurements were thus carried out to investigate the performance of a cell employing two EPR modified carbon-polypropylene end-electrodes.

$$i_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} A C_o^o D_o^{1/2} v^{1/2}$$

Where i_p is in amperes; A, the electrode area (cm); C_0^0, the bulk concentration of oxidant ($mol.cm^{-3}$); v, the potential sweep rate ($V.s^{-1}$); D_0, the diffusion coefficient of the oxidant ($cm^2.s^{-1}$), α ,the electron transfer coefficient and n_a, the number of electrons involved in the rate-determining step.

A plot of i_p vs $v^{1/2}$ should therefore give a straight line with slope proportional to D_0. The polt of anodic peak current versus $v^{1/2}$ is shown in Figure 12. Assuming a value of αn_a equal to 0.5 [1], the value of the diffusion coefficient can be calculated from the slope of this straight line, was $6.71 \times 10^{-7} cm^2.s^{-1}$.
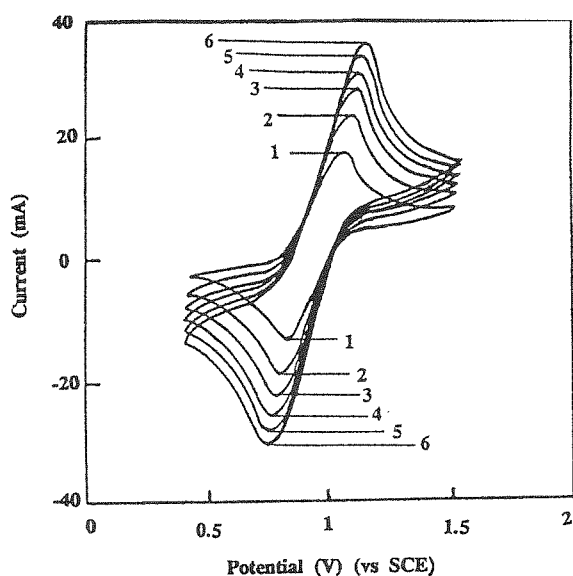

Figure (11) Cyclic voltammograms of graphite rod electrode with sweep rates from 1 to 6 $V.min^{-1}$ (numbers on the curves corresponds to scan rate).
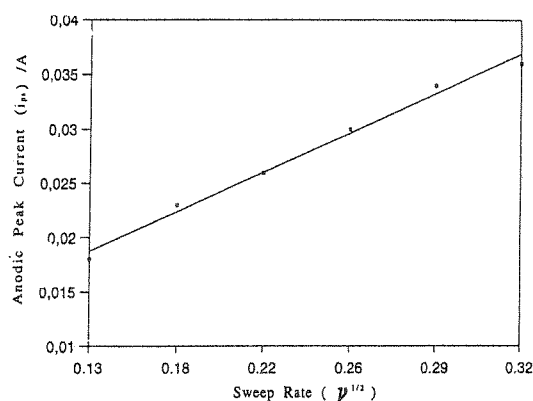
Figure (12) Plot of anodic peak currents (i_{pc}) versus sweep rates ($v^{1/2}$) for graphite rod electrode.

A series of cyclic voltammograms and the plot of anodic peak current versus $v^{1/2}$ corresponding to the V(V)/V(IV) redox couple at the graphite felt/composite electrode at various sweep rates in 1 M V(IV)+1M V(V)/3 M H_2SO_4 solution are also shown in Figures 13 and 14 respectively. Table 1 shows the values of i_{pc} from cyclic voltammograms of Figures 11 and 13. Therefore, using Equation 3 and as was mentioned before, assuming the same diffusion coefficient as obtained with graphite rod electrode, the active area of the graphite felt/ composite electrode was calculated as 2.06 cm^2. From the graphite sample(0.0051g), the active surface area of the graphite felt was thus determined to be 0.04 $m^2.g^{-1}$. As shown in Table 2, it can be observed that the active surface area of the felt calculated from the cyclic voltametric measurements is considerably lower than the specific surface area for main pores and for total measured pores as measured by mercury intrusion [5]. Thus the electrochemically active surface area of the graphite felt is only about 10% of the main pore surface area, this highlighting the need for an effective electrode activation treatment for the graphite felt electrodes to enhance the power density of the vanadium battery.

Figure 9 (curve (1)) shows a typical cyclic voltammogram of the conductive polymer electrode onto which a piece of Sigri graphite felt was bonded. Curve (2) in Figure 9 shows the electrochemical performance of the same graphite felt which had been bonded with epoxy glue to the surface of a graphite rod. As can be seen from this curve, the broader current peaks and larger peak potential separation can be related to a higher contact resistance leading to higher IR losses with this electrode. The smaller peak currents which appear in curve (2) would also be attributed to partial insulation of the graphite felt of the epoxy glue which would result in a reduced surface area.
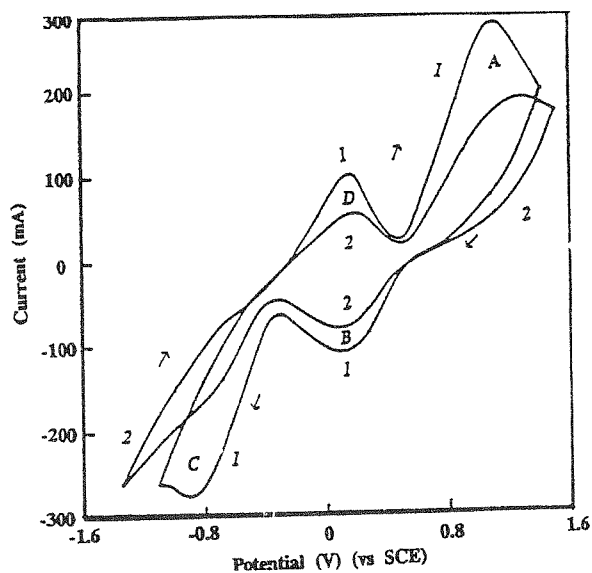

Figure (9) Cyclic voltammogram of (1) graphite felt bonded composite electrode (2) graphite felt bonded graphite rod electrode (sweep rate: 6 V.min^{-1}, vs SCE., electrode diameter : 0.6 cm).

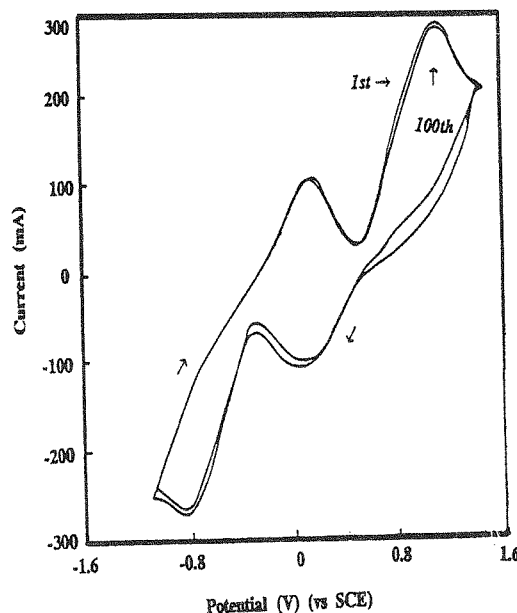Figure (10) Cyclic voltammograms of stability testing for composite electrode (sweep rate: 6V. min^{-1}, vs. SCE., electrode diameter: 0.6 cm).

From the comparison of these two curves, it can be concluded that the composite polymer is a better electrode substrate material because of the lower contact resistance between the polymer composite substrate and the graphite felt which is achieved by heat pressing.

Two cyclic voltammograms which show the stability behaviour of the graphite felt/composite electrode during operation are illustrated in Figure 10. It can be seen that after 100 cycles, only a negligible change in the electrode behaviour was recorded, indicating excellent long-term stability and characteristics of these electrodes over the potential range that would be experienced during normal operation of the vanadium flow battery.

There is agreement on the fact that it is only the macro pores of the felt which are involved in the electrochemical vanadium reactions [4]. Therefore, the actual area available for the electrochemical reactions is based in the macropores. It is thus desirable to characterize the active surface area of the graphite felt/composite electrode. Assuming the same diffusion coefficient of the vanadium ions at both the graphite rod and the graphite felt electrodes, the effective surface area of the graphite felt electrode can be calculated.

Figure 11 shows a series of cyclic voltammograms obtained at the graphite rod electrode at different scan rate in the acidic vanadium solution. It is generally agreed that the V(IV)/V(V) redox couple is electrochemically irreversible [1]. For such an electrochemical system at 25^0C, the peak current, i_p is given by:

modified carbon-polypropylene electrode in the 2M $VOSO_4$+3M H_2SO_4 electrolyte for which method was described before. The saturated calomel electrode and a clean high grade graphite rod were used as the reference and the counter electrodes, respectively. Figures 6, 7 and 8 show three typical cyclic voltammograms of the graphite rod, EPR modified carbon-polypropylene composite and graphite felt bonded composite electrode, respectively. Peaks A and B correspond to V(IV) oxidation and V(V) reduction respectively, while peaks C and D correspond to V(III) reduction and V(II) oxidation respectively. These four peaks represent the charge and discharge reaction in the positive and negative half cells of the vanadium redox battery. From comparison of these figures it can be observed that while the bare conductive composite electrode has poor electrochemical reactions of the V(II)/V(III) and V(IV)/V(V) redox couples.
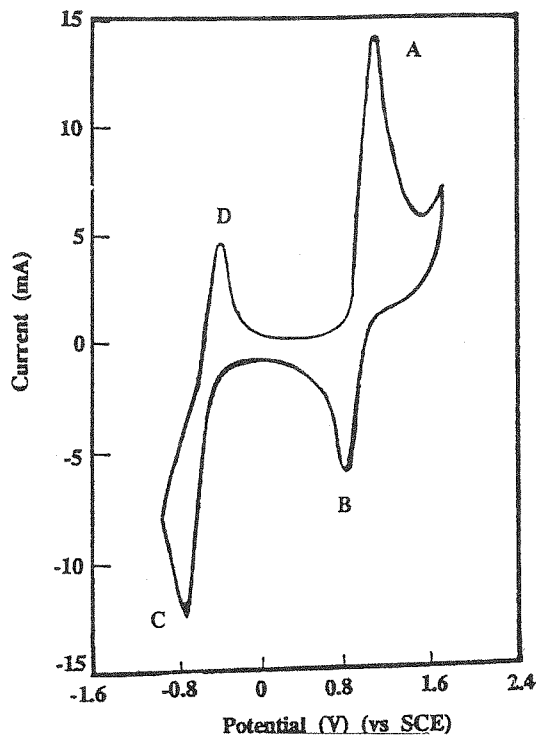

Figure (6) Cyclic voltammogram of graphite
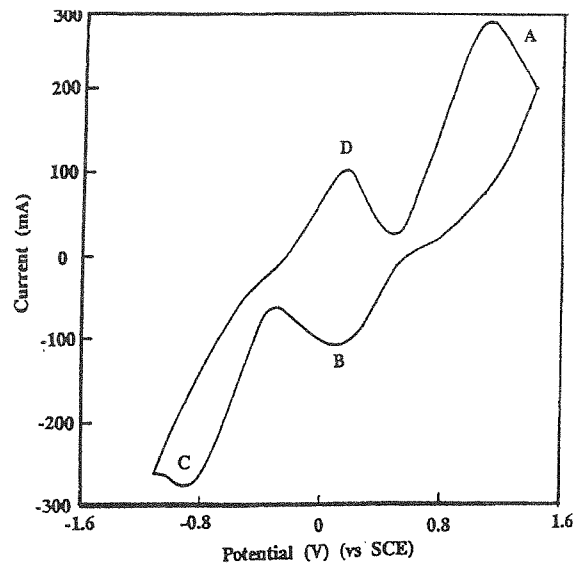rod electrode (sweep rate: 6 V.min
electrode diameter: 0.6 cm).

Figure (7) Cyclic voltammogram of EPR
carbon-PP composite electrode (sweep rate:
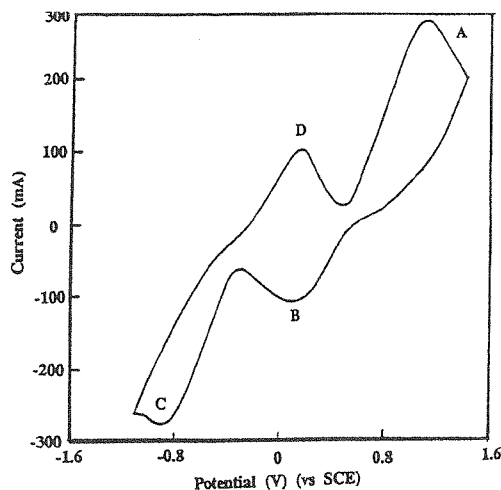6 V.min^{-1}, electrode diameter: 0.6 cm).

Figure (8) Cyclic Voltammogram of graphite felt bonded EPR carbon-PP
composite electrode (sweep rate: 6 V.min^{-1}, electrode diameter: 0.6 cm).
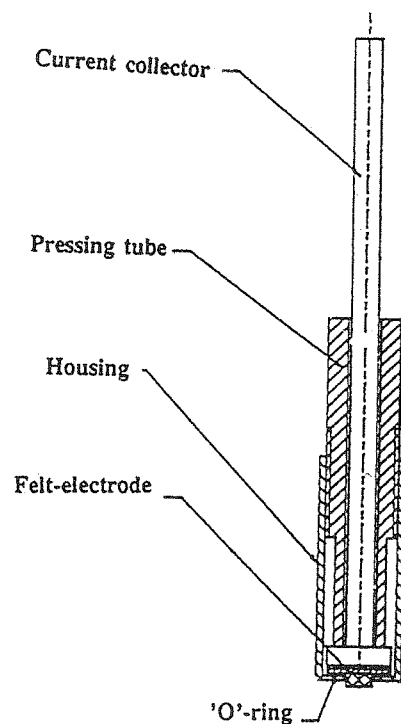
Figure (4) Construction of composite electrode for cycling voltametry.
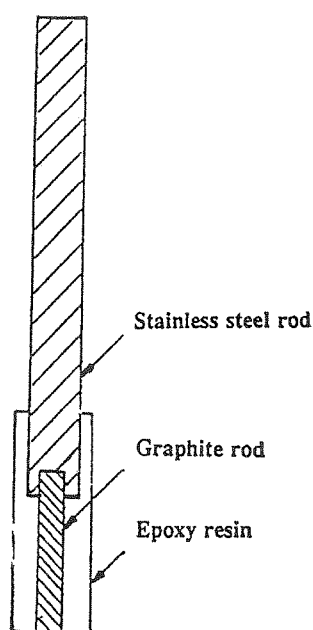

Figure (5) Construction of graphite rod electrode used for cyclic voltammetry.

The graphite rod electrode was polished with 600 grit silicon carbide polishing paper, followed by 800 grit Flexboc polishing paper and 0.3 micron alumina powder on a LECO polishing cloth. The electrode was then rinsed thoroughly with distilled water, followed by ultrasonification for 15 minutes using an LECO ultrasonic cleaner.

Results and Discussion
Electrochemical Activity and Stability of Electrodes
Cyclic voltammetry was employed to evaluate the electrochemical characteristic of EPR
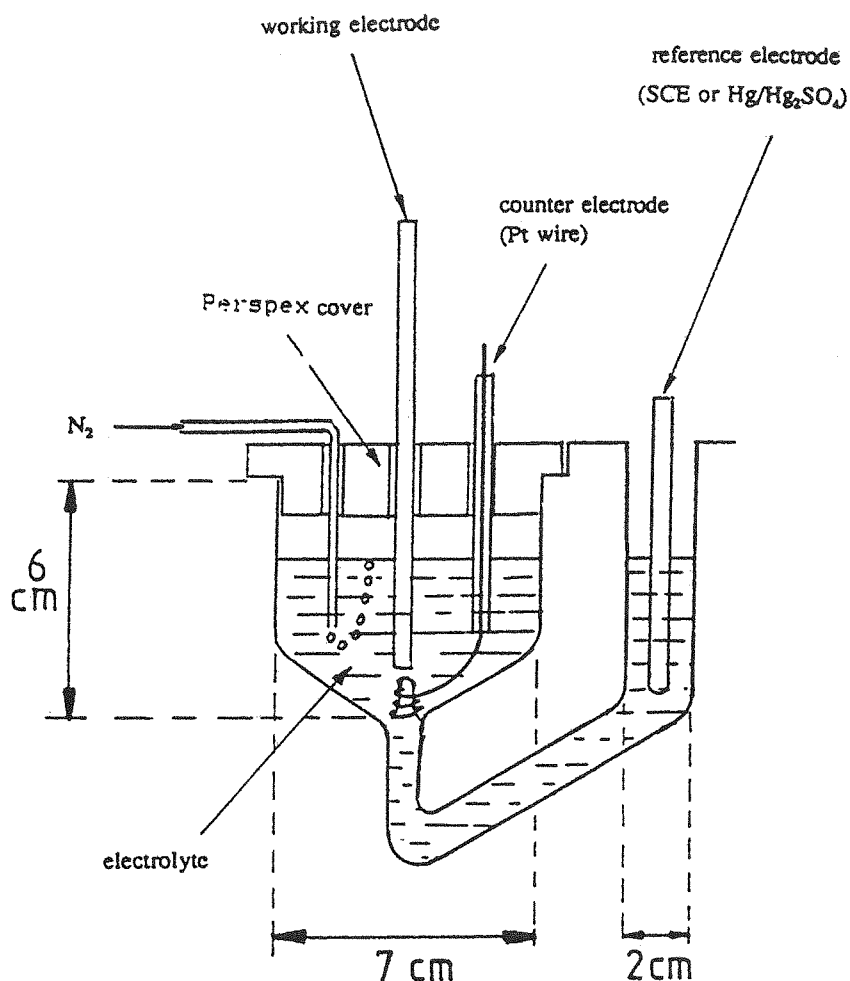
Figure (3) Electrochemical three-electrode cell for cyclic voltametry.

Cycling Voltametry Electrode Construction

The felt samples were punched with a 0.6 cm diameter puncher and then hot pressed to the surface of composite sheets/copper mesh. A metal plate with holes of 0.6 cm diameter was employed during the felt bonding, to prevent the felt from being crushed during processing. A release film with holes of the same diameter was also used between the metal plate and the composite sheet to prevent them sticking together. After hot-bonding the felt samples onto composite sheet, a 1.2 cm diameter puncher was employed to punch out the entire small composite electrode, i.e., a 0.6 cm diameter felt layer with a 1.2 cm diameter composite sheet. The extra 0.3 cm around the edge was required for placing an 'O' ring to stop solution leakage to the metal current collector. Several coats of epoxy resin were applied to ensure that no flaws due to air bubbles would allow electrolyte to contact the copper mesh on the back of the electrode (Figure 4).

A graphite rod working electrode was also employed for studying the electrode kinetics of the V(V)/V(IV) redox couple. A graphite rod of 0.6 cm in diameter was cut 2.5 cm long and then electrically connected to a stainless steel rod by inserting the graphite rod into the same diameter hole drilled in one end of the stainless steel rod. The graphite rod and lower part of the metal rod were sealed in epoxy resin. After the resin being cured, a machining process was applied to obtaine a graphite electrode for cyclic voltammetry. Figure 5 shows the construction of the graphite rod electrode.
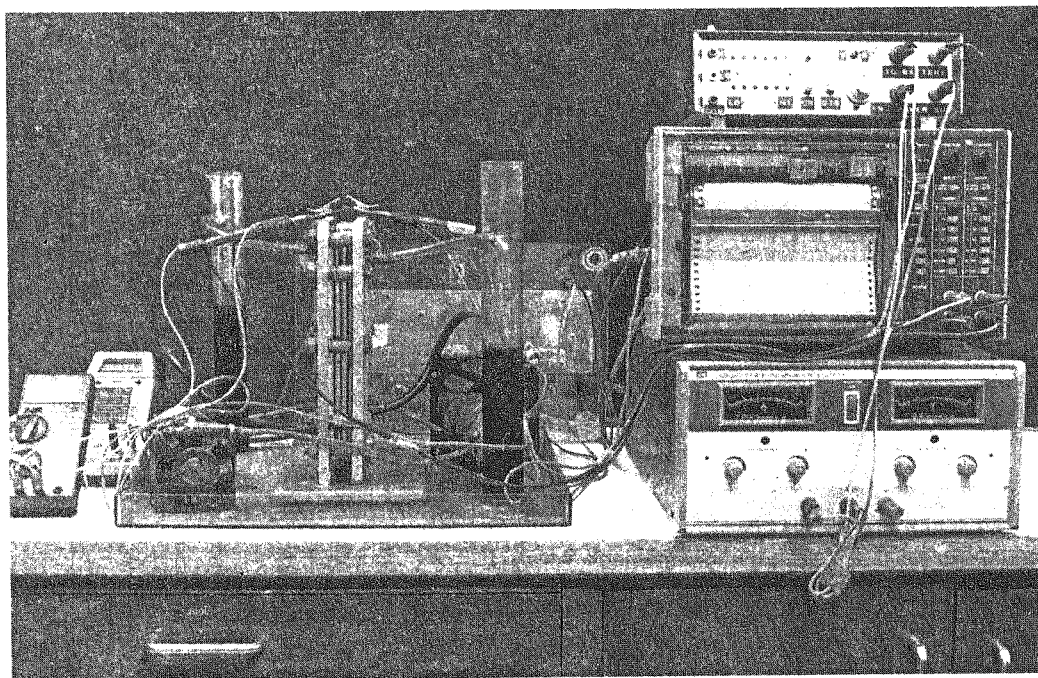
Figure (2) Laboratory-scale vanadium redox flow cell.

For single-cell performance tests, two composite end-electrodes were needed, while in the case of a multi-cell battery, a number of bi-polar electrodes plus two end-electrodes were required. For example, in a two cell multi-cell battery, two end-electrodes and bi-polar electrode are utilized.

Equal volumes of 2M $V^{3.5+}$ / 2.5M H_2SO_4 solution were used initially in each half cell to generate fully charged electrolytes from an initial charging cycle. It is necessary to balance the electrolytes in the initial cycle if the electrolytes in both sides of the cell are not charged to 100% state-of-charge at same time. After balancing the solution and making sure the system was leak proof, cell voltage, current and time for each charge-discharge cycle were recorded.

Electro-Analytical Technique

Cyclic voltametry was employed for studying the electrode behaviour in V(IV)/V(V) redox complex. A three-electrode cell was employed which was made of glass and contained a solution of $VOSO_4$ in H_2SO_4. The top of the cell was covered with a Perspex lid which had three openings in it to accommodate the three electrodes, as shown in Figure 3. The saturated calomel electrode and a clean high grade graphite rod were used as the reference and the counter electrodes, respectively.

Working conditions were:
Reference electrode: saturated calomel electrode (SCE)
Working electrode: graphite rod
Solution: $VOSO_4$ in 3M H_2SO_4
Temperature: 25^0C
Sparging: standard CIG N_2 cylinder

The three-electrode cell was connected to a potentiostate and cyclic voltammograms were recorded on a x-y recorder.

The potential sweeps always started from the open circuit potential. Unless otherwise stated the initial scan direction was positive and sweep rate was 6 $V.min^{-1}$. All studies were at room temperature. All voltage measurements in this work are done with respect to the SCE.
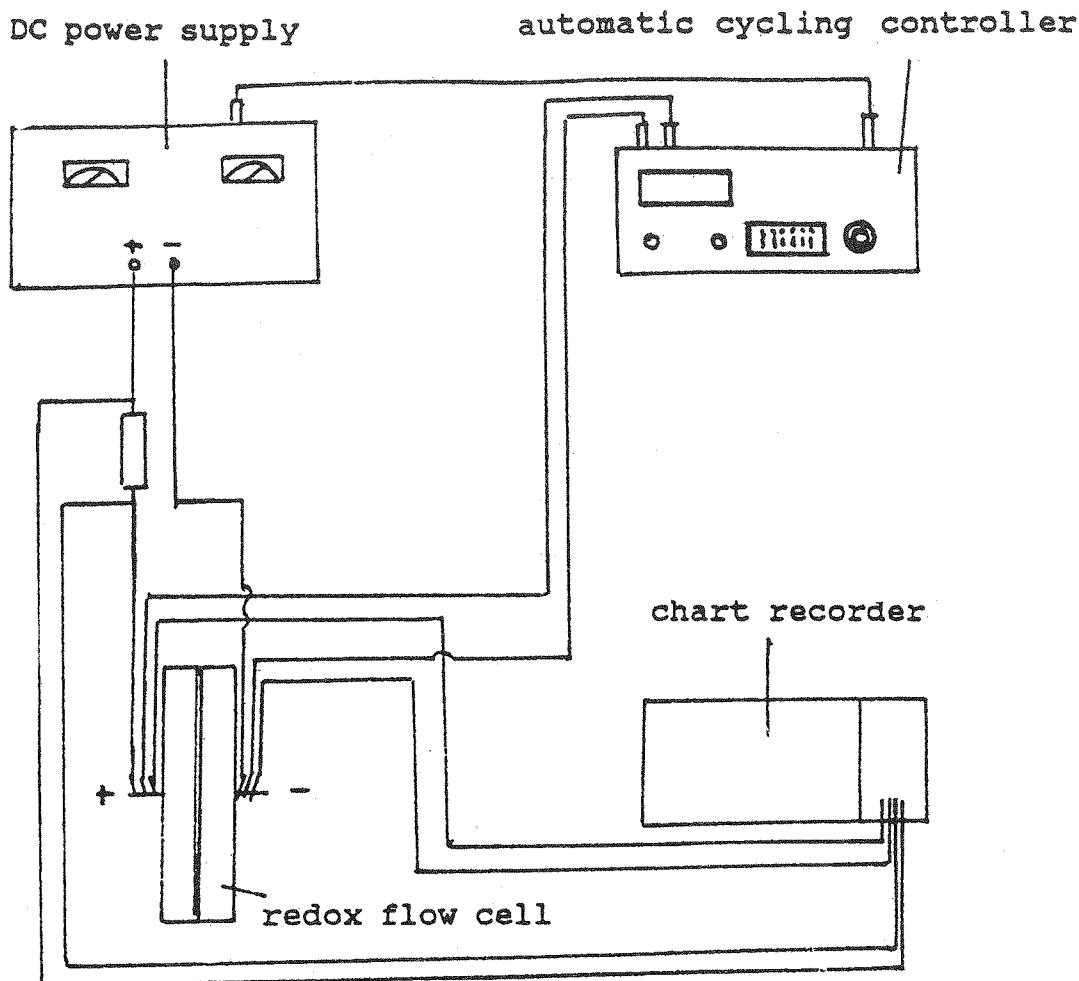
Figure (1) Electrical circuit used for cell performance test.

Evaluation of Charge-Discharge Performance of the Cell

In order to evaluate the applicability of the composite electrodes in the vanadium redox battery, two end electrodes were fabricated to fit into a cell with a working surface of 138 cm^2. The electrodes comprised EPR modified PP composite substrates (40% PP+20% EPR+25% Vulcan XC72+15% Graphite fiber) with heat treated Sigri GFD5 graphite felt active layer heat bonded on one side and untreated Sigri GFD2 graphite felt as a current collector heat pressed on the back.

The working conditions of the cell were as follows:

Positive half cell electrolyte: 2M V(IV)/3M H_2SO_4;

Negative half cell electrolyte: 2M V(III)/2M H_2SO_4;

Membrane: Nafion 112 (Asahi Glass, Japan);

The electrochemical properties of the electrodes are measured using a complete vanadium redox flow cell. The electrochemical properties can be evaluated by cyclic voltammetry as well as from measurement of the cell resistance and from the coulombic, voltage and energy efficiencies of the cell during charging and discharging.

The equipment which was used for evaluating the cell resistance, was connected to an automatic battery cycling controller and also used for cell performance testing (Figure 2). The cell charge-discharge cycles were controlled automatically and continuously by the controller between set upper and lower cell voltage limits.

studies were focused on evaluation of the electrochemical behaviour and cell performance tests of the composite electrodes including:
- Cyclic voltametric study of electrochemical activity and stability;
- Cell resistance measurements.

Experimental

Preparation Procedure

Polypropylene (LZM60CR, lCl Ltd. Australia) was pre-mixed in a "Haake 600" internal mixer with ethylene-propylene rubber (EPR Vistalon, Exxon Co., Australia) for 5 minutes followed by 10 minutes mixing with carbon black (Vulcan XC.72, Cabot Corp., USA). Graphite fiber was then added slowly for 20 minutes. The mixture was pressure-moulded with 250 kg/cm^2 pressure at 200^{0}C for at least 30 minutes. A piece of Sigri GFD2 graphite felt (2mm thick, Sigri Electrographite GmbH, Germany) was placed below the composite sheet inside the mould and a window was then placed on top of the composite sheet, a piece of thermally treated Sigri GFD5 graphite felt was placed in the window the mould was heated to 200^{0}C for 20 minutes under pressure. The mould was then cooled rapidly.

Measurements of Electrical Properties

To evaluate the area resistance of the composites, the "two-plate" method was employed (as described in a previous publication [2, 3]), which involved placing a copper plate above and below the composite sheet to be tested. These copper plates were compressed to a pressure of 50 g/cm^2. A series DC current was then applied to the composite test sample through the copper plates. Potential drop values were measured on a digital Hewlett Packard (3465B) multimeter which was connected to the other two corners of the copper plates. Plotting the potential drop in Volts versus the current density in A.cm^{-2} from the value of the slope, the resistance of the composite could be determined with units of $\Omega.cm^2$.

Measurement of Cell Resistance

One of the important and basic methods which is applied widely to evaluate the real performance of an electrochemical cell, is cell resistance measurement. This can be also used to study the individual cell components, such as electrodes, membrane, and electrolytes; the electrical circuit used for the cell resistance measurement is shown in Figure 1. The details of testing can be described as follows:

A DC power supply, two multimeters, a resistor of 0.1 Ω, two magnet pumps, a portable chart recorder, two glass reservoirs with polyethylene tubes connected to a complete vanadium redox cell and pumps were employed for the cell resistance tests. This equipment was also used for evaluating the cell performance of the composite electrodes. The electrolytes used in each half cell corresponded to 50% state-of-charge (SOC) vanadium solutions, i.e. lM V(IV)+lM V(V) in 3.5M H$_2$SO$_4$ solution as the catholyte, and 1MV(II)+1MV(III) in 2M H$_2$SO$_4$ solution as the anolyte. The cell was charged for 1 minute at a constant current density within the range 10-60 mA.cm^{-2}. After around 15 seconds rest interval, the cell was discharged for 1 minute at the same current density as that used for charging. The above procedure was repeated at various current densities to obtain plots of current versus voltage for the charge and discharge cycle. From the slopes of these I.V plots, values of cell resistance could be calculated for the charge and discharge processes at 50% state-of-charge.

Electrochemical Performance of Graphite Felt/Carbon-Polymer Composite Electrodes (I): Electrochemical Activity and Stability of Electrodes

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Abstract

Conducting plastic electrodes have been developed and investigated for the vanadium redox flow battery. Electrical and electrochemical properties of carbon-polypropylene composite material were evaluated. The composite electrode assembly has a matrix layer and an active layer, each performing different function. Since the electrochemical reactions of the redox couples in the battery take place at the active layer, particularly at the interface between the electrolyte and the surface active layer material, its physical, chemical and electrochemical properties are important factors in battery application.
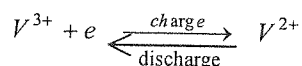
Keywords
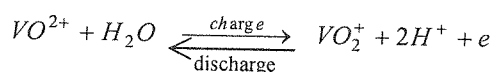*Carbon-Polymer Composite, Electrodes, Graphite felt.*

Introduction

During charging and discharging in the vanadium redox system, the following reactions occur:

Hydrogen and oxygen can also evolve at the negative and positive electrodes respectively. At the negative electrode:

$$V^{3+} + e \underset{\text{discharge}}{\overset{charge}{\rightleftarrows}} V^{2+}$$

At the positive electrode:

$$VO^{2+} + H_2O \underset{\text{discharge}}{\overset{charge}{\rightleftarrows}} VO_2^+ + 2H^+ + e$$

during charging at high states-of-charge (SOC), or if the battery is overcharged.

The composite electrodes which were evaluated in the vanadium redox battery consisted of a graphite felt layer bonded onto the conductive composite substrate, each performing different tasks. Functioning as a catalyst and/or catalyst support, the graphite felt electroactive layer is the surface where the vanadium redox reactions take place during charge and discharge whereas the conductive polymer substrate acts as a current collector as well as being a support for the felt layer. A good electrode for the vanadium redox battery should be stable in highly oxidative V(V) ions and oxygen which may be formed during charging. More importantly, the electrode should have a high electrochemical activity for the vanadium redox reactions to reduce activation overvoltage losses and a low activity for oxygen and hydrogen evolution so as to minimize gassing during charging. Thus, in this study, more intensive