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Novel bipolar electrodes for battery applications

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Abstract

A novel bipolar graphite felt electrode for use in redox flow batteries and other electrochemical systems is described. The new electrode features a unique approach in the design of bipolar electrodes, employing carbon black free, nonconductive polymer materials as substrates. This innovation allows a dramatic reduction of processing time and cost compared to conventional carbon polymer composite electrodes used in bipolar battery systems. The conductivity of the new electrode assembly is similar to that of conventional bipolar electrodes, however, it shows significant improvements in mechanical properties. The functionality of these novel electrodes has been evaluated in the vanadium redox battery application and the results show comparable performance with conventional composite materials. An important operational advantage, however, is that side reactions leading to the deterioration of conductive filler in the electrode substrate material (i.e., electrode delamination due to CO_2-evolution) during cell overcharging are eliminated, making these electrodes more durable than the conventional designs. To date, these bipolar electrodes have been applied in vanadium redox cells but their design and properties promise further applications in a range of other redox flow batteries and bipolar electrochemical cell systems.

1. Introduction

Much of the research on bipolar electrode designs has focused on finding an optimum material for the bipolar substrate. The main requirements of a suitable material are stability in the electrolyte, high oxygen and hydrogen overvoltage and good conductivity of the electrochemically active parts of the bipolar electrode [1]. Among such materials carbon–polymer composites have played an important and promising role in the last two decades of bipolar battery research which has included zinc–bromine, iron chromium, and more recently, bipolar lead–acid battery development [2–10]. A number of industrial electrochemical applications including waste and mineral processing [11] have also been suggested; however, state of the art formulations of such carbon plastic composites cannot fulfil all the requirements for various battery applications and commercial products are not yet widely available. Apart from metallic electrodes the electronic conductivity of alternative materials such as carbon-composites is of major interest.

Sufficient conductivity in conventional carbon polymer composites is usually obtained by the addition of 20–30% conductive filler material. Figure 1 illustrates the general relationship between resistance and carbon black content of these materials. Usually, the percolation level indicates the fill grade when the composite turns into a reasonable electrically conductive material. The percolation level indicates the conducting filler content needed to provide a conductive network within the polymer material. This varies with filler material and can be between 10 and 20% conductive filler content.

Although carbon–polymer composite materials offer many benefits over solid carbon or graphite substrates for bipolar electrode applications, such as lower costs and reduced weight, they tend to be labour intensive in their production and they have relatively poor mechanical properties due to high loadings of conductive filler.

A further problem caused by carbon black filler materials is associated with side reactions during battery overcharge operation, that is, water decomposition and gassing in lead–acid cells [13] or irreversible deactivation after severe overcharging in vanadium redox batteries [14,15]. In particular, overcharging conditions can lead to oxidation of the carbon black materials used in the bipolar electrode substrate leading to increased resistance. While oxidation of graphite felt materials will result in formation of carbon/oxygen functional groups, which are removable under reducing conditions, the oxidation of the more reactive carbon black filler material can also lead to CO_2 formation resulting in a destruction of the composite matrix and delamination.

The novel feature of the new electrode design is the use of a plain polymer sheet as the substrate material for

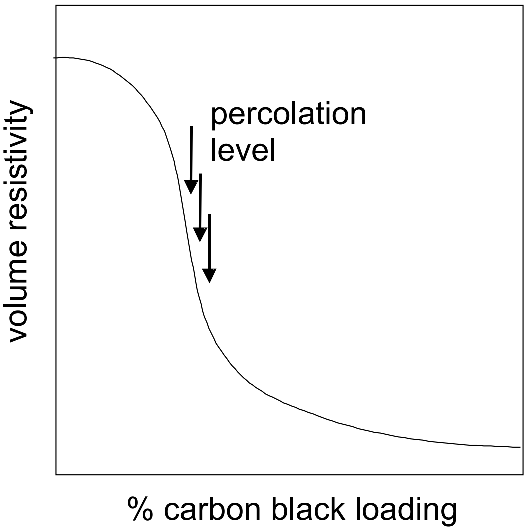

Fig. 1. General electrical resistance characteristic of carbon black polymer composites [10–12].

the bipolar electrodes. Surprisingly it was possible to obtain low area resistivities for the final bipolar graphite felt electrode assemblies when polymer substrate materials with certain flow properties were employed. The main parameters influencing the through conductivity of a conventional bipolar graphite electrode are given by the conductivity of the composite substrate and the attached, usually heat bonded, graphite felt employed as the electrochemically active material (Figure 2).

Optimized formulations are composite materials with relatively high conductive filler loadings, providing good conductivity but low mechanical stability. Furthermore, such materials show relatively low melt flow indices and therefore the penetration of fibres into the conductive substrate material during the heat bonding process is relatively poor. Good conductivity of the substrate material compensates the relatively long distance between opposing felt fibres through the substrate material.

The novel approach is basically characterized by using a completely nonconductive polymer sheet material with melt flow properties enabling a high penetration of carbon graphite felt fibres and interconnection of such fibres during the heat bonding process. The through conductivity is exclusively obtained by the interconnecting graphite fibres and the high melt flow index of the polymeric material guarantees sufficient sealing of the penetrating fibres so that electrolyte leakage cannot occur through the electrode assembly.

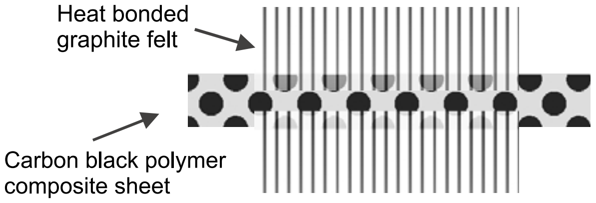

Fig. 2. Schematic of graphite felt bonded bipolar electrode assembly with nonconducting plastic substrate.

The conductivity of the novel bipolar graphite felt composite electrodes produced, however, is comparable to any former optimized electrode design for vanadium redox batteries [15–18]. This paper describes the effect of substrate material properties and felt bonding conditions on the conductivity of the resultant bipolar electrodes. Their performance characteristics during normal cycling and overcharge conditions in the vanadium redox battery are also presented.

2. Experimental details

The following materials were used as substrates for the bipolar electrode:

Material A: High density polyethylene (HDPE) powder, GA 7260H powder, Kemcor Australia.

Material B: Extruded HDPE material provided by E-Plas Pty, Australia, with a thickness of 1 mm was used as sheet material for electrode preparation. Physical properties given in Table 1.

Material C: Extruded low density polyethylene (LDPE) material provided by E-Plas Pty, Australia with a thickness of 1 mm was used as sheet material for electrode preparation. Physical properties given in Table 1.

Material D: Alkathene LDPE granule, grade WSM 168 (Orica Polythene, Australia).

Material E: Alkathene LDPE granule, grade WRM 124 (Orica Polythene, Australia).

Material F: Alkatuff, Grade 710 UV LDPE granules (Orica Polythene, Australia).

Materials A and D–F were used as granular materials for compression moulding. The sheets were pressed for 10 min in an aluminium mould with the inner mould dimensions of 110 mm × 100 mm × 1 mm under a pressure of 43 kg cm^{-2} and a temperature of 135–155 °C. The mould was preheated for 10 min before applying the pressure. After pressing, the mould was quenched in a cold water tank. Physical properties of resultant polymer sheets given in Table 1.

Materials A–F were used as substrate materials for producing bipolar graphite felt electrodes. The bipolar electrodes were obtained by heat bonding a sheet of graphite felt to each side of the substrate material. The graphite felt sheets (FMI Graphite, USA, 50 mm × 50 mm × 2 mm) were placed into frames on both sides of the polymer sheet and heat bonded to the centre of substrate materials A-F (100 mm × 110 mm × 1 mm). The felt bonding was conducted for various times at 155 °C and an applied pressure of 2.2 kg cm^{-2}, unless stated otherwise.

The properties of bipolar electrodes fabricated using standard high carbon black (20–30%, carbon black filled PE and PP) and low carbon black (1–3%, SIC electrode, for preparation see [15]); substrates were also evaluated for comparison and shown in Table 1.

Table 1. Mechanical properties (ASTM D-638) of composite sheets and melt flow index of substrate material (ASTM 1238)

Material	MFI 190/2.16 [g/10 min]	Tensile strength/MPa	Δ *L* /mm	Elongation /%	Elastic Modulus /GPa
A	17.5	26.0	No break	>400	–
B	N/A	26.0	No break	>400	–
C	N/A	23.7	No break	>400	–
D*	63	8.2		315	0.168
E*	22	8.9		290	0.158
F*	10	15		470	0.408
SIC [15]	18.5	26.2	1.65	4.1	0.62
Standard PE composite [17]	N/A	23.1	2.3	4.7	0.49
Standard PP + rubber composite [17]	5 (195/5)	22.1	0.68	1.7	1.30

* Data provided by Orica Polythene, Australia.

Mechanical properties of the substrate materials were characterized by the values of percentage elongation and tensile strength at break. This was measured using an Instron M 1185 universal testing machine. The bipolar electrodes were characterized according to the following tests:

Test I. Area resistivity characterization of the investigated electrodes was done by means of setting the bipolar electrodes between two copper plates and applying a pressure of 0.2 kg cm^{-2}. The potential drop was measured at various currents applied to the copper plates and the area resistance calculated.

Test II. For the static permeability, the bipolar electrode was assembled between two electrolyte compartments containing a 2 mol vanadium solution on one side (1 M V(III) + 1 M V(IV) in 2 M H_2SO_4 referred to as V(3.5+)) and a 2 mol H_2SO_4 solution on the other side of the graphite felt area. Permeation of the vanadium solution through the electrode at the graphite felt area was tested by means of u.v.–vis. analysis of the H_2SO_4 solution.

Test III. For the dynamic permeability, the bipolar electrode was assembled in a flow cell, where a 2 mol vanadium solution (V(3.5+)) was pumped through on one side and a 2 M H_2SO_4 on the other side of the graphite felt area. Permeation of the vanadium solution through the electrode at the graphite felt area was tested by means of u.v.–vis. spectroscopy (Varian, Cary 3 u.v.–vis. spectrophotometer) on the H_2SO_4 blank solution to determine the presence of any vanadium ions.

Test IV. Overcharging behaviour: The bipolar electrode was overcharged for various periods at 40 mA cm^{-2}. Area resistivity before (R_{start}) and after overcharging (R_{OC}) was measured according to test I. The resistivity of the electrodes was further measured after setting up the cell in a reverse polarity mode (R_{rev}).

Test V. For cell performance, vanadium redox cells employing the bipolar electrodes were cycled between 800 and 1800 mV cell voltage limits at 40 mA cm^{-2}. Cell voltage was recorded as a function of time using a Yokogawa 3057 X,t chart recorder. The main components of a typical test cell are illustrated in Figure 3. The test cell consisted of two end-electrodes (glassy carbon sheets on copper current collectors), the bipolar test electrode in the positive half cell and a graphite felt in the negative half cell. A sheet of Nafion® 112 membrane was placed between the test electrode and the negative graphite felt using two flow-frames and rubber gaskets.

3. Results and discussion

The properties of the polymer component of conventional carbon black polymer composites are usually characterized by a low melt flow index to obtain the required mechanical properties. Consequently, using low carbon black fill-grades with such low melt flow index polymers resulted in bipolar electrodes with very high resistance. Thus, under felt bonding conditions established earlier for carbon–polymer composite substrates, the heat bonded graphite fibres were not able to penetrate deeply enough to interconnect and build a conductive bridge between the opposing graphite felt layers. Using previously determined conditions with

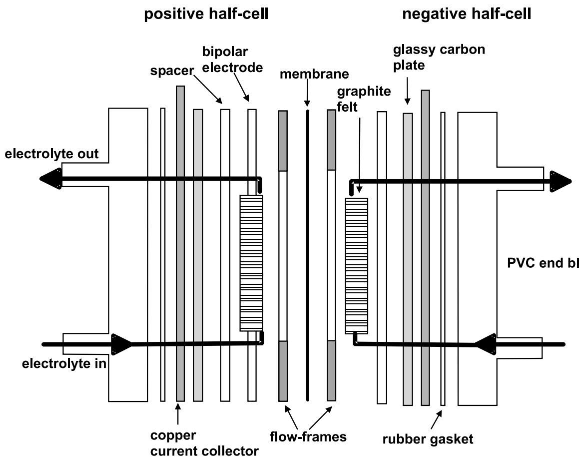

Fig. 3. Schematic diagram of stack components of a vanadium redox flow test cell (exploded cross-sectional view).

non-conducting substrate material resulted in final electrode assemblies with very high resistance.

It was thus necessary to increase the felt bonding temperature (which is undesirable since increased polymer degradation occurs at higher temperatures), or to select polymeric substrate materials with high melt flow index for adequate penetration of the graphite fibres.

Various polymeric materials used as substrates in the novel bipolar electrode design, were thus investigated for their mechanical properties. The tensile strength and melt flow index of a range of polyethylene materials were tested according to ASTM-Methods D-638 and 1238 respectively. Table 1 shows the mechanical properties of materials which were employed as substrates for preparation of bipolar electrodes in the present study. Area resistivity measurements were employed to compare the carbon black free bipolar electrodes with original carbon plastic composite electrodes employed in vanadium redox prototype batteries to date. Bipolar electrodes were also fabricated from low carbon black plastic substrates described elsewhere [15], and their resistance values measured for comparison.

As shown in Table 2, for a number of the substrates tested, resistivity values obtained according to test 1 described in Section 2, are comparable to any previous electrode type used in the vanadium redox battery.

Thus, material D with the highest melt flow index gave an area resistivity of 0.6 Ω cm^2 when used for the fabrication of a bipolar electrode. Material C produced a bipolar electrode C1 (with 8–18 Ω cm^2 resistance) when the 2 mm graphite felt was compressed on each side using a 2 mm window. When an additional 1mm reinforcing plate was inserted into the mould to decrease the cavity thickness however, the consequent higher applied pressure resulted in a bipolar electrode C3 with an area resistivity of 1.1–1.3 Ω cm^2. In addition, depending on the type of substrate used, the felt bonding time had a critical influence on the conductivity of the final bipolar electrodes. The effect of felt bonding time on conductivity using different substrate materials (materials A–C) is shown in Figure 4.

Table 2. Area resistivity of bipolar electrodes produced from different substrate types

Electrode type	Area resistivity /Ω cm^2
A1	0.5–0.8
B1	>1000
C1	8–18
D1	0.6
E1	0.7
F1	1.0
A2*	0.4
F2*	0.5
C3*	1.1–1.3

* Reinforcing copper plates added to mould during felt bonding process to increase applied pressure during bonding.

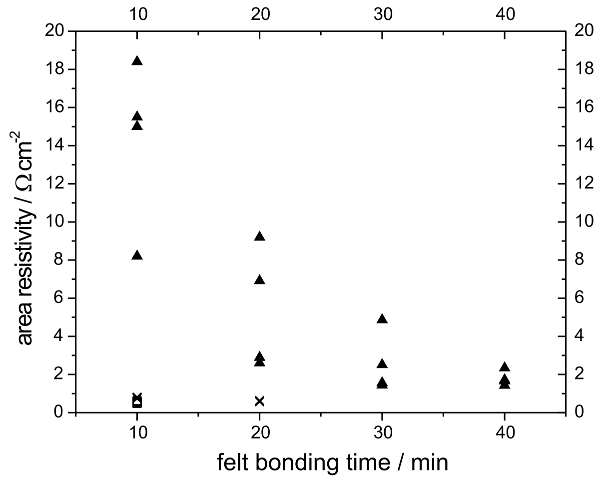

Fig. 4. Effect of felt bonding time on conductivity of bipolar electrodes. Key: (×) substrate A, (▲) substrate C, (□) Substrate D. Substrate B showed resistivities over 1000 Ω cm^2 after 40 min felt bonding.

Figure 4 illustrates that even with substrate materials characterized by relatively low melt flow indices reasonable interconnection of the felt fibres and therefore sufficiently low resistivity are achievable after sufficient time in the felt bonding step. Thus, even material F which showed the lowest melt flow index in Table 1, was able to produce low area resistivities under appropriate felt bonding conditions of temperature and applied pressure, as seen in Table 2. On the other hand, the materials with high melt flow indices required short felt bonding times under the same conditions of temperature and pressure.

A basic requirement for bipolar electrodes to hinder any cross-contamination or unintentional electrolyte transport through the cell is impermeability. In conventional high fill-grade electrodes the porous carbon black material cannot guarantee a lifetime impermeability of the material and processing conditions must be carefully controlled to prevent formation of voids. The reject rate is however, still quite high. The novel carbon black free electrode design produced with material A was tested according to procedures described under tests 2 and 3 and no evidence of electrolyte permeation was evident over a test period of two months.

In addition to the physical properties, the performance of novel bipolar electrodes was also investigated in a vanadium redox battery. By using the same electrochemically active graphite felt layer (FMI, USA), the evaluation of novel electrodes could be compared to test results achieved with former electrode designs. Further tests (tests 4 and 5) were carried out on electrodes produced with substrate material A and compared to standard bipolar electrodes used in vanadium redox cells.

A severe problem for bipolar electrodes based on carbon plastic composites is the electrochemical activity of the carbon black filler material. Especially under extended overcharging conditions, materials like carbon black or graphite fibres can be oxidized at the positive electrodes in a cell stack. Although the oxidation of graphite fibres is more or less reversible, oxidation of the carbon black filler in surface layers of the composite, can result in CO_2 evolution and decomposition of the composite material. In the case of standard composite electrodes where typically a graphite felt is heat-bonded to a carbon black filled plastic composite substrate, such overcharging results in delamination of the substrate surface film and breakdown of electrode functions. Due to the carbon black free nature of the new substrate material, this concern is eliminated and therefore, longer electrode life and high resistance against overcharging are imparted. The following results obtained after severe overcharging illustrate excellent stability of the bipolar electrode compared to standard materials which show delamination effects and therefore an irreversible increase in electrical resistance. The novel materials show slightly higher area resistivity values after overcharging which can be reduced by reversing the polarity of the cell. Due to this higher resistance against overcharging, monitoring of the state of charge of single cells in a battery stack becomes no longer necessary and reduces set up costs and maintenance of battery systems.

In Table 3 novel electrodes are compared to standard high carbon black (20–30% CB content) composites and already improved low carbon black electrode materials (2–3% CB content produced by SIC process [15]). Thus, in the case of the standard high carbon black polypropylene composite (standard PP) positive electrode, the area resistance increases from 0.5 to 33.5 Ω cm^2 after 60 min of overcharging at 40 mA cm^{-2}. Reversing the polarity of the cell to reduce any oxidation products on the graphite felt did not lead to any reduction in the area resistance showing that overcharging causes irreversible degradation of the standard composite electrode. Cell polarity reversal involved first discharging the cell to 800 mV and then reversing the polarity of the terminals. The cell was then charged under reverse conditions at a current density of 40 mA cm^{-2} for the same time as it was previously overcharged. In the case of the novel electrode A1 the same amount of overcharge caused the resistance to increase from an initial value of 0.6 to 5.5 Ω cm^2. Previous studies [18] have shown that this is due to the formation of oxygen functional groups on the surface of the carbon graphite felt under these highly positive voltage conditions. However, reversal of the cell polarity resulted in a significant decrease in electrode resistance showing that for the new material, overcharging gives rise to reversible processes and no permanent losses in performance occur.

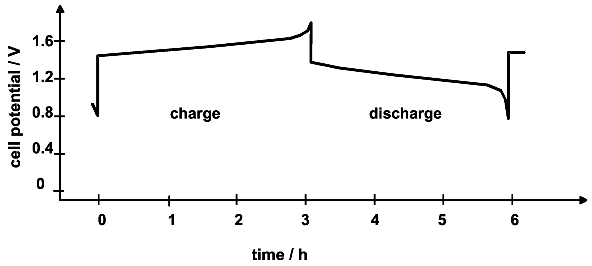

Fig. 5. Typical charge–discharge behaviour of novel bipolar electrode in vanadium redox cell. $i_{\text{charge}} = i_{\text{discharge}} = 40$ mA cm^{-2}.

Hence, if oxidation products during overcharging can be reduced by reversing the polarity of the cell, a recovery of the electrode is possible.

To complete the evaluation of the new electrode material, cycling tests were carried out according to the description under test V and cell performance was determined. A typical charge–discharge curve for the novel bipolar electrode is shown in Figure 5. From the average discharge and charge voltage values, a voltage efficiency of 80% is calculated, while from the ratio of discharge time to charge time a coloumbic efficiency of 91% is calculated. These values are comparable to those obtained with standard PP composite electrode tested under similar conditions. When an extra sheet of graphite felt was inserted into each half cell between the bipolar electrode and the membrane, greater compression of the felt causes a decrease in cell resistivity, thus leading to an increase in voltage efficiency. Comparison with standard electrode materials showed similar and acceptable performance in terms of coulombic, energy and voltage efficiencies. Results are summarized in Table 4.

The following explanation shows the importance of the melt flow behaviour on the conductivity of bipolar electrodes. A cross section of such a bipolar electrode is illustrated schematically in Figure 6. An important function of the composite material is to provide a conductive pathway between the facing graphite felt fibres. The distance of the graphite fibres depends on conditions used during the felt bonding process and on fluidity of the composite material, which is crucial for penetration of the graphite felt into the substrate layer.

Table 3. Overcharging effects on A1 electrodes, low carbon black electrodes (SIC, [15]) and conventional high carbon black loaded composite electrodes

Type	R_{start} /Ω cm^2	OC time /min	R_{OC} /Ω cm^2	R_{rev} /Ω cm^2
A1	0.5	30	3.3	1.0
A1	0.6	60	5.5	2.2
SIC	0.7	60	15.0	6.1
Standard PP	0.5	60	33.5	33.5

Table 4. Cell performance

Electrode-type	Electrode resistivity /Ω cm^2	i /mA cm^{-2}	Coulombic efficiency η_c	Energy efficiency η_E	Voltage efficiency η_V
A1	0.8	40	0.91	0.79	0.86
Standard PP	0.8	40	0.91	0.80	0.88
A1 plus extra felt	0.8	40	0.94	0.82	0.88

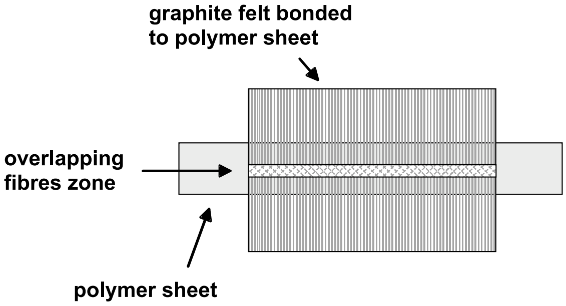

Fig. 6. Schematic of a bipolar electrode with nonconducting plastic substrate.

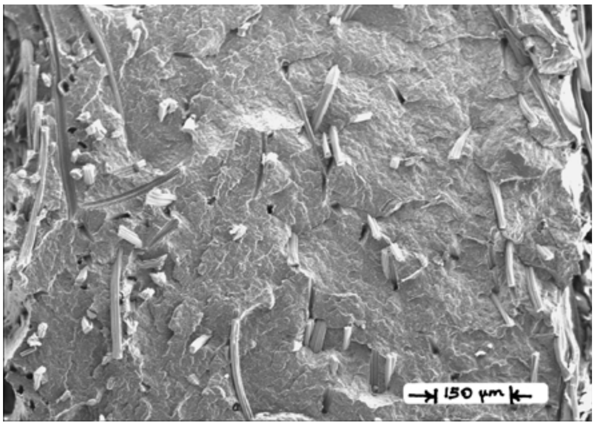

Fig. 7. FESEM micrograph of a cross-section of a bipolar electrode substrate with zero carbon black.

The micrograph of a cross section of a bipolar electrode illustrated in Figure 7, shows penetrating felt fibres from both sides of the composite sheet, overlapping and interfering with each other. The majority of the graphite felt fibres should penetrate into the composite from each side by at least 50% of the cross section of the composite so that overlapping opponent fibres are able to support the current transport exclusively. As can be seen in Figure 7 the arrangement of the bonded graphite fibres is of no specific order. The fibres are randomly oriented and form a dense electrically conductive network within the polymer sheet material.

4. Conclusions

A completely novel approach in the design of bipolar composite electrodes has been demonstrated in this study. The innovative bipolar electrode is characterized by nonconductive, electrochemically inert polymer materials used as substrate for bipolar electrodes. These electrodes simplify the fabrication process and show significant improvements in overcharge resistance for vanadium redox battery applications. At present the novel electrode is undergoing implementation in full size prototype vanadium redox batteries for golf cart applications. This provides a further step towards commercialization and application of the electrode for a variety of batteries or electrochemical systems employing bipolar electrode designs. The main disadvantages of previous developments are eliminated and further improvements in minimising maintenance as well as increasing reliability are achieved. Thus, the novel design will simplify electrode manufacture by eliminating difficult processing associated with conducting plastic composites. The improved mechanical properties of carbon black free electrodes will also lead to a decreased reject rate during manufacture, which is 50% for conventional composite electrodes. The new electrode design also allows simple assembly without any further precautions such as bonding of insulating frames to the electrode to avoid shunt currents or leakage currents. All of these advantages, coupled with comparable performance, will lead to a drastic cost reduction in the manufacture and realisation of a competitive commercial bipolar redox battery.

Most importantly, however, elimination of the carbon black filler has allowed excellent overcharge resistance to be achieved in redox flow battery applications, thus allowing longer stack life and improved reliability during operation.

These promising features will hopefully also lead to further utilisation of the novel bipolar electrode design in a wider range of electrochemical applications including heavy metal extraction from waste streams and in other redox battery systems such as the new Regenesys S/Br redox cell [19] developed by National Power in the UK and currently being commercialized by Innogy Technologies.

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