Effect of Electrochemical Cell Overcharge on Electrical and Electrochemical Properties of Polymer Composite Electrodes (II): Mechanism of Electrode Deterioration

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ABSTRACT

Electrical and electrochemical studies show that the carbon-polyolefin composite is a suitable electrode matrix material for the vanadium redox battery. The effect of overcharge on the performance of the vanadium redox cell that employs conductive carbon-polymer composite/graphite felt electrodes is examined. The electrical resistivity of the electrode and the cell resistance show a dramatic increase after overcharge. The effect of overcharge on the electrical resistivity and surface chemistry of the graphite felt are also investigated.

Key Words: carbon-polyolefin composite, vanadium redox flow battery, electrode, electrical resistivity

INTRODUCTION

It was reported earlier [1] that conductive plastic materials with volume resistivity as low as 0.5 Ω·cm can be fabricated from mixtures of carbon black and graphite fibre. On the positive electrode of the vanadium redox flow battery, the felt active layer works as an anode and contacts an oxidizing electrolyte during cell charging. Furthermore, at high states-of-charge, oxygen evolution takes place. Therefore, if the cell is overcharged, oxygen evolution becomes the predominant reaction in the positive half of the vanadium redox flow battery (Table 1).

The changes in the structure of composite electrode such as surface chemical characteristics of the graphite felt under these operating conditions are important, because they will directly affect the electroactivity and life cycle of the electrode in the vanadium redox flow cell.

EXPERIMENTAL

The materials and experimental procedures are as previously described [2]. The new materials and instrumentation are as follows:

Conductive filler: Vulcan XC-72 (Cabot Corp., Billerica Technical Centre, USA).

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Table 1. Effect of overcharging on the area resistivity of electrodes after 70 min total overcharge at 20 mA.cm$^{-2}$.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Area resistivity (R) (Ω.cm$^2$)</th>
<th>ΔR (Ω.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before overcharging</td>
<td>After overcharging</td>
</tr>
<tr>
<td>Positive</td>
<td>2.8</td>
<td>101.7</td>
</tr>
<tr>
<td>Negative</td>
<td>2.7</td>
<td>2.95</td>
</tr>
</tbody>
</table>


SEM Studies
To evaluate the surface microstructure of the selected samples, cross-section and surface of the composite materials were examined with a “Hitachi FESEM S-900” field emission scanning electron microscope. Samples were cut at a temperature of around 150 °C in liquid nitrogen. The surface was then covered with a thin chromium layer.

RESULTS AND DISCUSSION
Because of the conflicting conclusion from earlier overcharge studies [2], a more detailed investigation of this phenomenon was seen to be essential. Thus, an electrochemical study was undertaken in the present work to investigate the effect of cell overcharging on electrode active layer and substrate. As mentioned in a previous publication [2], the oxidation/reduction of hydroquinone/quinone-like groups on the surface of the graphite felt occurs during cycling of the positive electrode between the upper and lower voltage limits of the vanadium battery. Thus during charging at the positive potential, the concentration of surface –OH and –O groups increases, while during discharging a partial reduction of the graphite surface can occur. Application of a negative potential can further increase the degree of reduction of the C surface. After each 10 min overcharge cycle, therefore, the cell was subjected to over-discharging for the same period of time (a negative potential was applied to the cell) to reverse the graphite felt surface oxidation reactions. Figure 1 shows that after each over-discharging cycle, the cell resistance decreased slightly. This supports the theory that electrochemical oxidation of the felt layer by formation of high oxygen containing surface functional groups leads to a loss of its electroactivity toward the V(IV)/V(V) redox reactions. In addition, the conductivity of the graphite felt also depends on the transfer resistance of the individual fibres. An increase of oxygen containing

Figure 1. Effect of negative potential on cell resistance of vanadium redox flow cell with the EPDM modified carbon HDPE composite/heat treated Signi GF05 felt electrode (i: 20 mA.cm$^{-2}$, duration of each overcharge cycle: 10 min).

Figure 2. Surfaces of positive (a) and negative (b) electrodes after overcharging for 20 min (I: 20 mA.cm$^{-2}$; duration of each overcharge cycle: 10 min).
surface groups increases the transfer resistance and this has a negative influence on the electrical conductivity. The dark surface and "charred" appearance of the positive electrode after overcharge also confirmed the existence of these functional groups which were not observed on the negative electrode (Figure 2).

On the other hand, although discharging of an overcharged cell slightly reduced cell resistance, but it was not significant. This suggests, however, that while the deactivation of the graphite felt/composite electrode is slightly reversible, there should be another irreversible process responsible for electrode deterioration.

Effect of Overcharge on Electrical and Electrochemical Properties of Graphite Felt

To confirm the previous conclusion, as well as earlier claims that formation of high oxygen containing functional groups, especially –CO₃ are responsible for the felt/composite electrode deterioration under overcharge conditions [3], an experimental approach in which the physical detachment of the felt layer from its substrate would not interfere in the oxidation study of the graphite felt electrode was required. Therefore, by eliminating the possible effect of polymeric substrate deterioration or physical detachment of the felt layer from its substrate, the contribution of electrochemical oxidation of the graphite felt electrodes to any loss in electroactivity or increase in the activation overpotential component of the cell resistance, could be evaluated.

To study the effect of overcharge on the felt layer of the composite electrode and on cell performance and also to eliminate the possible problem of physical detachment of graphite felt, a modified NASA-design cavity fill-in flow cell was employed as a test flow cell (Figure 3). The design of the cell is such that graphite felt electrode is compressed between a membrane and a graphite plate current collector in either side of the cell. Therefore the relationship between surface functional groups and electrical resistance of the felt layer during overcharge or anodic oxidation could thus be investigated.

The X-ray photoelectron spectroscopy and cell resistance measurement were used before and after overcharge to understand more about the quality, quantity and influence of the functional groups on the surface of the Sigri GFD5 graphite felt electrode.

XPS Studies of Overcharged Graphite Felt.

The surface chemistry of the overcharged samples of electrode was compared with those samples which had been heat treated at 350 °C for 24 h. Comparison with heat treated sample was done because, as it was mentioned before, heat treated Sigri graphite felt was used in the vanadium redox cell rather than untreated felt.

Figure 4 illustrates the overall XPS spectra of the heat treated and GFD5 felt samples overcharged for 1 h. As can be seen, in both spectra there is only one strong and intense C(1s) peak at about 284.6 eV binding energy. Two weak O(KLL) and C(KVV) Auger peaks at around 760 eV and 1000 eV are, respectively, observed. The O(1s) peak which appears in both samples at about 533 eV, increases from the heat treated to the overcharged sample. There is no significant peak from other elements indicating that their contents should be very low.

Table 2 shows the atomic oxygen concentration of the felt increases slightly from 15% to 16.5% after overcharging.

To determine the oxygen functionality of the felt before and after overcharging, the high resolution spectra of the C(1s) peaks were obtained. Figures 5(a)
Effect of Electrochemical Cell Overcharge on Electrical and Electrochemical

Figure 4. XPS spectra of graphite felt (a) heat treated at 350 °C for 24 h, (b) heat treated under the same conditions and then overcharged for 1 h.

and (b) present the curve-fitted C(1s) spectra of heat treated and overcharged samples. The spectra have been fitted to various carbon/oxygen functional groups known to be found on carbon/graphite surfaces mainly based on Sherwood and co-workers’ assignment [4, 5].

The main peak at the lowest binding energy is the graphite peak at 283.6–284.6 eV. The four types of oxides designated as 1, 2, 3, and 4 were shifted by 1.5, 3, 4.5, and 6.1 eV from the main peak, respectively. Oxide 1 corresponds to carbon atoms in hydroxide (C–OH) or ether (C–O–C) groups. Oxide 2 is assigned to carbon atoms in carbonyl (C=O) type groups. Oxide 3 is the peak corresponding to ether carboxyl (COOH) or ester (COOR) types of groups. Oxide 4 is probably –CO₃ type groups, and the π–π* shake up satellite also falls in this range [6].

Table 2 presents the peak position and peak area percentage for the C(1s) spectra. As can be seen for both the samples the oxide 4 C(1s) peak is very weak and decreases slightly after overcharge. It can also be seen that overcharge results in an increase in the oxide 1 peak area. On the other hand, both C=O and COOH groups decrease after overcharge.

Operation under 1 h anodic oxidation condition of overcharge thus results in slight oxidation of the graphite felt and a change in the carbon/oxygen functional groups especially the –OH groups. More importantly, the results show that the –CO₃ type groups form only about 0.15% of the total oxide produced on the surface of the felt electrode even after 1 h under overcharge conditions. It can thus be concluded that the formation of this functional group on the surface of the felt electrode should not be a major contributor to any serious changes in the electrical and electrochemical properties of the felt electrodes.

### Table 2. The effect of overcharge on surface carbon and oxygen atomic concentration and carbon oxygen ratio in Sigri GFD5 graphite felt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of oxygen</th>
<th>Percentage of carbon</th>
<th>Percentage of oxygen/carbon ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treated</td>
<td>15.0</td>
<td>85.2</td>
<td>17.6</td>
</tr>
<tr>
<td>Overcharge</td>
<td>16.5</td>
<td>83.6</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Cell Resistance Measurement of Overcharged Graphite Felt

Cell resistance was also used as a criterion for evaluation of the entire system resistance before and after overcharge. To avoid any interference from...
oxidation of the positive graphite current collector which also occurs during overcharge, after each overcharge experiment, the cell resistance measurement was repeated after polishing and through washing of the positive current collector until an even, clean and conductive surface was obtained. The cell resistance measured should thus reflect the effect of overcharge on the oxidation of the graphite felt rather than oxidation of the current collector.

Furthermore, the electrical resistivity of the graphite felt was also measured before and after overcharge. Any changes in electrical resistivity of the graphite felt electrodes which might be caused by damaged graphite fibre or formation of very low conductive graphite oxide were thus investigated.

To compare the results of this study with those obtained with others [3, 7], the same graphite felt materials and also the same overcharge conditions, such as current density and oxidizing solution were employed.

Tables 4 and 5 show the effect of overcharge on the electrical resistivity of Sigri graphite felt material in 2M VO$_2^+$ / 3M H$_2$SO$_4$ solution at 20 mA.cm$^{-2}$ for 70 min. As can be seen, even after 1 h
overcharging, volume and area resistivities of the positive graphite felt only increased by 0.15 \( \Omega \cdot \text{cm} \) and 1.57 \( \Omega \cdot \text{cm}^2 \), respectively. In addition, very small increases in both volume and area resistivities of negative electrodes were observed.

Comparison of Tables 1 and 5 however, shows that although the area resistivity of the positive felt increased by 1.57 \( \Omega \cdot \text{cm}^2 \), this is negligible compared with the increase of 98.9 \( \Omega \cdot \text{cm}^2 \) observed in the area resistivity of the graphite felt/conductive polymer electrode. Furthermore, while the overall cell resistance of the cell employing the graphite plate current collector increases to 4.5 \( \Omega \cdot \text{cm}^2 \) after 70 min overcharge, for the cell employing graphite felt/conductive polymer electrodes the cell resistance was more than 50 \( \Omega \cdot \text{cm}^2 \) after the same amount of overcharge.

These results thus confirm that the formation of functional groups on the surface of felt electrode should not be a major contributor to any serious changes in the electrical properties of the graphite felt/conductive composite electrodes. In other words, anodic oxidation or overcharge conditions are more serious for the graphite/conductive polymer electrode than for graphite felt alone.

### Table 3. XPS Results from C(1s) peak curve fitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Main peak</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P(eV)</td>
<td>A(%)</td>
<td>P(eV)</td>
<td>A(%)</td>
<td>P(eV)</td>
</tr>
<tr>
<td>Heat treated</td>
<td>284.0</td>
<td>68.0</td>
<td>285.5</td>
<td>18.0</td>
<td>288.0</td>
</tr>
<tr>
<td>Overcharge</td>
<td>283.5</td>
<td>69.0</td>
<td>285.0</td>
<td>22.5</td>
<td>286.5</td>
</tr>
</tbody>
</table>

\( P = \text{position}; A = \text{area}; O = \text{oxide}. \)

### Influence of Overcharge on Carbon-Polymer Composite Electrode

Figure 6 shows XPS spectra of the graphite felt (separated from the surface of the conductive polymer substrate) after being subjected to the same overcharge conditions in the vanadium redox cell. Comparing Figures 4(b) with 6(a) and also 5(b) with 6(b) shows similar peaks, with no evidence of any volatile content from the polymeric substrate which could contaminate the graphite felt.

To establish the main contributor to the graphite felt/conductive polymer electrode deterioration, the overcharging time was increased to 2 h. At this point physical detachment of the felt layer from its substrate; i.e. formation of a gap between the felt layer and the conductive composite substrate was clearly observed. Further study and investigations revealed that, decomposition of the graphite felt did not occur at the interface of the graphite felt and composite substrate destroying the electrical contact between the felt and substrate. Instead, a thin layer (skin) of composite was lifted with the graphite felt from the surface of the polymeric substrate (Figure 7). Delamination of the conductive polymer substrate is thus responsible for positive electrode deterioration.

### Table 4. Effect of overcharge on volume resistivity of graphite felt (Sigri GFD5) material, overcharged with 2M \( \text{VO}_2^+/3\text{M H}_2\text{SO}_4 \) for 70 min at 20 mA.cm\(^{-2}\).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Volume resistivity ((\mu)</th>
<th>((\Omega\cdot\text{cm}))</th>
<th>(\Delta \mu)</th>
<th>((\Omega\cdot\text{cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before overcharge</td>
<td>0.1040</td>
<td>0.2557</td>
<td>0.1517</td>
<td>0.009</td>
</tr>
<tr>
<td>After overcharge</td>
<td>0.1113</td>
<td>0.1203</td>
<td>0.009</td>
<td>0.009</td>
</tr>
</tbody>
</table>

\( \Delta \mu = \mu_{\text{after overcharging}} - \mu_{\text{before overcharging}} \)

### Table 5. Effect of overcharge on area resistivity of graphite felt (Sigri GFD5) material, overcharged with 2M \( \text{VO}_2^+/3\text{M H}_2\text{SO}_4 \) for 70 min at 20 mA.cm\(^{-2}\).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Area resistivity ((R)</th>
<th>((\Omega\cdot\text{cm}^2))</th>
<th>(\Delta R)</th>
<th>((\Omega\cdot\text{cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before overcharge</td>
<td>0.35</td>
<td>1.92</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>After overcharge</td>
<td>0.36</td>
<td>0.53</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

\( \Delta R = R_{\text{after overcharging}} - R_{\text{before overcharging}} \)
Effect of Overcharge on Carbon-Polymer Composite

Since the degradation of the carbon-polymer composite substrate itself was found to be the main contributor to electrode failure, so during extended overcharge of the vanadium battery an attempt was made to find the reason for this degradation.

As there are only two phases in the composite, i.e., polymer and filler, two processes can contribute to the composite degradation under overcharge conditions in the vanadium redox system:

- Oxidation and degradation of the polymeric phase (e.g. HDPE).
- Consumption of carbon black by oxygen to produce CO$_2$ below the surface. This gas would be trapped in the composite matrix and subsequently crack and degrade the matrix.

In the first case, it is generally accepted that polymers are degraded by a free-radical mechanism. The term “degradation” is used to describe any undesirable changes in the properties of a polymer. Protection of a polymer against oxidative degradation can be achieved by blending the polymer with appropriate stabilizers. Antioxidants are required as a minimum to protect the polymer from chain scission during overcharging. However, antioxidants do not completely eliminate oxidative degradation, although they markedly retard the rate of autoxidation by interfering with radical propagation [8].

Secondary aromatic amines and hindered phenols belong to the family of antioxidants that inhibit oxidation by a chain-breaking antioxidant mechanism. Chain breaking antioxidants are those that retard the oxidation by intercepting either R$^\circ$ or ROO$^\circ$ free radicals that propagate the kinetic chain. The antioxidants give up an H$^\circ$ radicals to deactivate polymer free radicals, that is:

$$\text{R}^\circ + \text{AH} \rightarrow \text{RH} + \text{A}^\circ$$

where R$^\circ$ is the polymeric free radical and AH is the antioxidant. If the A$^\circ$ were to react with the polymer, further propagation of the oxidation reaction would...
occur. This is prevented by the aromatic nature of the antioxidants, which forms a resonance-stabilized phenoxy radical that, in many cases, reacts with an additional polymer radicals, thereby increasing the efficiency of the antioxidant [9].

To further improve the performance of the HDPE in the overcharged vanadium solution, three types of antioxidants (i.e., Irganox 1010, 1010 Master batch and 254) were separately blended with the composite. However, even up to 5% of these antioxidants did not prevent oxidative degradation of the composite and instead, the brittleness of the composite increased dramatically. The performance of certain antioxidants are thought to reduce in the presence of carbon black owing to the adsorption on the surface of carbon black particles [10]. This would explain the ineffectiveness of the antioxidants in this material.

The same susceptibility to attack by the strong oxidizing conditions, was also observed when the HDPE was replaced by PP in the composite. The same trend was observed with and without EPDM. In fact replacing the EPDM with SEBS resulted in a more severe oxygen degradation of the composite which can be related to the easier degradation of unsaturated bonds in this rubber.

On the other hand, in the case of second mechanism (oxidation of carbon black to CO₂), it is reported that carbon and graphite are stable in most

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**Figure 7.** Physical detachment of the positive graphite felt electrode under overcharge conditions. (Section A is the underlying composite surface; B is the graphite felt; C is the composite which is still attached to the felt even after physical detachment.)

**Figure 8.** SEM Surface micrographs of the surface skin of the carbon-HDPE composite substrate after overcharging (positive side).
boiling dilute acids, but are attacked by concentrated oxidizing acids, especially at elevated temperatures [11]. Sulphuric acid which is used in the vanadium solution is a relatively strong oxidant and its interaction with graphite/carbon electrodes has been reported in a number of studies [12, 13]. In addition vanadium is a good catalyst for CO₂ formation and subsequent carbon consumption in the composite matrix.

As can be seen from Figure 8, there are several holes and micro-cracks on the surface (upper skin) of the composite. Figure 9 also shows that degradation of the bulk of the composite has also occurred. Comparing the Figures 8 and 9 it reveals that destruction is higher in the bulk (with high carbon content) than in the skin (with lower carbon content) of the composite. The higher carbon content thus results in greater degradation.

In order to determine the effect of different carbon blacks on the composite degradation, the XE-2 and FW-200 were replaced by Vulcan XC-72. It was found that after 30 min overcharging, the cell resistance reached 6.9 Ω.cm² for Vulcan XC-72. Comparing these results with that obtained for XE-2 and FW-200 (20 Ω.cm²) under the same conditions, it can be seen that type and obviously the structure of the carbon black is a major parameter in the composite degradation under highly oxidizing overcharge conditions. This behaviour may be related to the oxygen evolution on the surface of the carbon black. A separate study of the oxygen evolution reaction on conductive polymer composite did in fact show that the rate of this reaction is higher for XE-2 than for Vulcan XC-72 [14].

Therefore, it can be concluded that due to the microporous surface of the composite, the acidic solution can penetrate into the bulk of the composite sheet where a higher concentration of carbon black particles is available. Oxygen evolution on the carbon black leads to CO₂ formation which results in consumption of the carbon particles. Furthermore, the evolution of these gases below the surface skin layer destroys the substrate, resulting in electrode delamination and consequently very high electrical resistivity of the electrode.

CONCLUSION

The XPS analysis revealed that the surface oxygen content of the Sigri GFD5 felt increased with increasing severity of oxidation due to overcharge. Overcharge conditions will result in a slight oxidation of graphite felts by formation of various carbon/oxygen functional groups particularly -OH group. These results show that the -CO₂ type groups form only about 0.15% of the total oxide produced on the surface of the felt electrode, even after 1 h being under overcharge conditions in the vanadium redox cell. In addition, although discharging of the overcharged cell and applying a negative potential can remove the functional groups from the surface of the graphite felt, the cell resistance decreased only slightly and this decrease was not significant. It was thus concluded that although graphite oxidation in the cell leads to a slight decrease in its conductivity due
to formation of carbon/oxygen functional groups, it is not the major contributor to the increased cell resistance after extended overcharge. Results of this study have in fact shown that oxidation of carbon black particles leading to CO$_2$ formation and subsequent destruction of the composite matrix, is the main contributor to the electrode deterioration.

**REFERENCES**