

## References

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vanadium half-cell solutions from cycle to cycle which is caused by changes in solution flow rate. After neglecting the interfering effects of the membrane on the cell stability therefore, the electrodes exhibit excellent long-term stability and activity in the vanadium cell as evidenced by the relatively constant voltage efficiency values.

The performance of the EPR modified conductive plastic electrodes developed here were also compared in Table 5 with the earlier graphite fiber-SEBS composite developed by Zhong [6] as well as with an electrode composite sheet purchased from Toray (Japan) which had a graphite felt sheet bonded on one side and copper foil attached to the back. The EPR modified conduction plastic electrode thus shows the highest voltage efficiency in the vanadium battery but as discussed previously, should also be considerably lower cost than the SEBS composite material.

**Table (5) Voltage Efficiency Comparison of Three Types of Conductive Carbon-Polymer Electrodes in the Vanadium Redox Cell (membrane = Nafion112  $i= 20 \text{ mA.cm}^{-2}$ ).**

Electrode	Voltage Efficiency (%)
Toray Electrode (with Toray felt)	90.0
Graphite fiber-SEBS/heat Treated Sigri GFD5 felt Electrode	89.0
EPR modified carbon-PP/heat Treated Sigri GFD5 felt electrode	95.0

## Conclusion

PAN based Sigri graphite felt exhibited better electrical conductivity and electrochemical activity compared with rayon based FMI and Toyobo felts. Although air oxidation of the felt resulted in a slight decrease in electrical conductivity, a significant increase in the activity of the felt was obtained with thermal treatment of the felt at  $350^{\circ}\text{C}$  for 24 hrs. Furthermore, the cyclic voltametric study indicated that the heat treated graphite felt bonded EPR modified carbon-polypropylene composite electrode structure has good electrochemical performance and activity in the vanadium electrolyte.

Cell performance tests with the graphite felt/EPR modified carbon-polypropylene composites electrode in the vanadium redox battery have shown that these electrodes are promising for vanadium battery applications. An voltage efficiency of up to 95% can be achieved with these electrodes in cell testing at a charge/discharge current density of  $20 \text{ mA.cm}^{-2}$ . Long-term cycling tests have been conducted over more than 6506 hours (1300 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 the, temperature 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  $23^{\circ}\text{C}$ .

Increasing the current was seen to increase the coulombic efficiency since the rate of self-discharge decreases with the decreasing charging and discharging time. On the other hand the voltage efficiency decreases due to higher resistance and polarization losses at the higher currents.

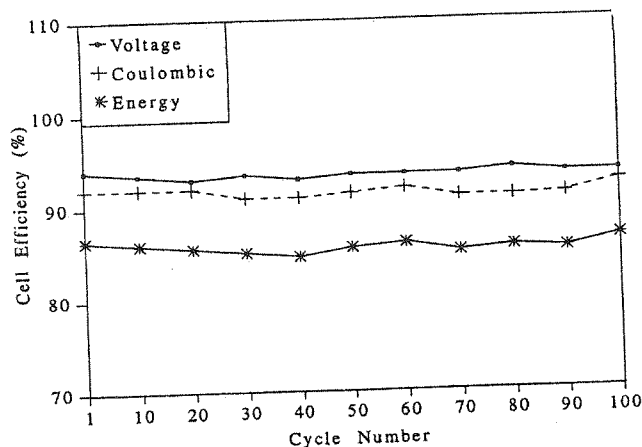


Figure (10) Short-term multi cell performance of heat treated Sigri graphite felt/EPR modified carbon-PP composite electrodes with Nafion 112 membrane ( $i = 30 \text{ mA.cm}^{-2}$ ).

### Single Cell Long-Term Stability and Charge/Discharge Testing

In order to evaluate the cycle life and cell performance of the PP composite electrodes, long-term testing of the electrochemical activity was carried out in a single cell employing Nafion 112 membrane. Continuous charge/discharge cycling was carried out over 6506 hours and 1300 cycles at a current density of  $20 \text{ mA.cm}^{-2}$ . The coulombic and energy efficiency values are presented in Figure 11, while the voltage efficiency values are plotted in Figure 12. During the first 100 cycles, this was relatively constant and up to 95% voltage efficiency was achieved. The slight decrease in voltage efficiency was due to break down of the controller which caused overcharging in the cell resulting in a reduction in the activity of the positive electrode. This was corrected by employing a new controller. The life of the composite electrodes under overcharging conditions was thus highlighted as a critical issue that requested detailed evaluation both to understand the mechanism of deterioration of the electrodes as well as to establish the operational limits required to avoid such a problem during use.

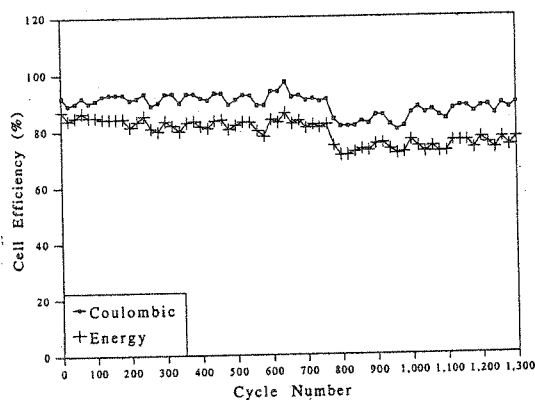


Figure (11) Long-term single cell performance of heat treated Sigri graphite felt/EPR modified carbon-PP composite electrodes with Nafion 112 membrane ( $i = 20 \text{ mA.cm}^{-2}$ ).

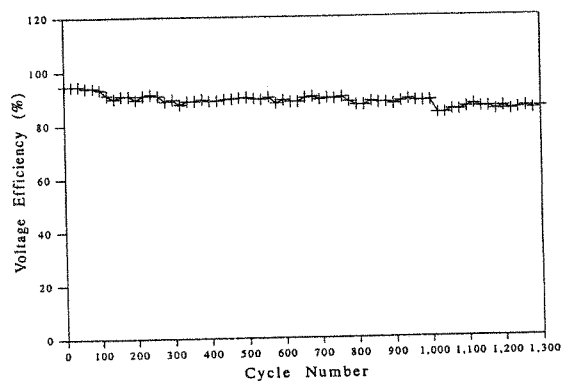


Figure (12) Long-term voltage efficiency of heat treated Sigri graphite felt/EPR modified carbon-PP composite electrodes with Nafion 112 membrane ( $i = 30 \text{ mA.cm}^{-2}$ ).

As can be seen from Figure 11, when the cell is operated between the normal limits of 1.8V for charge and 0.8 V at the end of discharge, the voltage efficiency decreases by only approximately 10% over the 1300 cycles of testing, showing that the electrode is promising for application in the vanadium redox battery. The coulombic efficiency is seen to fluctuate slightly. As explained before, and this may due to membrane fouling/degradation, variation in temperature between day and night and the imbalance in the state-of-charge of the two

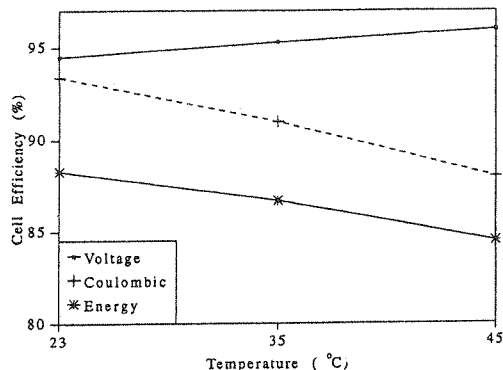


Figure (7) Effect of temperature on the cell performance for heat treated Sigri graphite felt/EPR modified carbon-PP composite electrode and Nation 112 membrane ( $i = 20 \text{ mA.cm}^{-2}$ ).

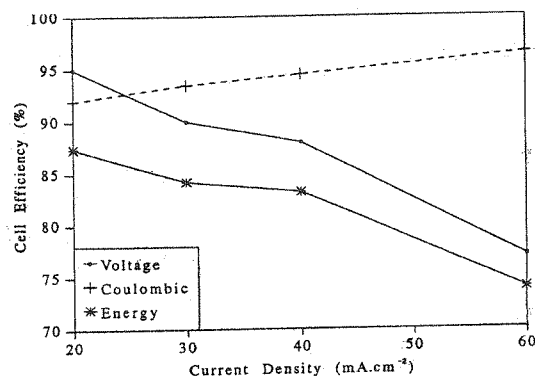


Figure (8) Effect of current density on the cell performance for heat treated Sigri graphite felt/EPR modified carbon-PP composite electrode and Nation 112 membrane.

### Single Cell Short-Term Stability and Charge/Discharge Test

Figure 9 shows the efficiencies obtained during short-term cell charge/discharge cycling tests for the EPR modified carbon-PP composite electrodes. Two end electrodes and Nafion membrane were used in a single cell and a current density of  $20 \text{ mA.cm}^{-2}$  was applied. As can be seen, fairly constant voltage efficiencies ( $\pm 0.5\%$ ) with slightly fluctuating coulombic and energy efficiencies versus cycle number were obtained over the 100 cycles. The fluctuation in the energy efficiency thus reflects the coulombic efficiency which depends on the membrane and the state of balance of the solutions.

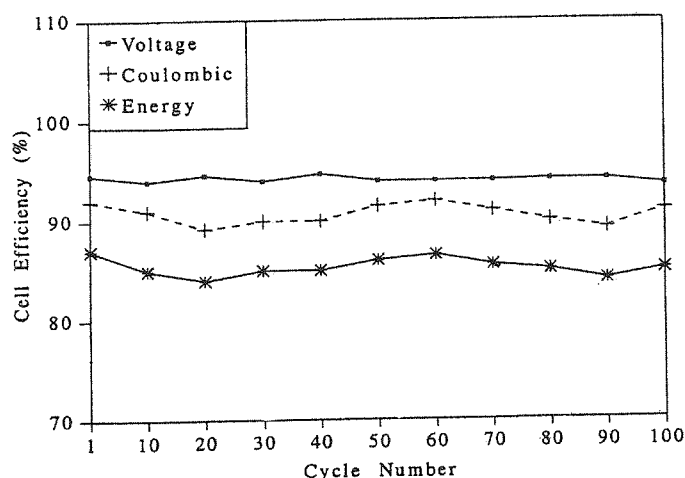


Figure (9) Short-term single cell performance of heat treated Sigri graphite felt/EPR modified carbon-PP composite electrodes with Nation 112 membrane ( $i = 20 \text{ mA.cm}^{-2}$ ).

### Multi Cell short-Term Charge/Discharge Tests

As mentioned before, in the redox flow batteries, multi cell stacks can be used to increase the output power of the system. Such stacks require both end-electrodes and bipolar electrodes, term cell charge/discharge behavior for the composite electrodes in a two-cell vanadium redox battery in the centre. Two sheets of Nafion membrane were employed as the separators and a current density of  $30 \text{ mA.cm}^{-2}$  was applied. As can be seen, because of higher applied current density, a slightly lower voltage efficiency and higher coulombic efficiency were achieved again. The slight fluctuation in the energy efficiency relates to trends in the coulombic efficiency which decreases gradually over the 100 cycles as solution is transferred across the membrane [6].

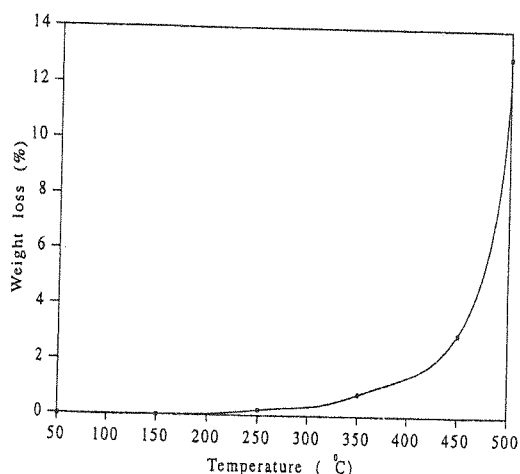


Figure (5) Effect of thermal treatment temperature on weight loss of Sigri graphite felt.

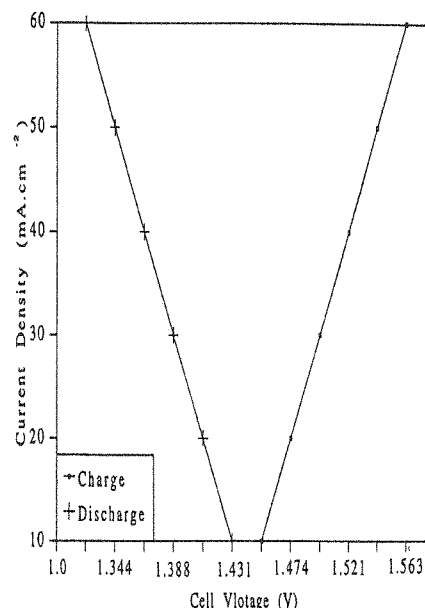


Figure (6) Polarization curves of charge and discharge for heat treated Sigri graphite felt/EPR modified carbon-PP composite electrode.

Table (4) Comparison of Cell Resistance for Carbon-PP Composite Electrode Bonded with Different Graphite Fibres.

Graphite Felt Type	Thickness (mm)	Membrane Type	Cell Resistance ( $\Omega \cdot \text{cm}^2$ )
FMI	6.0	Nafion	3.9
Heat treated FMI	6.0	Nafion	3.5
Sigri	5.0	Nafion	3.0
Heart treated Sigri	5.0	Nafion	2.2
Heart treated Sigri	5.0	CMV	3.8
Heart treated Sigri	5.0	AMV	3.9

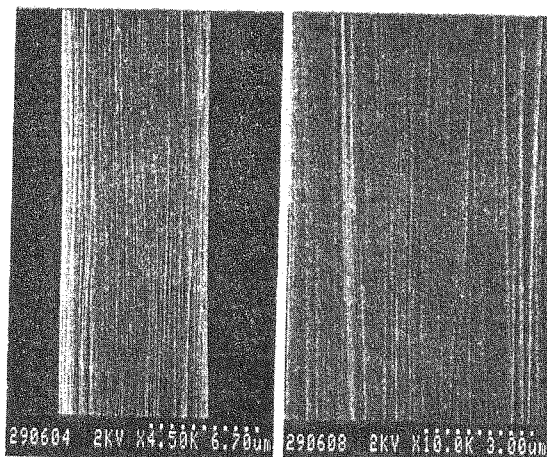
### Effect of Temperature on Cell Performance of Composite Electrodes

Results obtained from the 100th cycle performed at various temperatures also show that increasing the temperature increases the voltage efficiency of the cell (Figure7). This is expected since at higher temperatures, the activation overvoltage losses for the vanadium redox reactions are reduced. On the other hand, a slight decrease is observed in coulombic efficiency which is attributed to an increase in diffusion of vanadium ions through the membrane at the higher temperatures [6]. However, within the temperature range studies, the combined effect of coulombic and voltage efficiency trends produce a maximum overall energy efficiency of 88.3% at 23°C.

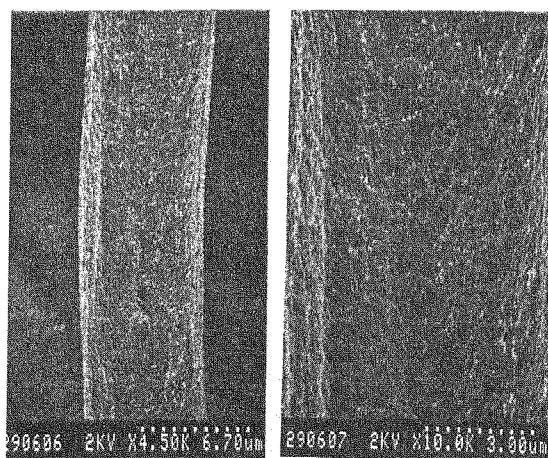
### Effect of Current Density of Cell Performance of Electrodes

Figure 8 illustrates the effect of increasing charge/discharge current density on the cell efficiencies for the composite electrodes. Increasing the current is seen to increase the coulombic efficiency since the rate of self-discharge decreases with the decreasing charging and discharging times. At higher currents, however the voltage efficiency decreases due to higher resistance and polarization losses. For the current density range 20 to 60 mA.cm<sup>-2</sup> therefore the overall energy efficiency decreases with increasing current density with a certain value of 87% obtained at 20 mA.cm<sup>-2</sup>.

resistances have values of 0.9 and 1.0  $\Omega \cdot \text{cm}^2$  (including contact resistance) respectively. From this information, the electrical cell resistance can be estimated as 1.9  $\Omega \cdot \text{cm}^2$ . Comparing this value with the experimental cell resistance of 2.2  $\Omega \cdot \text{cm}^2$ , the polarization resistance can be estimated as 0.3  $\Omega \cdot \text{cm}^2$  which is a measure of the electrochemical activity of the heat treated graphite felt. These results show that while small improvements in power density could still be achieved with better electrode activation methods, the most significant gains would be derived from further reductions in the electrical resistance of the electrodes and membrane.



(a)



(b)

Figure (4) FESEM micrographs of a) untreated, b) heat treated Sigri graphite felt (500<sup>o</sup>C for 30 hrs) at different magnifications.

Table (3) Polarization Test for Heat Treated Sigri Graphite Felt/EPR Modified Carbon-PP Composite Electrode.

Current (A)	Current Density (mA.cm <sup>-2</sup> )	Voltage (V)	
		Charge	Discharge
0	0	1.449	1.449
1.37	10	1.474	1.431
2.76	20	1.498	1.409
4.14	30	1.521	1.388
5.52	40	1.543	1.365
6.90	50	1.563	1.344
8.28	60	1.586	1.322

information on the performance of the electrodes. This test involves the charge-discharge of a redox test flow cell and was performed at constant current density up to  $60 \text{ mA.cm}^{-2}$ . Table 3 shows the polarization test results obtained for the heat treated Sigri graphite felt/EPR modified carbon-PP composite electrode with  $1\text{M V(II)} + 1\text{M V(III)}$  in  $2\text{M H}_2\text{SO}_4$  solution as negative electrolyte and  $1\text{M V(IV)} + 1\text{M V(V)}$  in  $3\text{M H}_2\text{SO}_4$  solution as positive electrolyte corresponding to the 50% state of charge (SOC) electrolytes.

The polarization curves for the composite electrode were obtained by plotting applied current (I) versus cell voltage, as shown in Figure 6. The cell resistance values which were calculated from the slope of the lines were  $2.26$  and  $2.13 \Omega.\text{cm}^2$  for charge and discharge, respectively. Because of the inverse ratio between the slope of the polarization curve and cell resistance, the greater the value of the slope causes the lower the resistance of the cell. The ratio of the discharge cell voltage for the charge cell voltage is also a measure of the cell voltage efficiency since 50% SOC electrolytes were employed in the measurement. For example, when a constant current density of  $20 \text{ mA.cm}^{-2}$  was employed during charge and discharge, the cell voltage at 50% SOC was  $1.498 \text{ V}$  and  $1.409$  for the charge and discharge cycles respectively. Therefore the cell voltage efficiency can be calculated by:

$$\eta_v = \frac{1.409}{1.498} \times 100\% = 94\%$$

This agrees well with the value of 95% obtained from the full charge-discharge cycle at  $20 \text{ mA.cm}^{-2}$  (Table 1).

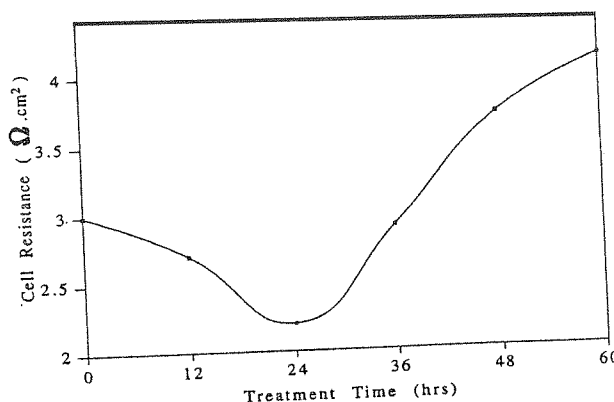


Figure (3) Effect of thermal treatment time of the Sigri GFD5 graphite felt on the average cell resistance for Sigri graphite felt/EPR modified carbon-PP composite electrode (temperature =  $350^\circ\text{C}$ ).

### Cell Resistance Test

The cell resistance ( $R_{\text{cell}}$  with units of  $\Omega.\text{cm}^2$ ) was used as a criterion for evaluation of the entire system resistance. This term is an overall quantity which includes both electrical losses and polarization in a cell and has been employed throughout this study to evaluate the overall cell felt/composite polymer electrodes were measured using a complete single cell and associated apparatus with 50% SOC electrolyte in both negative and positive half cell. Cell resistance values for various graphite felts are shown in Table 4. It can be seen that the composite electrode employing the heat treated Sigri graphite felt and Nafion 112 membrane gave the lowest cell resistance of  $2.2 \Omega.\text{cm}^2$ . This can be attributed to the high surface area, electrical conductivity and electrochemical properties of the heat treated Sigri felt materials, and also the low resistivity of Nafion membrane ( $0.9 \Omega.\text{cm}^2$  vs.  $2.6$  and  $2.8 \Omega.\text{cm}^2$  for CMV and AMV respectively).

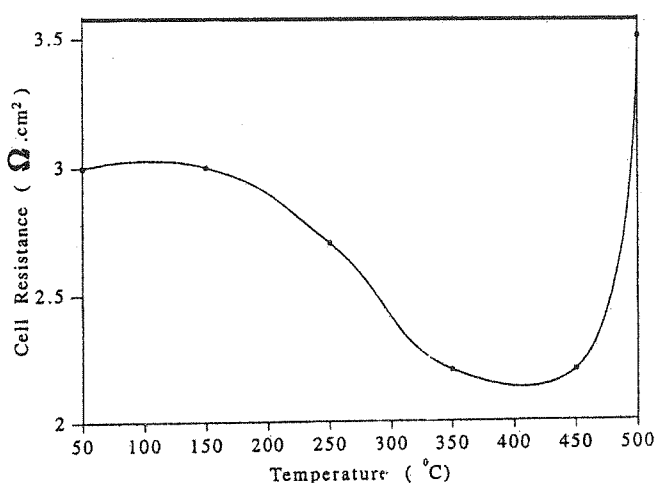
As already mentioned, the cell resistance is made up of the membrane, electrode, polarization contact resistances in the cell. The Nafion membrane resistance and two end-electrodes

**Table (2) The Wetting Properties of Sigri Graphite Felt in Acidic Vanadium Solution.**

Graphite Felt Samples	Time of Start Wetting
Untreated Sigri Graphite Felt	41 days
Treated Sigri Graphite Felt at 250 <sup>0</sup> C for 24 hrs	19 days
Treated Sigri Graphite Felt at 350 <sup>0</sup> C for 24 hrs	Immediately
Treated Sigri Graphite Felt at 450 <sup>0</sup> C for 24 hrs	Immediately

Electrode activation is also believed to catalyze the oxidation reduction reaction at the negative electrode by introducing functional groups on the graphite felt surface which accelerate electron exchange along a -C-O-V bond on the surface. While these oxygen functional groups on the surface of the graphite felt electrodes provide active sites for the vanadium reactions, they also result in an increase in electrical resistance.

Figure 2 shows the effect of treatment temperature on the cell resistance for thermally treated Sigri graphite felt bonded to EPR modified carbon-PP composite in the vanadium redox flow battery. It can be seen that the cell resistance decreased dramatically when the treatment temperature was increased up to 400<sup>0</sup>C but then increased with increasing treatment temperature for constant treatment time of 24 hours.



**Figure (2) Effect of thermal treatment temperature of the Sigri GFD5 graphite felt on the average cell resistance for Sigri graphite felt/EPR modified carbon-PP composite electrode (treatment time = 24 hrs).**

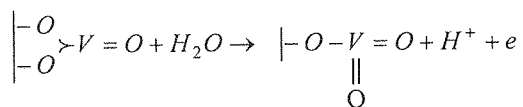
The effect of activation time on the cell resistance was also investigated at a constant temperature of 350<sup>0</sup>C. As can be seen from Figure 3, the minimum value was obtained at a treatment time around 24 hours. For shorter or longer activation time, the graphite felt exhibited a lower activity in the vanadium redox flow cell. In addition, it was observed that although increasing the treatment time and temperature increased the hydrophilicity and activation properties of the graphite felt, the bonding strength of the felt to the surface of composite polymer substrate decreased dramatically due to degradation of the graphite felt fibres caused by the reaction between carbon and oxygen producing CO<sub>2</sub> at high temperatures (see Figure 4). As can be seen from Figure 5, the burn off of the graphite felt increases with increasing temperature. The optimum conditions for the thermal activation of the graphite felt electrodes were thus found to be around 350<sup>0</sup>C for 24 hrs.

### **Polarisation Test**

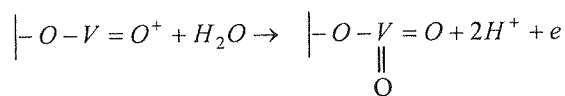
Results from polarization testing in the vanadium redox cell can give important



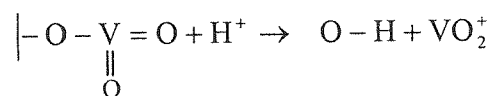
In the second step, electron transfer occurs from the  $\text{VO}^{2+}$  to the electrode along the  $-\text{C}-\text{O}-\text{V}-$  bond as well as the transfer of one of the oxygen atoms on the  $\text{C}-\text{O}$  functional group to the  $\text{VO}^{2+}$  forming a surface  $\text{VO}^{2+}$ .



or



Finally, the  $\text{VO}^{2+}$  exchanges with a  $\text{H}^+$  from solution and diffuses back into the bulk solution.



From the above hypothetical reaction sequence for the charge process involving the  $\text{V(IV)/V(V)}$  redox couple, it can be seen that electron transfer reaction can be accelerated along the  $-\text{C}-\text{O}-\text{V}-$  bond, and oxygen transfer from the  $\text{C}-\text{O}-\text{H}$  functional group will also be easier than directly from  $\text{H}_2\text{O}$ . The rate of the overall process would thus be increased leading to reduced activation over potential and increased cell efficiencies.

For the discharge process, the above reactions would occur, although the steric hindrance associated with the more bulky  $\text{VO}^{2+}$  ion attaching itself to surface  $-\text{C}-\text{O}$  group would make this process more difficult than the charge process and would explain the higher activation overvoltage often observed for the  $\text{V(V)} \rightarrow \text{V(IV)}$  reaction in cyclic voltammetry.

At the negative electrode of the vanadium redox cell, the electrode reactions are follows:

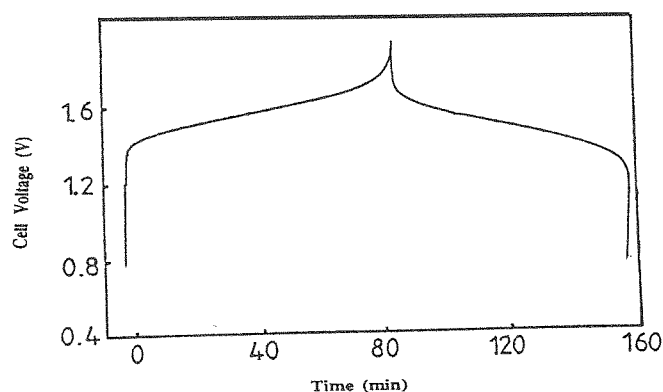
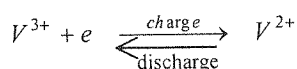


Figure (1) Charge/discharge curve of cell employing heat treated graphite felt/EPR modified carbon-PP composite electrode ( $i = 20 \text{ mA} \cdot \text{cm}^{-2}$ , cell voltage upper limit = 1.75 V, lower limit = 0.8 V).

Table (1) Effect of Thermal Treatment of Graphite Felt on Cell Performance of The Electrode.

Thermal Treatment	Area Resistivity of felt ( $\Omega \cdot \text{cm}^2$ )	Voltage Efficiency (%) (at $20 \text{ mA} \cdot \text{cm}^{-2}$ )
Before	0.27	88.5
After	0.35	95.0

## FESEM Studies

To evaluate the surface microstructure of the selected samples, the surface of the fibers were examined with a "FESEM S-900 Hitachi" field emission scanning electron microscope. The surface was then covered with a thin chromium layer.

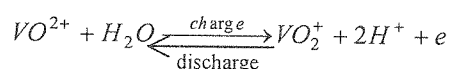
## Results and Discussion

### Effect of Thermal Treatment of Graphite Felt on Cell Performance

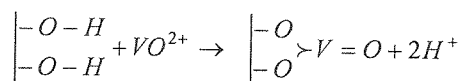
It was previously reported that some graphite felts can be easily activated for the vanadium redox reactions by various oxidation methods [2-7]. Understanding the factors which influence graphite felt activity, will assist in the selection of a more suitable felt as the electrode active layer. Alternatively, an effective activation method for a particular type of felt can be chosen, so that the efficiency of the vanadium redox flow battery can be further improved.

Table 1 shows that although the treatment of the Sigri graphite felt air at 350°C for 24 hours resulted in a decrease in electrical conductivity of the felt, a significant enhancement in the voltage efficiency was achieved for the vanadium redox flow cell. The typical charge/discharge behavior of the vanadium redox cell with the heat treated felt bonded onto the EPR modified carbon-polypropylene electrode at a charge/discharge current density of 20mA.cm<sup>-2</sup> is illustrated in Figure 1. The hydrophilicity of the graphite material was observed to improve after thermal treatment and activation of the samples. The surface wetting properties of the Sigri graphite felt were studied initially in acidic vanadium solution. It was observed that the graphite felt surface was hydrophobic and the time for untreated Sigri to show signs of wetting in 2M VOSO<sub>4</sub>/2M H<sub>2</sub>SO<sub>4</sub> solution was 41 days (by visual examination). As can be seen from Table 2, the wetting properties of the graphite felt were improved by thermal treatment. The reason for the improved hydrophilic properties is believed to be due to the formation of surface oxides which provide adsorption sites for water and other polar compounds [8]. The enhancement in the electroactivity of the felt was attributed to the electrocatalysing effect of increased C=O and C-OH functional groups [7]. The oxygen functional groups on the carbon surface behave as active sites for the vanadium reaction as well as for many electrochemical reactions [9]. Sun hypothesized a mechanism of catalysis for reactions on the electrode surface as follows [2]:

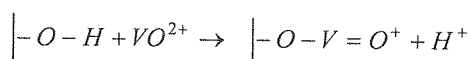
In the positive half cell, the reactions occur as:



As can be seen from this reaction, the charge and discharge processes at the positive electrode involve the transfer of an oxygen atom which is likely to be the rate determining step in the overall mechanism. The availability of oxygen groups on the electrode surface would thus be expected to affect the overall rate of the reactions. Thus, during charge, the first step involves the transport of VO<sup>2+</sup> ions from the bulk of the solution to the electrode surface and ion-exchange with hydrogen ions of the phenolic functional groups on the graphite surface;



or:



# Electrochemical Performance of Graphite Felt/Carbon-Polymer Composite Electrodes (II): Effect of Thermal Treatment of Graphite Felt on Cell Performance

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## Abstract

*Conducting plastic electrodes have been developed and investigated for the vanadium redox flow battery. It was found that although air oxidation of the felt resulted in a slight decrease in electrical conductivity, a significant increase in activity of the felt was obtained with thermal treatment of the felt. Finally, the performance of a vanadium redox flow cell employing the carbon-polypropylene composite electrode was evaluated and voltage efficiencies as high as 95% were achieved at a charge/discharge current density of  $20\text{mA}\cdot\text{cm}^{-2}$ .*

## Keywords

*Carbon-Polymer Composite, Electrodes, Graphite felt.*

## Introduction

A good electrode for the vanadium redox battery should be stable to the 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 studies were focused on evaluation of electrochemical behavior and cell performance tests of the composite electrodes including:

- Constant current charging/discharging;
- Cell efficiencies vs. temperature;
- Cell efficiencies vs. current density;
- Single cell short-term stability and charge/discharge testing;
- Multi cell short-term charge/discharge testing;
- Single cell long-term stability and charge/discharge testing.

## Experimental

Preparation Procedure, electrical properties measurements and cell resistant measurement were described in previous paper [1].

## Thermal Treatment of Graphite Felts

Thermal treatment was used to increase the electrochemical activity of the graphite felt for the vanadium reaction [2]. Samples were placed in a furnace and heated to  $350^{\circ}\text{C}$ . After exposure to air at this temperature for 24 hrs., the samples were removed from the furnace and cooled.