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Conductive carbon–polypropylene composite electrodes for vanadium redox battery

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Carbon–polymer composite electrodes have been developed and investigated for application in the vanadium redox flow battery. Electrical, electrochemical, physical and mechanical properties as well as chemical resistance and solution permeability of a wide range of carbon-polymer composite materials were evaluated. Volume resistivities as low as 0.21 Ω cm were achieved with composites based on polypropylene, this being combined with excellent stability. Finally, the performance of a vanadium redox flow cell employing the best composite electrode was evaluated and voltage efficiencies as high as 91% were achieved at a charge/discharge current density of 20 mA cm^{-2}.

1. Introduction

The need for a move to renewable energy systems and a reduced dependence on fossil fuels by the more efficient use of energy has become a more important issue in the last few years. Initial research on the UNSW vanadium redox battery began in the mid-1980s; since then overall energy efficiencies of up to 90% with 1 kW stacks have been reported by Skyllas-Kazacos and coworkers [1–3]. In this system, V(V)/V(IV) and V(III)/V(II) redox couples are used in the catholyte and anolyte, respectively, the vanadium electrolytes being produced by electrolytic dissolution of V_2O_5 powder in H_2SO_4 [2]. As one of the most important components of the battery, the electrode and its related characteristics including cost and processability, has become one of the key aspects of the research and development of the vanadium battery system.

A styrene–ethylene–butylene–styrene thermoplastic elastomer (SEBS) modified carbon-high density polyethylene (HDPE) composite material has been shown to have good electrical and mechanical properties as well as being impermeable [4]. Unfortunately, however, during recent electrode manufacturing trials with this material, difficulties were encountered in the blending of the components. Further work was thus undertaken to investigate alternative polymeric materials for improved processability as well as further cost reduction. Since SEBS is a relatively expensive thermoplastic elastomer, lower cost alternatives were examined. The present work thus centres upon carbon–polypropylene composite electrodes modified with a range of rubbers.

2. Experimental details

Polypropylene (LZM60CR, ICI Ltd Australia) was pre-mixed in a 'Haake 600' internal mixer with SEBS thermoplastic elastomer (SEBS, Keraton, Shell Co., Australia), butyl rubber (Exxon Chemicals Australia), ethylene–propylene rubber (EPR), ethylene–propylene diene monomer (EPDM) rubber (Vistalon, Exxon Co., Australia), nitrile rubber (NBR, Nipol, Polysar, Australia) or isobutylene-co-high density polyethylene (BMX42) (ICI Co., Australia) for 5 min followed by 10 min mixing with carbon black (Cabot Corp., USA and Degussa Co., USA). Graphite fibre (3 mm, Kureha Co. Ltd, Japan) was then added slowly for a range of times and temperatures. The mixture was pressure moulded as previously described [7] at 200° C. The mould was then cooled down overnight under pressure. ASTM D-991 and 638 (with Instron M1115) were employed for evaluating the electrical and mechanical properties of the composite electrodes respectively. Gamma radiation crosslinking was carried out at 0.4 kGy h and 7.5 kGy as total dose.

3. Results and discussion

3.1. *Effect of carbon black*

To increase the conductivity of the PP, three types of high surface area carbon blacks were used to prepare composite samples with composition 60% PP + 40% carbon black (Table 1). It was observed that although the high surface area Black Pearl 2000 resulted in higher composite conductivity due to its low particle size, the mechanical properties of the material diminished with the high carbon loading. Decreasing the amount of the carbon black to 10 wt % not only resulted in high resistivity but did not improve the mechanical properties. Vulcan XC72 was thus selected as the conductive filler material for further optimization.

Figure 1 shows the effects of increasing levels of carbon black on the conductivity of the composite containing PP, EPR and carbon black. The addition

Table 1. Effect of carbon black on volume resistivity of compound. (60% PP + 40% carbon black)

Carbon black type	*Surface area* /$cm^2\ g^{-1}$	*Density* /$g\ dm^{-3}$	*Thickness* /*mm*	*Volume resistivity* /$\Omega\ m$	*Description*
Acarb–P	41	352	1.25	0.36	Brittle
Black pearl 2000	1475	152	1.20	0.15	Brittle
Vulcan XC72	254	273	1.06	0.19	Flexible

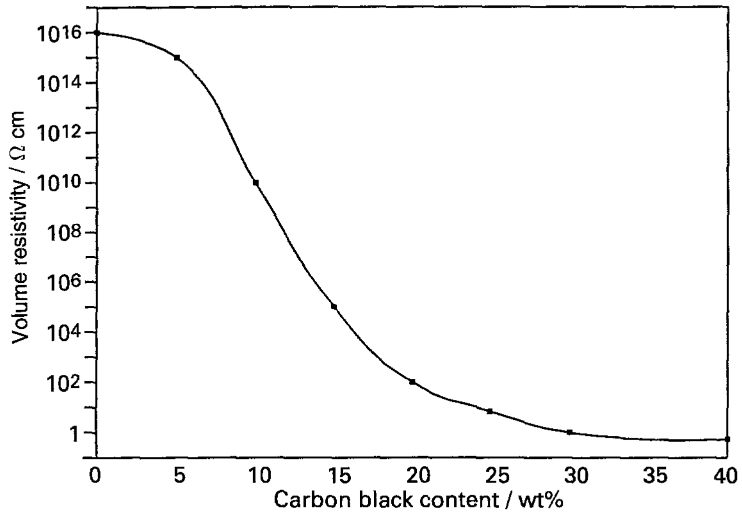

Fig. 1. Effect of carbon black concentration on volume resistivity of the EPR modified PP.

of conductive carbon black to the polymer blend is a nonlinear relationship. It can be seen that for up to 5 wt % carbon black the composite is still as insulating as the polymer. As the level of the carbon black additive increases to a critical level the conductivity increases very rapidly. This percolation level can be placed in the region of around 10 wt % carbon black. Conductivity is strongly dependent not only on the carbon black concentration but also on the filler particle size distribution [5]. Samples with more than 30% carbon black were difficult to mix since the resultant compound was in the form of a powder that would not flow. The melt flow rate of the composite was strongly dependent on filler concentration. The rapid decrease in fluidity of the carbon black and PP mixtures is attributed to their strong interaction [6]. In the absence of these interactions, according to the Einstein equation, viscosity at low filler concentrations increases and it is independent of particle size [5].

3.2. *Effect of graphite fibre*

The preliminary experiments showed that addition of the optimum amount of graphite fibre [4, 7] results in higher conductivity and better mechanical properties. The increased conductivity is due to a network-like structure formed by the graphite fibres and the carbon particles. Table 2 shows that reducing the ratio of graphite fibre to carbon black increases the volume resistivity of the PP–EPR composites. It was observed that fibre is more effective than powders in increasing the conductivity parallel to the plane of the moulded composite sheets. This can be attributed to orientation of fibres during the compression moulding of the composite. Although the orientation of the fibres improves the conductivity in the parallel direction of the sheets, it does not improve the conductivity in the perpendicular direction. Furthermore, using the graphite fibre not only makes the processing of the composite too difficult, but also leads to curvature of the moulded composite sheets. The lowest amount of graphite fibre should thus be used to solve these problems, while ensuring good mechanical properties and low resistivity.

3.3. *Effect of mixing time on conductivity*

The resistivity of the composite is strongly dependent

Table 2. Effect of graphite fibre on volume resistivity of EPR modified PP composites

Polypropylene /*wt %*	*EPR (Vistalon 404)* /*wt %*	*Carbon black* /*wt %*	*Graphite fibre* /*wt %*	*Volume resistivity* /$\Omega\ cm$
40	20	20	20	0.21
40	20	30	10	0.27
40	20	35	5	0.36
40	20	40	–	0.54

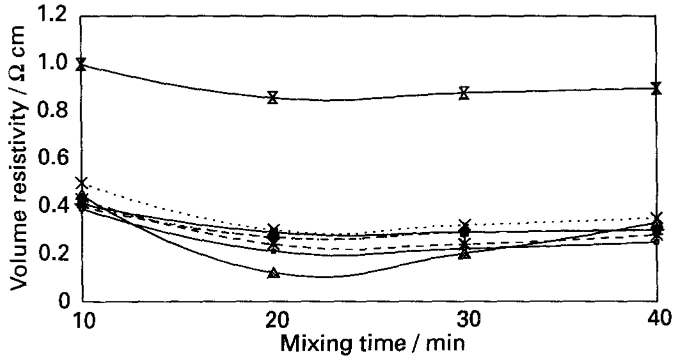

Fig. 2. Effect of mixing time on volume resistivity of the compound. Key: (—□—) EPR (Vistalon 404), (+) EPR (Vistalon 805), (∗) EPDM (Vistalon 2504), (■) EPDM (Vistalon 7000), (×) SEBS, (◆) butyl rubber, (▲) BMX42, (⌧) NBR.

Table 3. Effect of rubber content on conductivity of composite (40% PP + 20% rubber + 20% Vulcan XC72 carbon black + 20% graphite fibre)

Rubber	*Ethylene content /wt %*	*Diene content /wt %*	*Volume resistivity /Ω cm*	
			*5% GF**	*20% GF**
EPR (Vistalon 404)	40	–	0.36	0.21
EPR (Vistalon 805)	77	–	0.40	0.27
EPDM (Vistalon 2504)	50	3.8	0.38	0.24
EPDM (Vistalon 7000)	68	5.0	0.45	0.29
NBR (Nitrile rubber)	–	–	1.2	0.86
SEBS (Styrene–ethylene–butylene–styrene)	–	–	0.45	0.30
Butyl rubber	–	–	0.28	0.27
BMX42 (Isobutylene-co-HDPE)	–	–	0.28	0.12

* Graphite fibre

on the processing parameters. Figure 2 shows that as mixing time increases, resistivity decreases as a result of improved dispersion until a conductivity plateau is reached (20 min). Additional mixing after this point eventually results in break down of the graphite fibres and aggregation of carbon particles [5] leading to an increase in resistivity. The control of the fibre length in the polymeric blend matrix was very difficult because extensive fibre breakage occurred during processing. While mixing graphite fibre with composite in the internal mixer, severe breakage of fibre was observed. Fibre breakage increased with increasing mixing time as well as with the increasing rotor speed.

3.4. *Blending with rubber*

Although an increase in the concentration of conductive particles leads to improved conductivity, it is unfortunately accompanied by a deterioration in the mechanical properties of the composites. A range of chemically resistant rubbers was thus blended in the composites to overcome this drawback. It is generally accepted that the interaction between carbon black and rubber is both chemical and physical [8]. It is believed that carbon black can be strongly bound in blends of EPR and PP [9]. The results in Table 3 show that in the case of EPR and EPDM rubbers, not only does the increasing ethylene and diene content in the rubber decrease the conductivity, but also that increasing the rubber content, causes an increase in the volume resistivity of the compound. This may be attributed to a decrease in crystallinity of the compound, which can lead to better orientation of the conductive particles and thus to a higher conductivity. Although the use of highly crystalline BMX42 did result in higher conductivity, the resulting composite cracked during processing. As can be seen from Table 3, EPR (Vistalon 404) modified PP was found to be best composite, combining acceptable mechanical properties and the lowest resistivity.

3.5. *Mechanical properties*

Table 4 shows the mechanical properties of carbon–PP composites modified with different kinds of rubber. Although some of the composites gave higher tensile strengths, with the exception of EPR and EPDM rubber, the samples cracked under processing. Increasing the rubber content decreases not only tensile strength but also the conductivity of the composite (Table 5). To further improve the properties of the EPR rubber composites, two crosslinking

Table 4. Mechanical properties of composites (40% PP + 20% rubber + 20% Vulcan XC72 carbon black + 20% graphite fibre)

Rubber	*Thickness of sample/mm*	*% Elongation at break*	*Tensile strength at break/mPa*
EPR (Vistalon 404)	0.82	3.0	11.7
EPDM (Vistalon 2504)	0.94	1.2	20.2
EPDM (Vistalon 7000)	0.94	2.8	39.6
BMX42	1.04	1.2	35.4
SEBS	1.23	3.4	48.2
Butyl	1.06	2.4	23.7

Table 5. Effect of percent of rubber content on volume resistivity of compound (carbon black 20% + *graphite fibre 20%)*

PP /wt %	EPR 404 /wt %	Crosslinking	Thickness /mm	Volume resistivity /Ω cm
40	20	–	0.75	0.21
30	30	–	0.87	0.32
20	40	–	0.90	0.75
20	40	Peroxide	1.04	0.91
20	40	Gamma ray	0.80	0.85

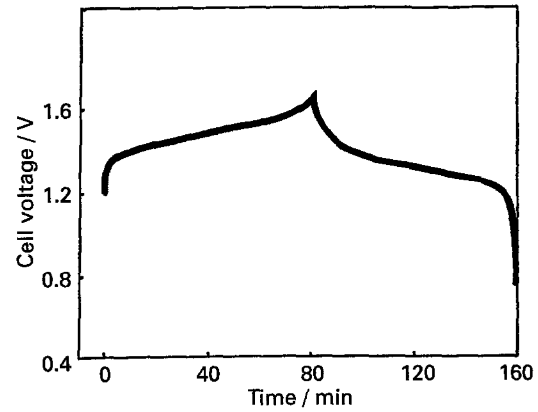

Fig. 3. Typical charge/discharge curve of vanadium redox cell employing EPR modified carbon–PP composite electrode (matrix layer: 40% PP + 20% EPR + 35% Vulcan XC72 carbon black + 5% graphite fibre; active layer: heat treated Sigri GFD5 graphite felt).

procedures were used to cross-link the rubber phase of the composite, i.e. dicumyl peroxide and gamma radiation. The results in Table 5 show that crosslinking the conductive composite tends to reduce conductivity probably as a result of lower density and less crystallinity. Moreover the mechanical properties were dramatically diminished particularly in the case of gamma radiation. This can be attributed to chain scission of PP [10].

3.6. *Permeation*

When employing the conductive plastic in electrode fabrication for redox cell applications, an electrochemically active layer is heat bonded to the top and a current collector (normally a metal foil or mesh) to the back of the composite sheets. With sheet thicknesses less than 1 mm, it is essential that the composite substrates are impervious and free of pin-holes, otherwise, the electrolyte (which in the present system is vanadium ions in sulfuric acid) will pass through the sheet and attack the current collector, and also possibly leak out of the battery during operation. To evaluate the permeation and stability of the material a small cell with solution pumping system was employed. After six months no permeation of electrolyte through the electrodes was observed.

3.7. *Cell application*

To evaluate the applicability of the composite electrodes in the vanadium redox 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 (40% PP + 20% EPR + 35% Vulcan XC72 + 5% graphite fibre) with Sigri GFD5 graphite felt active layer heat bonded on one side and phosphor bronze mesh current collector heat pressed on the back.

The working conditions of the cell were as follows:
Positive 1/2 – cell electrolyte: 2 M V(IV)/3 M $\mathrm{H_2SO_4}$
Negative 1/2 – cell electrolyte: 2 M V(III)/2 M $\mathrm{H_2SO_4}$
Membrane: Selemion CMV (Asahi Glass, Japan)
Charging/discharging current density: 20, 30 and 40 mA cm^{-2} (constant)
Temperature: 23, 35 and 45° C.

The cell with these electrodes at conditions described above was run for up to 100 cycles, a typical charge–discharge curve being presented in Fig. 3. The voltage efficiency of the cell (calculated from the ratio of the average voltage during discharge to the average voltage during charging) is presented in Table 6. Voltage efficiencies of 91% and 88% 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. Results obtained from the 100th cycle

Table 6. Effect of current density and temperature on voltage efficiency of electrode

Electrode	Voltage efficiency				
	Current density, i/mA cm^{-2}				
	20	20	20	30	40
	1st cycle	20th cycle	100th cycle	20th cycle	20th cycle
Toray Electrode (with Toray felt)	75	–	–	–	–
SEBS modified carbon–HDPE/heat treated Sigri GFD5 felt electrode	83	–	–	–	69
EPR modified carbon–PP/heat treated Sigri GFD5 felt electrode (23° C)	91	90	88	80	75
EPR modified carbon–PP/heat treated Sigri GFD5 felt electrode (35° C)	–	–	89	–	–
EPR modified carbon–PP/heat treated Sigri GFD5 felt electrode (45° C)	–	–	90	–	–

performed at various temperatures also show that increasing the temperature increases the voltage efficiency of the cell. This is expected since at higher temperatures, the activation overvoltage losses for the vanadium redox reactions are reduced. The performance of the EPR modified conductive plastic electrodes is compared in Table 6 with the earlier SEBS–HDPE composite [7] as well as with a purchased electrode composite sheet (Toray, Japan) which had a graphite felt sheet bonded on one side and copper foil attached to the back. The EPR modified conducting plastic electrode thus shows excellent performance in the vanadium battery and should be considerably lower cost than the SEBS modified PE composite material.

4. Conclusion

Carbon–PP composite material modified with rubber, has been shown to have good electrical and mechanical properties, as well as being impermeable. However, depending on precursors and processing conditions, the characteristics of the composite vary considerably. It was found that, although HDPE composite electrodes show better mechanical properties, the overall conductivity of the PP composite electrodes is better. Cell performance tests with these composites in the vanadium redox battery have shown that these electrodes are promising for vanadium battery applications.

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