

Carbon-Polymer Composite Electrodes for Redox Cells

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SYNOPSIS

Conductive carbon-polymer composite electrodes for the vanadium redox flow battery were developed and their properties investigated. Conductive polymer composite materials were fabricated by mixing PVC, nylon 6, nylon 11, LDPE, and HDPE with conductive fillers. To overcome the deterioration in the mechanical properties of carbon-polymer composites with high carbon loading, a range of chemically resistant rubbers was blended into the composites. Electrical, mechanical, permeation, and electrochemical studies show that the HDPE composite is the best electrode matrix material for the vanadium redox battery. The performance of a vanadium redox flow cell employing the best composite electrode was also evaluated and voltage efficiencies as high as 88% were obtained with electrodes employing graphite felt active layers bonded to the carbon-polymer composite substrates.

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INTRODUCTION

Many properties are required of materials to be employed as electrodes, the most important of which are conductivity, mechanical integrity, low permeability, electrochemical activity, and stability in the electrolyte. Conductive polymers or polymer blends would be ideal electrode materials for a large number of industrial electrochemical applications since they offer a low-cost, low-weight, alternative to the commonly used graphite or carbon electrodes. They offer high chemical resistance and excellent physical and mechanical properties and can be easily formed into any shape and size.¹⁻⁶ On the other hand, intrinsically conductive polymers, such as polypyrrole, are easily attacked by acidic and oxidative electrolytes.⁷ Therefore, in applications such as the vanadium redox battery,⁸ these conductive polymers are unsuitable for use as electrodes. Carbon/graphite composite plastics have, however, been successfully employed in applications such as the Zn/Br₂ battery⁹ as well as in the vanadium redox battery.^{10,11} Indeed, energy efficiencies of up to 90% have been achieved with Japanese materials (Toray, Japan) in 1 kW prototype vanadium redox batteries at currents of

20 mA cm⁻².¹² While other workers¹³ have achieved similar efficiencies at up to 100 mA cm⁻² current densities using glass carbon substrates, the cost of this material is too high for commercial applications. Because of the high cost of currently available material, therefore, the objective of the present work was to develop formulations and processes to give a more cost-effective and processable electrode material for commercial applications.

EXPERIMENTAL

Preparation of Composites

The following materials were used in the preparation of the composites:

Polymers: high-density polyethylene (HDPE, Hostalen, Hoechst Ltd., Australia), low-density polyethylene (LDPE, Manis Pty. Ltd., Brookvale 2100, Australia), poly(vinyl chloride) (PVC, ICI Co., Australia), nylon (6, 11, Rilsan, France), styrene-butadiene-styrene copolymer (SBS, Aldrich Chemical Co., USA), styrene-ethylene-butylene-styrene thermoplastic elastomer (SEBS, Kraton®, Shell Co., Australia), ethylene-propylene rubber (EPR), ethylene-propylene diene monomer (EPDM) rubber (Vistalon, Exxon Chemicals, Australia), nitrile rubber (NBR, Nipol, Polysar, Australia), butyl rubber

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(IIR, Exxon Chemicals, Australia), and isobutylene-co-high-density polyethylene (BMX-42 Vistaflex, Esso Chemicals, Australia).

Conductive fillers: carbon black (Cabot Corp., USA, and Degussa Co., USA), graphite powder (Lonza KS-2.5, Lonza Inc., USA), and graphite fiber (Kureha C-203s, 3 mm, Kureha Co. Ltd., Japan).

Graphite felts: Sigri GFD5 (5 mm thick, Sigri Electrographite GmbH, Germany).

Metal mesh: 100 mesh (150 microns) brass mesh (Swiss Screen Pty. Ltd., Australia).

Membrane: Selemion CMV (Asahi Glass, Japan).

Preparation Procedure

Each grade of plastic was premixed in a "Haake 600" internal mixer with the elastomer for 5 min followed by 10 min mixing with the conductive powder. Graphite fiber was then added slowly for 20 min. The mixture was pressure-molded with 250 kg/cm² pressure at 200°C for at least 30 min. A metal mesh sheet was placed below the composite sheet inside the mold and the mold was heated up to 200°C for 20 min. A window was then placed on top of the hot sheet and a piece of graphite felt was placed in the window and again heated up for another 10 min under pressure. The mold was then cooled down overnight.

Thermal Treatment of Graphite Felts

Thermal treatment was used to increase the electrochemical activity of the graphite felt for the vanadium reaction.¹⁴ Samples were placed in a furnace and heated up to 350°C. After exposure to air at this temperature for 24 h, the samples were removed from the furnace and cooled down.

Electrical and Mechanical Properties Measurements

ASTM D-991 and 638 (with Instron M1115) were employed for evaluating the electrical and mechanical properties of the conductive composite materials, respectively. To evaluate the area resistance of the final electrode, the "two-plate" method was employed (as illustrated in Fig. 1). The resistance of the electrode is determined by measuring current-voltage curves and then working out the slope of the I-V curve by the linear regression method. Two electrodes are faced to their surfaces and set between two copper plates. These copper plates are compressed with a pressure of 50 g/cm². A series DC current is then applied to the testing electrodes

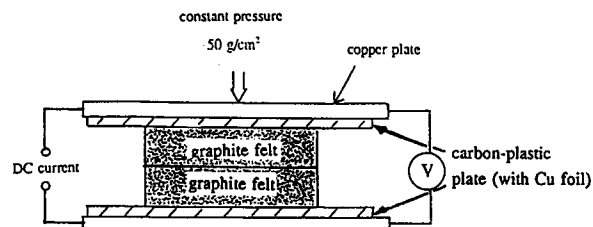


Figure 1 Two-plate method for measuring the resistance of carbon composite end electrodes.

through the copper plates. Potential drop values are obtained by a multimeter which is connected to the other two corners of the copper plates. Plotting the potential drop in volts vs. the current density in A cm⁻² and working out the value of the slope, the resistance of two electrodes can be determined with units of Ω cm². The resistance of an individual electrode is taken as half of the value determined above.

Optical Microscopy, SEM, and DSC Studies

To evaluate the surface microstructure of the selected samples, the cross section and surface of the composite materials were examined with an Olympus Vanox A041 optical microscope and morphologies of the blends and composites were characterized with a Cambridge 360 scanning electron microscope. Samples were cut at a temperature of around -150°C in liquid nitrogen and the rubber particles were extracted during 5 min in boiling *n*-heptane vapor. The surface was then covered with a thin gold layer. DSC studies were carried out with a DuPont 910 differential scanning calorimeter.

RESULTS AND DISCUSSION

Conductive Filler Effect

It was reported earlier¹⁰ that conductive plastic materials with volume resistivity as low as 0.5 Ω cm can be fabricated from mixtures of carbon black and graphite fiber. To increase the conductivity of the polymer, therefore, a high surface area carbon black was used in the present study and preliminary experiments confirmed that addition of the optimum amount of graphite fiber (20% as reported by Zhong et al.¹⁰) results in higher conductivity and better mechanical properties as seen in Table I. The increased conductivity is due to a networklike structure formed by the graphite fibers and the carbon particles. It was reported previously¹¹ that the conductivity of the composite increases nonlinearly with

Table I Effect of Carbon Black on Volume Resistivity of Composite (60% HDPE + 20% Carbon Black + 20% Graphite Fiber)

Carbon Black Type	Surface Area (m ² g ⁻¹)	Density (g L ⁻¹)	Composite Sample Thickness (mm)	Composite Volume Resistivity (Ω cm)	Description
Activated carbon	—	—	1.09	4.4	Brittle
Activated charcoal	—	—	0.86	2.4	Brittle
Graphite powder	—	—	1.11	1.9	Brittle
Acarb-P	41	352	1.25	0.36	Brittle
Black pearl 2000	1475	152	1.20	0.20	Brittle
Vulcan XC72 R	254	97	0.89	0.22	Good
Vulcan XC72	254	273	1.06	0.22	Difficult handling

the addition of conductive carbon black. Up to 5 wt % carbon black, the composite is still as insulating as is the polymer. As the level of the carbon black additive increases, aggregation and agglomeration of carbon blacks occur (Fig. 2), and at a critical level of conductive filler, 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.¹² It was also observed that graphite fiber is more effective than are graphite powders in increasing the conductivity parallel to the plane of the molded composite sheets. Reducing the ratio of graphite fiber to carbon black increases the volume resistivity of the composites. As can be seen in Figure 3, this can be attributed to orientation of fibers during the compression molding of the composite. While the orientation of the fibers improves the conductivity in the parallel direction of the sheets, however, it does not improve the conductivity in the perpendicular direction. Further-



Figure 2 Optical cross-section micrograph of the aggregation of carbon blacks in the EPDM-modified HDPE composite polymeric matrix.

more, using the graphite fiber not only makes the processing of the composite too difficult, but also leads to curvature of the molded composite sheets. The lowest amount of graphite fiber should thus be used to solve these problems, while ensuring good mechanical properties and low resistivity.

The melt-flow rate of the composite was strongly dependent on filler concentration. Samples with more than 40% carbon black were difficult to mix since the resultant compound was in the form of a powder that would not flow. Carbon black grades with a higher surface area, higher structures, and lower volatile content showed higher conductivity.¹² Therefore, to increase the conductivity of the polymer, some types of high surface area carbon blacks were used to prepare composite samples with composition 60% HDPE + 20% carbon black + 20% graphite fiber. The results in Table I show that for the same loading the inclusion of graphite powder leads to a less conductive composite than carbon black.

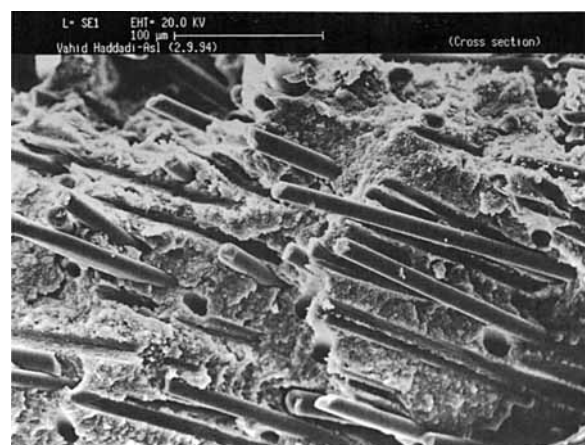


Figure 3 SEM cross-section micrograph of the orientation of graphite fibers in the EPDM-modified HDPE composite polymeric matrix.

Table II Effect of Plastic Types on Volume Resistivity of Composite (60% Plastic + 20% Carbon Black + 20% Graphite Fiber)

Plastic	Intrinsic Volume Resistivity (Ω cm)	Thickness (mm)	Volume Resistivity (Ω cm)
Nylon 6	10^{12} – 10^{15}	1.5	1.1
Nylon 11	2×10^{11}	1.6	2.3
PVC			
(plasticized)	10^{11} – 10^{15}	1.6	0.51
PP	10^{16}	1.17	0.23
LDPE	$> 10^{16}$	1.2	0.32
HDPE	$> 10^{16}$	1.23	0.23

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. Based on results shown in Table I, therefore, Vulcan XC72 was selected as the conductive filler material for further optimization.

Effect of Plastic Structure

Although nylon materials are engineering plastics, the composites prepared from nylon 6 were found to be unstable in an acidic vanadium solution and are therefore not suitable for this application. The nylon 11 samples were difficult to compression-mold and also gave high resistance, as seen in Table II. Although the intrinsic volume resistivity of PVC is lower than of other plastics, the final composite prepared from PVC showed higher resistivity than did polyolefins. In addition, rigid PVC is hard to process, and plasticising decreases the stability of the PVC composite in the acidic vanadium solution. Therefore, polyolefin thermoplastic materials were se-

lected as the main substrate because of their excellent chemical resistance and easy processing. Among the polyolefins, HDPE showed better mechanical properties and electrical conductivity (Table II). The results of Table III also show that the highest-density HDPE which has the highest crystallinity (i.e., Hostalen G.C 7260) produces the lowest resistivity composite. In other words, conductivity of the composite increases with the crystallinity of the plastic. This may be attributed to the fact that in the higher crystalline polymer orientation of the polymeric chains causes an orientation of conductive particles. Using the low melt-flow index (MFI) HDPE, results in not only easier processing but also a tougher final composite.

Blending with Rubber

While 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.¹⁵ However, increasing the rubber content resulted in higher resistivity which may be related to the amorphous structure of rubber. Table IV shows that the highest conductivity is achieved when HDPE is blended with BMX-42, which is isobutylene-*co*-HDPE. The cause for these differences in conductive behavior lies in the combination of several factors which result from different rubber characteristics such as different rheological behavior in the processing stages and different wettability of the rubber for conductive particles.¹⁶ In addition, the high conductivity of the HDPE/BMX-42 composite may also be attributed to the higher crystallinity of the BMX-42 and the blend. As can be seen from the DSC curve in Figure 4, the long sharp peak indicates that at the melting point of the HDPE/BMX-42 blend the crystallization enthalpy (ΔH_c) is 61.45 J/

Table III Effect of HDPE Type on Volume Resistivity of Composite (60% HDPE + 20% Carbon Black + 20% Graphite Fiber)

HDPE Type	MFI (190/5) ($\text{g } 10 \text{ min}^{-1}$)	Density (g L^{-1})	Volume Resistivity (Ω cm)
Hostalen C.M 7655	0.6	0.953	0.29
Hostalen G.C 7255	12	0.955	0.27
Hostalen G.A 7260H	75	0.956	0.24
Hostalen G.C 7260	23	0.958	0.22

Table IV Effect of Rubber Content and Mixing Time on the Conductivity of Composite (40% HDPE + 20% Rubber + 20% Carbon Black + 20% Graphite Fiber)

Rubber	Mixing Time (Min)				Volume Resistivity (Ω cm)	
	10	20	30	40		
	Ethylene Content (% Wt)	Diene Content (% Wt)				
Vistalon 404	40	—	0.35	0.28	0.30	0.36
Vistalon 2504	50	3.8	0.36	0.23	0.25	0.30
Vistalon 3708	65	4.0	5.1	3.8	4.0	4.1
NBR	—	—	0.45	0.31	0.35	0.4
SEBS	—	—	0.4	0.29	0.30	0.35
SBS	—	—	1.6	1.1	1.7	1.9
Butyl rubber	—	—	0.4	0.23	0.24	0.26
BMX-42 (isobutylene-co-HDPE)	—	—	0.35	0.19	0.22	0.23

g. This is nearly two times greater than the values obtained from similar DSC curves for HDPE/EPDM ($T_m = 132.92^\circ\text{C}$, $\Delta H_c = 34.46$ J/g) and HDPE/butyl blends ($T_m = 131.61^\circ\text{C}$, $\Delta H_c = 35.50$ J/g) and also three times greater than the HDPE/EPR blend ($T_m = 129.07^\circ\text{C}$, $\Delta H_c = 23.93$ J/g). The results in Table IV also show that in the case of EPR and EPDM rubbers increasing the ethylene and diene content in the rubber decreases the conductivity of the compound. Although the use of butyl rubber or highly crystalline BMX-42 did result in

higher conductivity, unfortunately, the resulting composites cracked during processing. As can be seen from Table IV, EPDM (Vistalon 2504)-modified HDPE was found to be the best composite, combining acceptable mechanical properties and the lowest resistivity.

Effect of Mixing Time

The resistivity of the composite is strongly dependent on the processing parameters. Table IV shows

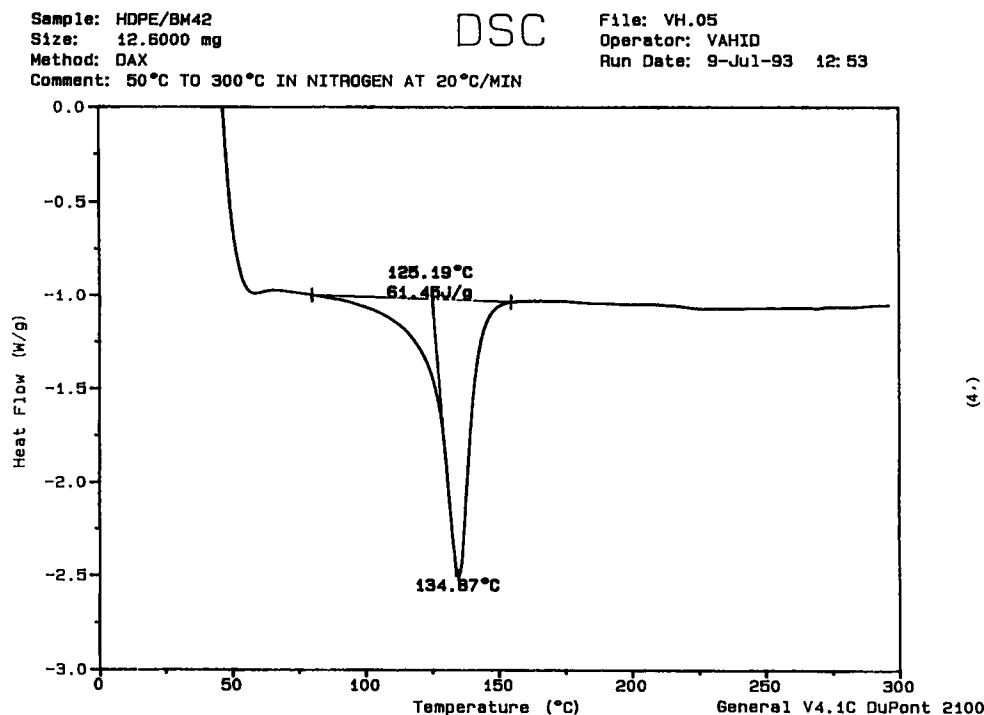


Figure 4 DSC curve of HDPE blended with BMX-42.

Table V Effect of Processing Method on Volume Resistivity of Composite (40% HDPE + 20% SEBS + 20% Carbon Black + 20% Graphite Fiber)

Processing Method	Volume Resistivity (Ω cm)	Thickness (mm)
Veneering	48.2	1.00
Calendering	29.5	1.50
Extrusion	0.56	2.0
Mixing with an internal mixer followed by compression molding	0.29	1.00

that as mixing time increases resistivity decreases as a result of breaking the pellets of the conductive carbon black into smaller pieces at an early mixing stage (10 min). After this, a semidiscontinuous phase of carbon black aggregates distributed in the continuous phase of the polymer matrix forms until a conductivity plateau is reached (20 min). Additional mixing after this point eventually results in the breakdown of the graphite fibers and aggregation of carbon particles,¹² leading to an increase in resistivity. As seen in Table IV, this behavior is not the same for all the polymers and can be related to the microstructure of the polymer and properties such as crystallinity, viscosity, and interaction of the polymer with carbon black.

The control of the fiber length in the polymeric blend matrix was very difficult because extensive fiber breakage occurred during processing. During the mixing of graphite fiber with the composite in the internal mixer, severe breakage of the fiber was observed. Fiber breakage increased with increasing mixing time as well as with increasing rotor speed.

Effect of Processing Methods and Conditions

The processing method and conditions have a significant effect on the volume resistivity of the composite, as seen in Table V for the HDPE/SEBS/carbon black/graphite fiber. The lowest conductivity was obtained by veneering and calendering of the composite materials. This may be because of the high applied shear stress which breaks down the polymeric chains and graphite fibers and changes their arrangement. Extrusion of the composite material results in not only higher conductivity but also better mechanical properties. This can be attributed to better mixing and shear stress in the extrusion. In the case of extrusion, anisotropic conductivity

was observed in that the conductivity in the with-flow direction was twice that in the across-flow direction. From these results, it may be concluded that extruding the composite orients the conductive fillers among the polymeric chains. In other words, orientation of polymeric chains and conductive fillers aggregates along the lines of flow leads to these anisotropic properties of the composite. In particular, alignment of the graphite fibers in the direction parallel to the extrusion plane would lead to a high conductivity in that direction but a low conductivity perpendicular to the plane. However, the results in Table V show that mixing in an internal mixer followed by compression molding the composite gave the highest conductivity. This may be due to a shorter mixing time in the internal mixer, which results in lower fiber breakage. In addition, in the compression-molding process, because of a longer cooling time, fibers have time to be oriented better in a parallel direction. While graphite fiber enhances the conductivity of the composite in the parallel direction of the sheet, therefore, this property is not significant for bipolar electrode applications where the current must flow perpendicular to the plane of the electrodes. It should thus be possible to reduce graphite fiber content for this application.

Mechanical Properties

Table VI shows the mechanical properties of carbon-HDPE 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. As described above, a combination of carbon black and graphite fiber in the ratio 1 : 1 (total fraction being 40% of the composite) produces a composite with a resistivity less than 0.3 Ω cm. Further experiments showed that even lower resistivity could be obtained by increasing the conductive fillers. Increasing the proportion of carbon black,

Table VI Mechanical Properties of Composites (40% HDPE + 20% Rubber + 20% Carbon Black, + 20% Graphite Fiber)

Rubber	Thickness of Sample (mm)	% Elongation at Break	Tensile Strength (MPa)
EPR (404)	1.03	2.0	15.0
Butyl	0.77	2.0	21.1
SEBS	0.6	4.8	29.0
EPDM (2504)	1.32	4.0	27.1

Table VII Effect of Percentage of Rubber Content on Volume Resistivity of the Compound (20% Carbon Black + 20% Graphite Fiber)

HDPE (Wt %)	EPDM (Wt %)	Thickness of Sample (mm)	Volume Resistivity (Ω cm)
60	—	0.75	0.22
40	20	0.87	0.23
30	30	0.9	0.36
20	40	1.04	0.80

however, resulted in a deterioration in the mechanical properties of the composite, i.e., both tensile strength and elongation decreased. Although increasing the rubber content increases the impact properties of the composite, it decreases not only tensile strength but also the conductivity of the composite, as seen in Table VII.

Permeation

When employing the conductive plastic in electrode fabrication for redox cell applications, an electrochemically active graphite felt layer is heat-bonded to the top and a current collector (normally, a metal foil or mesh) to the back of the composite sheets to produce an end-electrode for the cell stack. With sheet thicknesses less than 1 mm, it is essential that the composite substrates are impervious and free of pinholes; 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

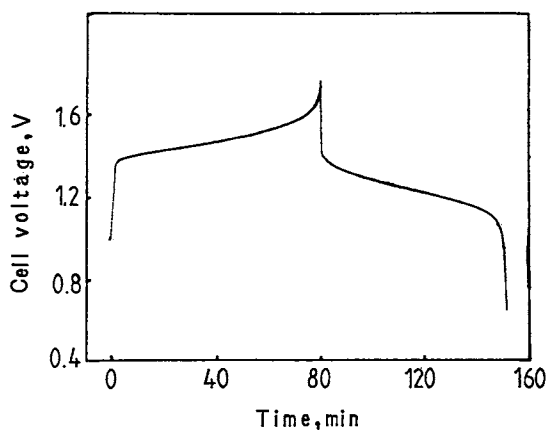


Figure 5 Typical charge/discharge curve of vanadium redox cell employing EPDM-modified carbon-HDPE composite electrode. $i_{ch.} = i_{dis.} = 20 \text{ mA cm}^{-2}$; cell voltage upper limit = 1.75, lower limit = 0.75 V.

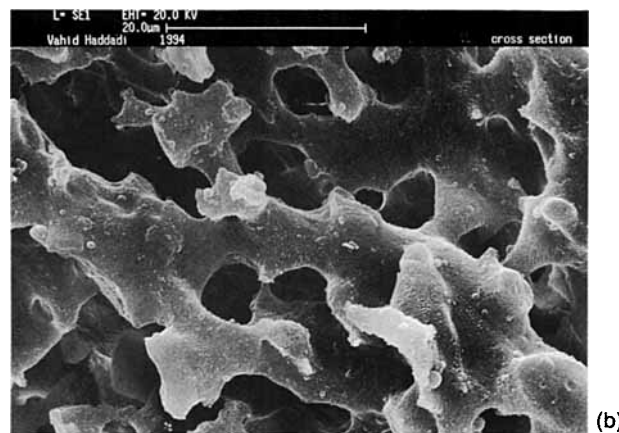
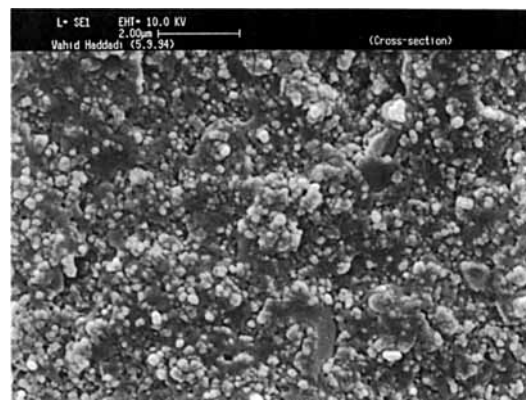


Figure 6 SEM cross-section micrographs of the EPDM-modified HDPE composite polymeric matrix: (a) before etching; (b) after etching.

during operation. The permeation behavior is therefore one of the most important characteristics of the composites. To evaluate the permeation and stability of the material, a small cell with a solution pumping system was employed. After 3 months of charge-discharge cycling, no evidence of oxidation of the copper mesh (current collector) was observed, showing that there was no permeation of electrolyte through the electrodes.

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 com-

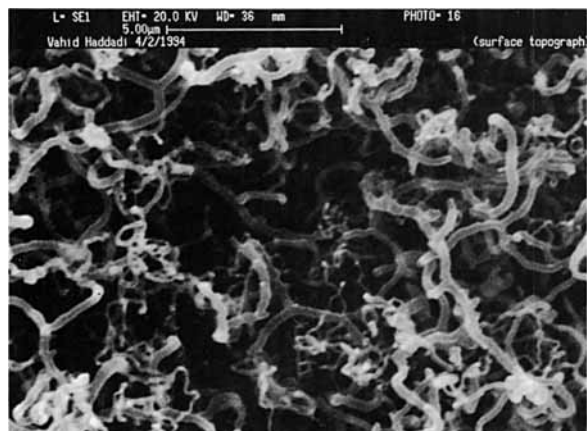


Figure 7 SEM surface micrographs of the EPDM-modified HDPE composite polymeric matrix.

prised EPDM-modified HDPE composite substrates (40% HDPE + 20% EPDM + 20% Vulcan XC72 + 20% graphite fiber) which had been fabricated by compression molding. A Sigri GFD5 graphite felt active layer was heat-bonded on one side and the metal mesh current collector heat-pressed on the back. Surface contact between the conducting plastic sheet and the metal current collector has been found to lead to high contact resistances due to the insulating effect of the polymer materials which tends to coat the conducting filler particles. The metal mesh is thus partially embedded into the back of the conductive plastic sheet so as to achieve a good electrical contact with the electrical network inside the composite material and produce electrodes with low area resistance. The area resistance of these electrodes was 2.3 and 2.5 $\Omega \text{ cm}^2$, respectively, which is still relatively high for high-power application (ideally, area resistances of less than 1 $\Omega \text{ cm}^2$ are required for high-power output). Further optimization of the electrode fabrication procedure is thus required to achieve high-power densities and reduce stack size and cost.

The working conditions of the cell were as follows:

Positive 1/2

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

Negative 1/2

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

and charging/discharging current density (i_{ch} and i_{dis}): 20 $\text{mA}\cdot\text{cm}^{-2}$ (constant); temperature: 25°C.

The cell with these electrodes at conditions described above was run for up to 50 cycles and a typical charge-discharge curve is presented in Figure 5. From such curves, the voltage efficiency of the

cell was determined from the ratio of the average discharge voltage to the average charging voltage. Voltage efficiencies of 88 and 85% were achieved for the first and fifth cycles, respectively, in the cell charge/discharge testing at a current density of 20 $\text{mA}\cdot\text{cm}^{-2}$ at room temperature. The EPDM-modified HDPE conducting plastic electrode thus shows excellent performance in the vanadium battery under low-power application. While the cost of this material should be significantly lower than that of graphite or glassy carbon substrates, as mentioned above, further improvements in the metal current collector bonding are required to reduce the contact resistance and allow higher-power densities to be achieved.

Morphology

The surface and cross-section topographies of the compression-molded EPDM-modified conductive HDPE composite were studied by use of scanning electron microscopy. The morphologies of some of the blends are shown in Figures 6 and 7. After etching the rubber by boiling heptane, a continuous structure of HDPE is observed [Fig. 6(b)] in the cross section of the sample. On the other hand, the surface topography revealed an aggregation of polymeric fibrillar (Fig. 7). In general, when comparing Figures 6(a) and 7, it can be said that compression molding of this composite results in a different bulk and surface structural morphology.

CONCLUSION

Carbon-HDPE composite material modified with EPDM 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. 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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