

GRAFT COPOLYMER SEPARATORS — DEVELOPMENT AND USE

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Summary

Graft copolymer membranes have been used for a number of years as interelectrode separators in alkaline batteries either singly, laminated to cellophane, or in conjunction with other materials such as felts.

The preparation details of some of the Royal Military College of Science's copolymers are summarised with emphasis on the production of commercial quantities having a high degree of uniformity and reproducibility. Important properties in a battery environment are discussed and, where possible, compared with other separator materials; notably cellophane.

The use of graft copolymers in a number of primary and secondary alkaline battery systems is reported and test data given. Conclusions are drawn relating the properties of these separators to their performance in cells.

1. Introduction

Graft copolymer membranes have been used as battery separators for a number of years, mainly as an alternative to cellulosic materials, and commercial processes for their manufacture have been developed [8]. This paper summarises the preparation of RMCS-type copolymers and illustrates some of the advantages and disadvantages of using these materials in various types of alkaline cells, ranging from button cells with typical current densities of 2 A per square metre to high rate secondary cells where 1000 A per square metre may be required.

2. Graft copolymer preparation

There are many general routes to prepare graft copolymers [4]. A typical reaction scheme is shown diagrammatically in Fig. 1 where monomer A is combined with polymer B to give a copolymer B-g-A which then possesses many of the physical and chemical properties associated with its two constituents. By varying A and B and their relative proportions in the copolymer a wide range of materials may be prepared.

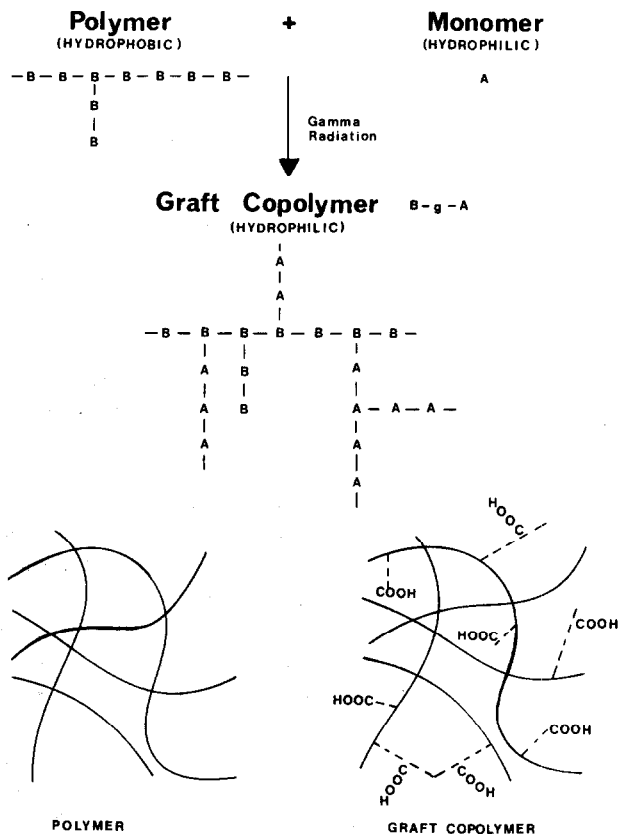


Fig. 1. Schematic diagram of graft copolymer preparation.

Graft copolymer preparation at RMCS originally used organic solvents such as benzene to act as a diluent for the monomer solution and as a swelling agent for the polymer being grafted. The principal disadvantage of this approach is the amount of free homopolymer formed which is extremely difficult to remove from the copolymer. Furthermore, the exotherm associated with the homopolymerisation reaction often leads to inhomogeneities appearing in the grafted material. It is much easier to prepare copolymers from aqueous grafting solutions, and laboratory tests have shown that separators with similar graft levels prepared by either technique have similar properties [1], although materials from aqueous solutions generally have marginally higher electrolytic resistances and show improved resistance to zinc dendrite penetration.

The present method uses an aqueous grafting solution containing an inhibitor to prevent homopolymer formation, thus removing the exothermic reaction and the need for extensive cleansing of the copolymer. This technique has given better copolymer uniformity, which has been maintained on scaling up to pilot trials quantities. The process also combines with the basic

copolymerisation a range of post graft treatments designed to tailor the properties of the material more closely to its application [3]. Acrylic acid monomer is used to confer the cationic exchange properties to the copolymer, permitting ionisation in the electrolyte and current flow across the separator. The backbone matrix, usually in the form of sheet or film, is chosen from a range of polymers with high and low density polyethylene, polypropylene and polytetrafluoroethylene being commonly used. The copolymerisation is initiated by cobalt 60 gamma radiation and the reaction is performed in aluminium vessels capable of preparing batches up to 150 square metres (250 m × 0.6 m). The resultant copolymer is washed to remove reaction residues and post-graft treated as necessary prior to being dried and wound up.

The properties of a separator, in terms of its chemical stability, exchange capacity, resistance in electrolyte and hydroxyl ion mobility, are controlled, though not all independently, by the preparation parameters, and it is possible to make a wide range of materials, as shown in Table 1, using the RMCS technique.

TABLE 1

Working range of RMCS graft copolymers

Base polymer	Dry thickness (μm)	Graft level* (%)	Electrolytic resistance** ($\Omega \text{ cm}^2$)
Low density polyethylene	12 - 120	30 - 70	0.02 - 3.0
High density polyethylene	10 - 40	26 - 70	0.03 - 5.0
Polypropylene	15 - 35	18 - 45	0.03 - 1.0
Polytetrafluoroethylene	6 - 50	12 - 25	0.02 - 1.0

$$\text{*Graft level \%} = \frac{\text{Weight of monomer in copolymer}}{\text{Weight of copolymer}} \times 100.$$

**In 5.8M KOH, 25 °C.

Quality control of the product depends greatly on an understanding of the copolymerisation and subsequent post graft reactions, and on being able to build into each stage a sufficient degree of latitude in each of the process variables so that the product quality is not critically dependent upon any one parameter. Some correlations between the reaction variables and copolymer properties are shown in Figs. 2 to 4. Figure 2 illustrates how electrolytic resistance varies with graft level and base polymer, and Figs. 3 and 4 show typical relationships between graft level, radiation dose, and monomer concentration obtained in laboratory experiments. For good quality control it is important to establish that these relationships still apply on scaling up and to choose preparation conditions corresponding to the plateau regions of

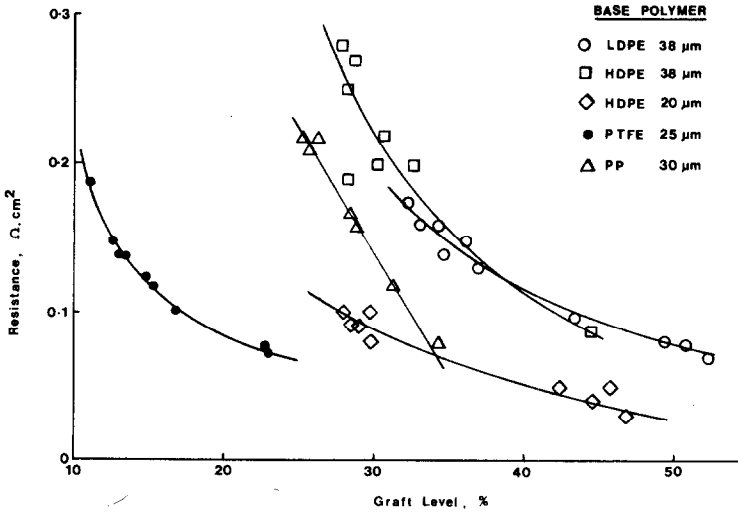


Fig. 2. Variation of separator resistance with graft level in 5.8 M KOH, 25 °C.

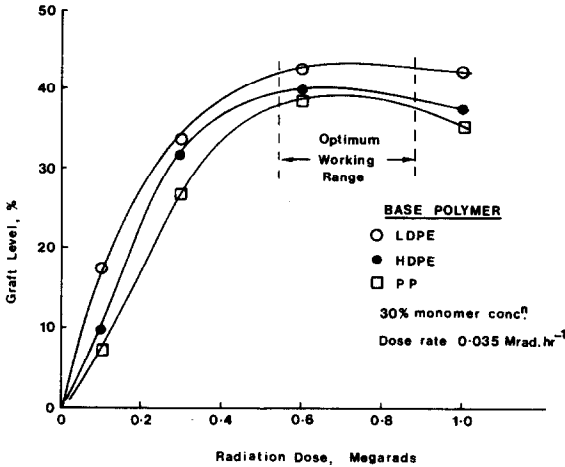


Fig. 3. Variation of graft level with radiation dose.

Figs. 3 and 4. Similar correlations can be established for many other process variables and, by careful optimisation, it is possible to achieve good product control and maximum working flexibility from the process.

It is extremely important to use high grade polymer film stock in the process, with particular attention being paid to thickness variation, molecular weight distribution, and the avoidance of pinholes and other blemishes (fish eyes). It is the procurement of a base polymer film of good thickness uniformity that poses a major problem, as may be seen from some typical quality assurance data on production material given in Table 2. It is this thickness

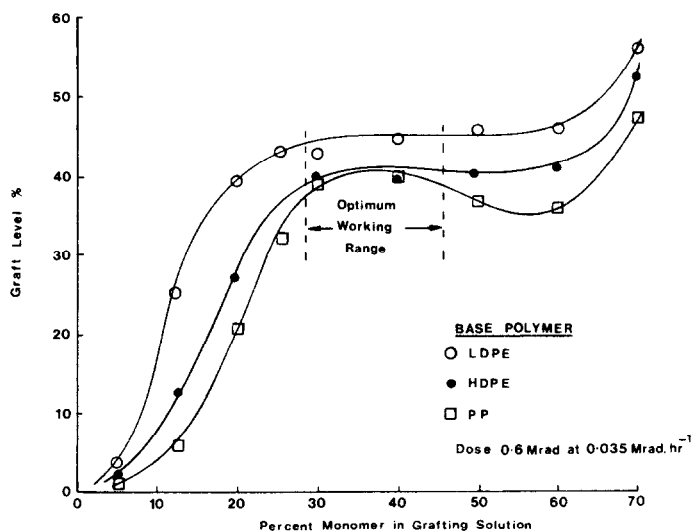


Fig. 4. Variation of graft level with monomer concentration in grafting solution.

uniformity that ultimately governs the overall resistance uniformity of the finished graft copolymer separator. The data in Table 2 were obtained from separators prepared by the aqueous route and the uniformities quoted are better than those previously obtained from organic solvent grafting processes.

The abbreviations to be used in this paper in the identification of RMCS type graft copolymer separators are given in Table 3, and the majority of the physical properties of these materials were determined using the techniques outlined in an earlier paper [2]. Separator resistances were determined by the a.c. technique. Other properties were measured using techniques outlined by Cooper and Fleischer [7].

3. Graft copolymer separators and comparisons with cellophane

The choice of separator for a particular battery system is vitally important since it often controls the storage life, cycle life, and discharge performance of the battery. Table 4 compares some properties of a typical battery grade cellophane, PUDO 193 (Du Pont), with two RMCS graft copolymers and P-2291 (RAI), an extensively used, commercially available, copolymer of methacrylic acid and a pre-crosslinked LDPE substrate. The most noticeable difference is in the amount of electrolyte absorbed by the cellophane (up to 350%); the commensurate increase in thickness, but not in other dimensions, is widely used to achieve tight cell packing, although allowance for this swelling will reduce the overall energy density of the cell. Graft copolymers, on the other hand, are generally incapable of taking up more than their own weight of electrolyte and rarely increase in thickness by more than 20%, but suffer from the disadvantage of varied dimensional changes in length and breadth, sometimes by up to 20%.

TABLE 2

Inter and intra batch uniformity of RMCS copolymer separators

RMCS batch code	Graft level (%)		Dry thickness (μm)		Electrolytic resistance* ($\text{m}\Omega \text{cm}^2$)	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
209	31.8	0.5	15.2	2.0	34	7
211	31.6	0.8	15.4	1.2	34	4
212	31.1	1.1	17.4	1.7	39	7
213	33.0	0.7	16.6	2.3	34	8
214	31.0	1.6	17.5	2.2	42	9
231	33.7	0.9	16.7	1.3	33	7
232	33.1	0.9	16.3	2.0	40	5
233	33.4	0.6	17.9	1.7	39	6
234	33.3	0.6	17.6	2.3	34	9
337	33.9	0.4	19.5	1.3	52	9
340	34.5	0.8	17.1	1.5	43	7
341	35.0	0.8	18.2	1.2	41	5
423	33.9	1.2	42.2	2.8	150	10
424	33.8	0.9	40.8	2.6	140	10
425	33.9	1.2	42.0	2.5	140	20
426	32.6	1.0	42.0	3.5	160	10

Notes

1. 209 - 214, 231 - 234, 337 - 341 made from different batches of the same base polymer.
2. 423, 424; 425, 426 made from different batches of base polymer.
3. The numbers of readings for each batch varied but, in general, a minimum of 50 thickness and 30 resistance measurements were taken. Graft levels were calculated from measurements along roll length; 16 measurements in total.

*In 5.8M KOH, 25 °C.

TABLE 3

RMCS separator codes used in this paper

Separator base polymer	Abbreviation in text	Separator code prefix
Low density polyethylene	LDPE	RL-
High density polyethylene	HDPE	RH-
Polypropylene	PP	RP-
Polytetrafluoroethylene	PTFE	RF-

Notes

1. All the RMCS separators described in this paper are copolymers containing Acrylic Acid (AA).
2. The number in the code refers to the percentage of AA in the graft copolymer; an additional letter P indicates that the copolymer has been post graft treated.
3. Separators with a suffix O were prepared using an organic solvent route, all other RMCS materials described were prepared using aqueous grafting solutions.

TABLE 4

Some properties of cellophane and graft copolymers

Property	Material			
	PUDO 193 Cellophane	RL-35	RL-35P	P-2291 (40/30)
Dry thickness (μm)	25	28	28	32
Percent. thickness increase in 5.8M KOH, 25 °C	290	15	8	2
Electrolytic resistance ($\Omega \text{ cm}^2$) in 5.8M KOH, 25 °C	0.02	0.09	0.07	0.16
9.7M KOH, 25 °C	0.04	0.31	0.14	0.33
12.5M KOH, 25 °C	0.03	1.43	0.42	0.77
Electrolyte permeability (mmole KOH $\text{cm}^{-2} \text{ min}^{-1}$)	0.23	0.18	0.30	0.12
Equilibrium electrolyte uptake of 5.8M KOH (% of dry weight)	368	85	96	51

Cellophanes exhibit relatively low electrolytic resistances over a wide temperature range, probably due to their high electrolyte retention, and this is not markedly affected by electrolyte concentration [2]. Graft copolymers, conversely, tend to show some sensitivity in resistance, not only to electrolyte concentration but also, as will be seen later, to the presence of dissolved species such as zinc oxide.

The RMCS graft copolymers shown in Table 4 illustrate the effect of post graft treatment on separator properties, since RL-35 and RL-35P are the same copolymer with the latter having received treatment to reduce its resistance and improve its electrolyte permeability. Graft copolymers cannot, however, combine all the desirable separator properties into a single material, and in any battery development programme work will be needed firstly to identify the essential separator properties and thereafter to tailor a material as closely as possible to meet these requirements. The practice of replacing a cellulosic material with a graft copolymer on a one for one basis is unlikely to give the best results.

4. Uses of RMCS separators

The following examples, drawn from collaborative work with many battery companies, summarise the results which have been obtained in battery trials and highlight some of the problems associated with the application of graft copolymer separators.

4.1. Primary cells

The graft copolymer separators have been tested in a wide range of primary alkaline cells. The results discussed in this paper are restricted to measurements on button cells where the main requirement is for good capacity retention over long storage periods.

Two types of silver-zinc cells were studied, one designed for a low current drain of 0.2 mA (~ 2 A per square metre) and the other for a higher rate of 2.5 mA (~ 25 A per square metre) and able to withstand pulses of 50 mA for short durations. Separators were also evaluated in two sizes of mercury-zinc cells, and a mercury-cadmium cell required to have a low temperature discharge capability after long term high temperature storage.

4.1.1. Silver-zinc

Cell construction and test procedures

The studies were carried out on cells having nominal capacities of 125 mA h and of 140 mA h made by different manufacturers. Both sets of cells contained a felt absorber adjacent to the separator: in the 125 mA h cells this was a viscose material and in the 140 mA h cells a non-woven cellulosic from the 'Webril' range. The electrolyte in the 140 mA h cells was 35% KOH containing 5% zinc oxide, the composition in the 125 mA h cells is not reported.

Cells of 125 mA h were discharged at 0.2 mA at 35 °C either within a few days of manufacture or after storage at 45 °C for 90 days. Two electrical tests were carried out on the 140 mA h cells; nominally fresh cells were either subjected to a continuous 2.5 mA drain or to 50 mA pulses of 2 s duration repeated at 28 s intervals.

Separators from used 140 mA h cells were analysed for silver retention by titration with a standardised potassium iodide solution using an iodine sensitive electrode as end-point indicator.

Results

125 mA h cells. The separators have not been identified individually in the results shown in Fig. 5 where discharge capacities are plotted against separator resistance. For fresh cells the capacities were independent of separator resistance and similar to that of the control material P-2192 (a laminate of P-2291 between 2 layers of cellophane). After storage, however, the cells with lower resistance separators had lost capacity while those with the higher resistance materials had virtually retained all their capacity.

These differences in capacity are probably unconnected with separator resistance at the very low current drain of 0.2 mA, and must result from the lower metal migration within the cell associated with high resistance separators. Inspection of the cells after discharge revealed that, although all the graft copolymers were highly stained, the cells with the best performances had the cleanest felt absorbers, that is, the copolymer had noticeably prevented silver migration. The control material with the two extra cellulosic layers also showed good silver barrier properties.

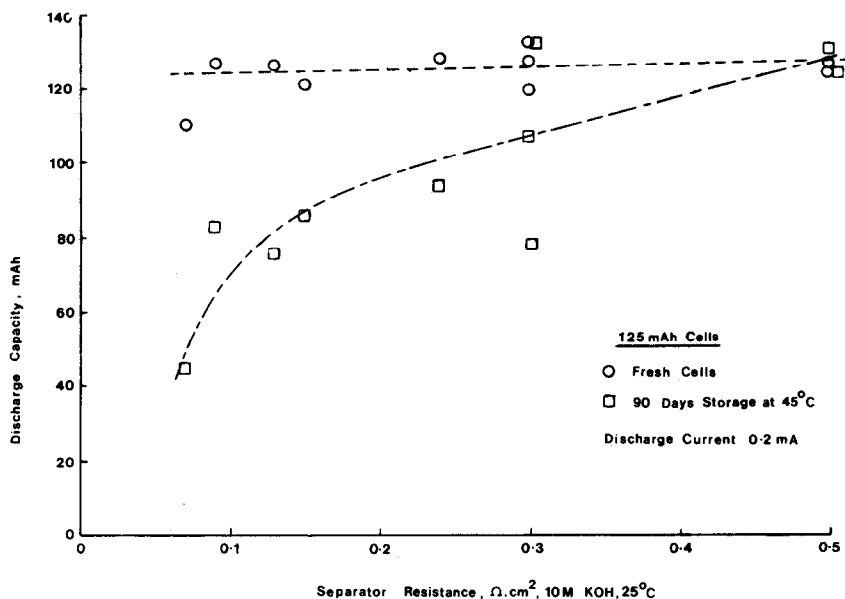


Fig. 5. Discharge capacity of silver-zinc button cells containing RMCS separators.

140 mA h cells. The results obtained from the two discharge tests are shown in Fig. 6 where capacity is plotted against separator resistance. As for the 125 mA h cells, on a continuous discharge at 2.5 mA the separator resistance in the range 0.05 - 0.25 $\Omega \text{ cm}^2$ had little effect on capacity. During the pulsed discharge regime, however, the importance of resistance became evident, with values of the order of 0.25 $\Omega \text{ cm}^2$ causing a loss in available capacity of up to 30%.

This loss is possibly due to a combination of two effects, the migration of silver being accelerated on pulsing and the limiting effect of separator resistance, since a 50 mA pulse represents a current density of the order of 500 A per square metre.

Crosslinking of the graft copolymer base film by irradiation to high doses around 60 Mrad tightened the molecular structure of the separator, reduced the metal migration, and resulted in some improvement in cell capacity, as shown in Fig. 6, but the separator resistance still remained a limiting factor on cell life. The control material, P-2190 (P-2291 and PUDO 193), being both cross-linked and a laminate to cellophane, also showed improved metal barrier properties and performance.

Results from the silver analysis showed that for continuously discharged cells capacity loss was not directly related to metal migration within the cell, with amounts of silver retained in the copolymer separator varying between 0.2 and 2.3 mg, and similar amounts on the felt absorbers. On pulsed discharges, however, some copolymers and felts retained larger amounts of silver, up to 7 mg, and these coincided with observed reductions in cell capacity.

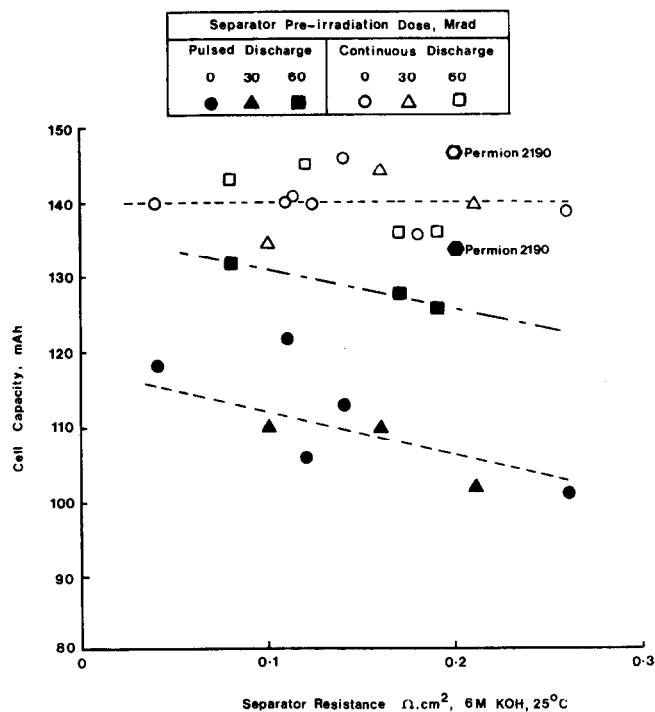


Fig. 6. Discharge capacities of 140 mA h silver-zinc button cells containing RMCS separators.

4.1.2. Mercury-zinc

Cell construction and test procedures

The tests were carried out on two sizes of cell having nominal capacities of 210 mA h and 350 mA h. In both cases the separators were used in conjunction with a non-woven cellulosic felt absorber (Webril), and the electrolyte, 40% KOH, contained 6% zinc oxide. The 210 mA h cells were discharged at 10 mA one week after manufacture and the 350 mA h cells at 0.5 mA and 10 mA after storage at 55 °C for periods of 1, 3, and 6 months.

Results

210 mA h cells. The discharge capacities of the 210 mA h cells are shown in Fig. 7 as a function of the separator resistance. Cells of two slightly different methods of construction were used in these tests, in one case (A) the separator was wetted with water during assembly and in the other (B) the separator was wetted with electrolyte saturated with zinc oxide. A pre-conditioning effect may have emerged because of the effect which dissolved zinc oxide has on separator resistance, as can be seen in Figs. 8 and 9.

Figure 8 shows the effect that adding different amounts of zinc oxide to the electrolyte has on the separator resistance of a typical graft copolymer RL-35, and Fig. 9 compares the resistance values of a range of separators

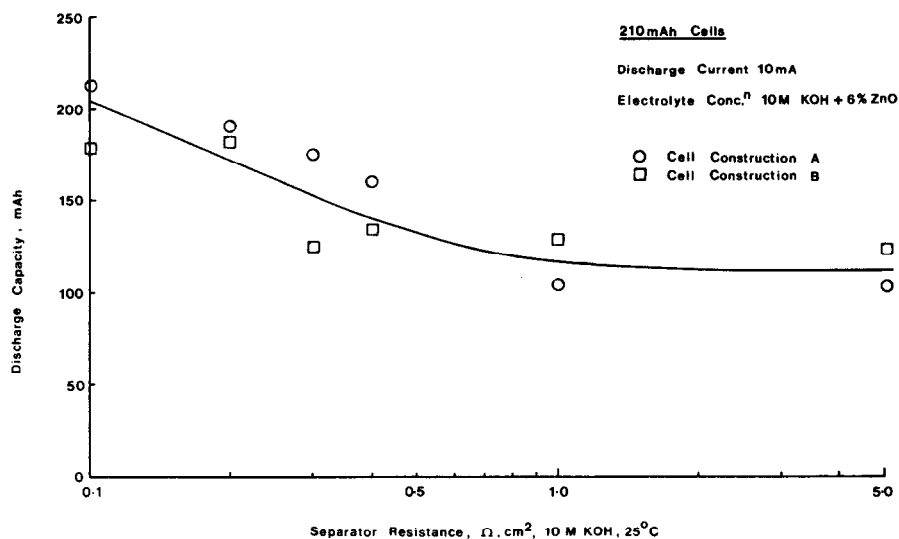


Fig. 7. Discharge capacity of mercury-zinc button cells containing RMCS separators.

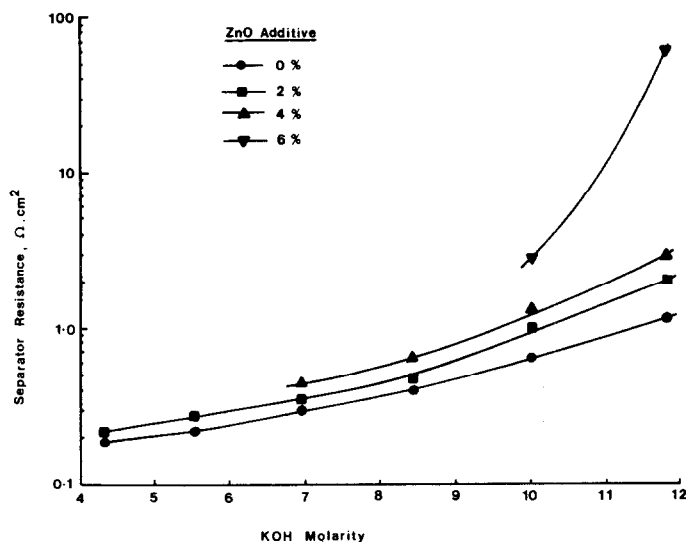


Fig. 8. Effect of electrolyte composition on resistance of RMCS separator RL-35.

measured in electrolyte with and without 6% zinc oxide added. The discharge results do not, however, show evidence of a conditioning effect and it is the cells containing the higher resistance separators which showed significant reductions in capacity.

350 mA h cells. The capacities of some 350 mA h cells are given in Table 5. The results are restricted here to three different separators based on

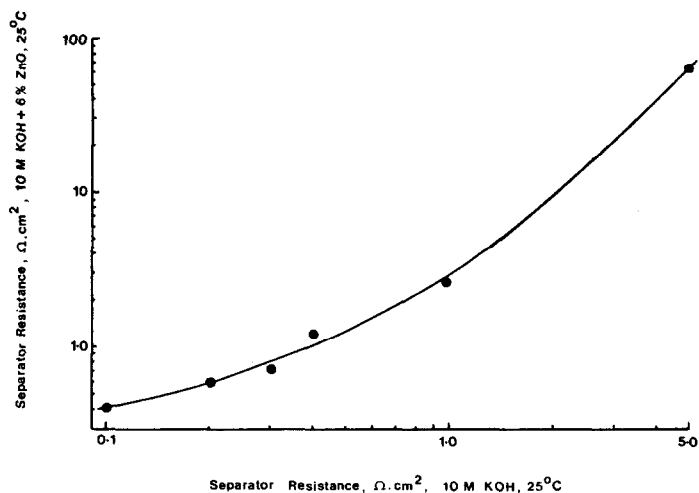


Fig. 9. Effect of electrolyte composition on resistance of a range of RMCS separators.

TABLE 5

Discharge capacities of mercury-zinc button cells (350 mA h) containing graft copolymer separators after storage at 55 °C

Separator	Dry thickness (μm)	Electrolytic resistance* ($\Omega \text{ cm}^2$)	Discharge current (mA)	Discharge capacity (mA h)** Storage period (months)		
				1	3	6
RL-35	40	0.12	10	249	270	252
			0.5	308	286	238
RL-21-0	35	0.15	10	227	190	205
			0.5	300	283	278
RL-13-0	35	3.1	10	0	0	0
			0.5	320	319	312
Synpor (porous PVC)	260	0.06	10	275	290	280
			0.5	308	171	206

*10M KOH, 25 °C.

**Average for 6 cells.

LDPE with widely varying graft levels (and resistances) and the control material Synpor. It can be seen that no single material within the range shown is capable of adequately meeting the requirements of long storage life and high rate discharge capability.

The cells containing the lowest graft level separator possessed the best low drain capability and stored well for up to 3 months, but did not discharge at all at higher currents of 10 mA. Conversely, those cells with the highest graft level separator discharged well at the high rate, even after storage,

but their low rate performance diminished with ageing. The separator with an intermediate graft level gave intermediate performances at both rates and on storage. Cells with Synpor (microporous polyvinyl chloride) had a better high rate capacity than the copolymers but gave a poor low rate performance.

The cell behaviour appears to be significantly influenced by the graft level and thus the resistance of the separator material in the electrolyte. If the resistance is too high then high drain rates are not possible, though storage and low drain capability are good. If the resistance is too low then the opposite is generally the case. The diffusion of mercury within the cell is thought to be responsible for the loss of capacity on storage.

4.1.3. Mercury-cadmium

Cell construction and test procedures

The studies were carried out on cells with a nominal capacity of 430 mA h at 20 °C (260 mA h at -40 °C). Each cell contained one or two layers of non-woven polypropylene felt absorber in addition to one, two or three layers of the graft copolymer, and an absorbent cotton pad was placed next to the anode in each case. Table 6 shows the various cell assembly combinations, the graft copolymer separators having been chosen for their good metal barrier properties, handleability, and resistance to curling during cell assembly. The control cell contained P-2291 40/60 and the electrolyte was nominally 30% KOH.

The electrical tests, carried out on five cell batches, consisted of a 5 mA constant current drain on both freshly made cells and also on those stored for up to 3 months at 70 °C. The discharges were taken at 20 °C and -40 °C. Cell voltages were also measured after 20 ms during nominal 50 mA pulsed discharges on fresh and aged cells.

TABLE 6

Cell composition of long life mercury-cadmium button cells

Cell number	1	2	3	4	5	6	7	8	9
Graft copolymer separator	P-2291 (40/60)	RF-13	RH-27	RH-27P1	RL-33	RH-27P2	RP-34	RH-27	P-2291 (40/60)
Number of separator layers	1	1	1	1	2	2	3	1	1
Σ Separator layer thickness (μm)	30	55	43	43	80	86	96	43	30
Number of felt* layers	2	1	1	1	1	1	1	1	2
Anode pad	Cotton	Cotton	Cotton	Cotton	Cotton	Cotton	Cotton	Felt**	Felt**
Σ graft copolymer resistance (Ω cm ²)	0.20	0.50	0.55	0.85	0.75	0.50	0.65	0.55	0.20

*Grafted non-woven PP felt E1488 (69 μm) (RAI).

**Acrylic acid grafted HDPE felt.

TABLE 7

Capacities and half life voltages of fresh mercury-cadmium button cells discharged at 5 mA

Cell number	Capacity (mA h)		Half-life voltage (mV)	
	20 °C	-40 °C	20 °C	-40 °C
1	391	263	893	762
2	424*	(No current drawn)	891	—
3	435	203	891	663
4	443	(3 out of 5 very low capacity)	884	—
5	443	249	892	726
6	403	248	892	710
7	415	(245), (263)** one cell very low	893	740
8	425	157	889	642
9	413**	256	891	731

Values quoted are averages of 5 cells.

*2 cells.

**4 cells.

Metal analysis was carried out on separator components after storage and discharge using X-ray fluorescence spectroscopy, and the mercury content of the anode compartment (the cadmium electrode, absorbent pad, graft copolymer separator, and non-woven felt on the anode side of the separator) was determined by atomic absorption spectroscopy.

Results

The discharge capacities and half-life voltages of fresh cells are shown in Table 7. The cells containing RMCS materials (cells 2 - 8) generally gave higher capacities and comparable voltages to the control cells (cells 1 and 9) when discharged at 20 °C. In discharges at -40 °C, however, the control cells performed better; some copolymer separator combinations either failed to discharge at 5 mA or gave widely spread results.

The capacities measured for stored cells on a 5 mA drain at -40 °C are given in Fig. 10 (restricted for clarity to the values for the best cell batches). All cells gave greatly reduced capacities after ageing at 70 °C, but those cells with RMCS separators (5, 6, and 7) compared well with the controls (1 and 9) at the end of 3 months storage.

The comparison of cell voltages measured on fresh cells during the 25 - 50 mA current pulses at -40 °C shows again that cells 5, 6, and 7 gave a better performance (710, 680, and 720 mV) than cells 2, 3 and 8 (0, 620, and 570 mV), despite the greater thicknesses and higher resistances in 5, 6 and 7. Control cells gave 780 mV. After storage for 3 months at 70 °C the voltages of both control and test cells 5, 6 and 7 were comparable at 700 mV.

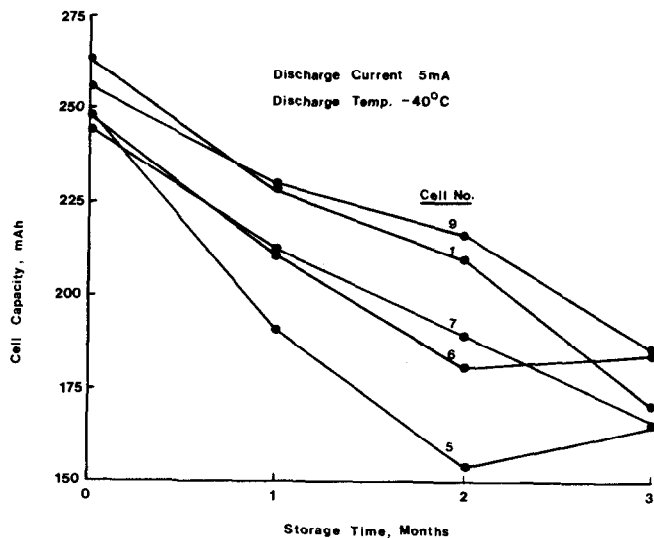


Fig. 10. Discharge capacities of mercury-cadmium button cells containing RMCS separators after storage at 70 °C.

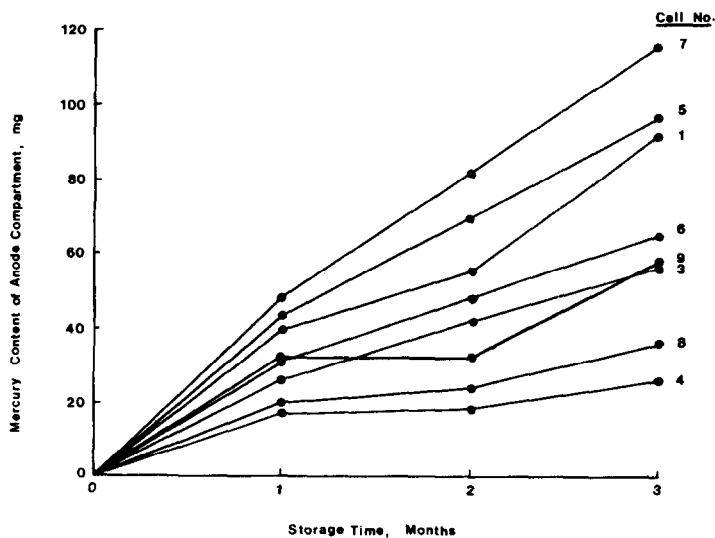


Fig. 11. Mercury diffusion in mercury-cadmium button cells containing RMCS separators after storage at 70 °C.

The results from the mercury metal analysis are shown in Fig. 11. The metal content of the anode compartment varied from 20 mg to 120 mg after storage at 70 °C for 3 months, though much of this appears to have passed through the separator and felt layers and into the anode, since the total content of the separators was found to be typically only a few milligrams. In some cells, notably from batches 2, 3 and 4, mercury globules weighing up

to 37 mg were found in the separator layers, indicating considerable parasitic redox activity within the cell. In general, the felt absorber contained up to twice as much mercury as its corresponding graft copolymer material.

Measurement of the cadmium content of the graft copolymer and felts revealed that a total of up to 150 mg of metal was present in these layers, the majority being retained in the felt, which is not surprising since it was placed in the cell adjacent to the cadmium electrode. In those cells (1 and 9) which had an extra layer of felt against the mercury electrode, the layer was found to contain only very small amounts of cadmium, indicating that there was minimal cadmium migration across the cell.

The mercury electrode in these cells contained up to 10% by weight of silver, and analysis showed that this had also migrated through the cell, with concentrations in the copolymer separators (0.01 - 0.1 mg) being larger than in the felts (0.001 - 0.04 mg), indicating that the separators were retarding silver migration.

4.2. Secondary cells

The application of graft copolymers in secondary systems was first studied at RMCS in what is referred to in this paper as a medium rate silver-zinc cell having a maximum current density output of 300 A per square metre. These cells were developed for use in the United Kingdom satellite programme and the main requirements of the system were an improved cycle life and a longer storage life in the activated state than that achieved by cells with cellulosic separators.

The work was later extended to produce separators for a high rate silver-zinc cell (current density up to 1000 A per square metre) although the cycle life required of this system was relatively low at 15 - 20 cycles.

Graft copolymer separators are currently being evaluated in nickel-zinc batteries to be used primarily for traction applications, where the need is for a high energy density, long cycle life system.

The final secondary application described is the vented nickel-cadmium aircraft battery. A cellulosic separator degrades in the oxidising environment within this battery, losing its separator properties, and the degradation can, in some cases under constant overcharge conditions, lead to catastrophic breakdown in the cell known as thermal runaway.

4.2.1. Silver-zinc

Cell construction and test procedures

Medium rate. The test cell, having a nominal capacity of 5 A h, consisted of 3 positive electrodes sealed into 100 μm thick, woven nylon fabric bags and four equivalent area negatives, 'U'-wrapped with 5 layers of graft copolymer separator. The separators were chosen from a range of materials and were made by both the organic and aqueous grafting techniques: their basic properties are given in Table 8. The electrolyte was 30% KOH and the cells were positive limited.

TABLE 8

Properties of graft copolymer separators tested in medium rate silver-zinc cells

Separator	Grafting medium	Dry thickness (μm)	Electrolytic resistance* ($\Omega \text{ cm}^2$)	Dimensional stability (%)				Zinc penetration time (min)**	
				l	b	t	w	(i)	(ii)
RL-36-0	Organic	44	0.21	7	8	11	50	108 \pm 35 (13)	380 \pm 90
RP-46-0	Organic	25	0.20	12	-3	28	80	52 \pm 4 (2)	230 \pm 85
RH-37-0	Organic	46	0.17	9	9	8	55	168 \pm 70 (10)	340 \pm 90
RH-32	Aqueous	43	0.20	7	5	-18	30	260 \pm 100 (16)	—
RL-57	Aqueous	48	0.09	16	17	18	80	176 \pm 90 (18)	—
Diophane (washed)	—	22	0.06	-2	2	162	185	214 \pm 90 (10)	—
PUDO 134	—	37	0.05	5	-2	210	350	—	350 \pm 165
P-2291 (40/30)	Organic	32	0.21	8	4	2	50	(150 - 240)***	—

*7M KOH, 25 °C.

**(i) Laboratory A — values include standard deviation and number of measurements (in brackets).

(ii) Laboratory B — average of 5 measurements.

***Trade literature.

Two electrical tests were performed, an activated long stand and a cycling test. The activated stand life was measured at normal temperature and at 40 °C, although for brevity only the 40 °C results are reported here. At the end of the stand time, cell capacities were measured by discharging at 4 A to a 1.0 V cut-off. The cycling tests were carried out at normal temperature according to the following regime: charged at 300 mA for 16 h or to a 2.06 V cut-off, charged stand time of 6 h, discharged at 2.5 A (300 A per square metre) to a 1.0 V cut-off.

High rate. The test cell was a nominal 5 A h cell containing eight positive and eight negative electrodes with pairs of negatives 'U'-wrapped in four layers of separator. The cells were flooded with 11M KOH as electrolyte.

After two forming cycles the cells were cycled as follows: charged at 250 mA to a 2.0 V cut-off, charged stand time varying between 5 and 14 days, discharged at 27 A (1000 A per square metre) to a 1.0 V cut-off and then drained at 500 mA to a 1.0 V cut-off.

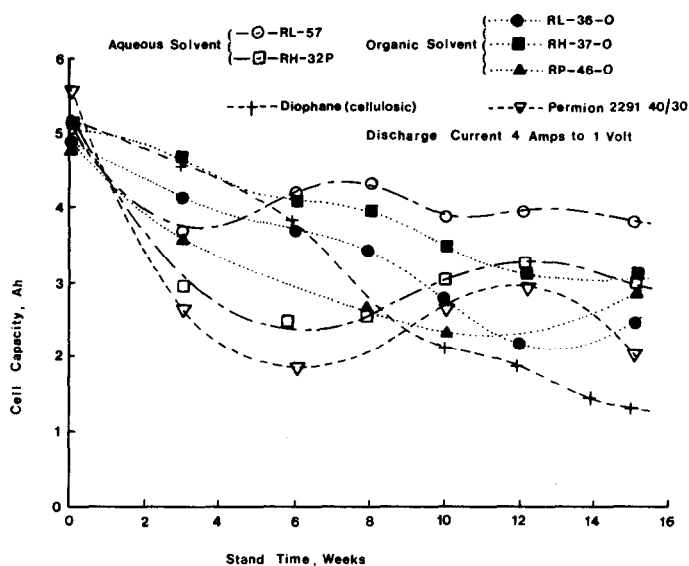


Fig. 12. Effect of activated stand at 40 °C on capacity of medium-rate silver-zinc cells containing RMCS separators.

Results

Medium rate. The results of the long stand tests are shown in Fig. 12 in which each point is the average of 2 cells. After a 15 weeks stand all cells containing graft copolymer separators showed better charge retention than control cells containing a cellulosic (Diophane) separator. There was no significant difference in performance between the copolymers prepared by aqueous or by organic routes, including P-2291 40/30, with the exception of RL-57, a high acrylic acid content separator made by the aqueous process, which, after a 6 weeks stand, was consistently better than the other materials.

The results of the cycling tests are given in Figs. 13 and 14 where capacities are plotted against cycle life for both graft copolymer separators alone and when used in conjunction with cellophanes. Figure 13 clearly illustrates the superior cycling behaviour of cells containing the cellulosic separator, and demonstrates the fairly rapid decline in cells containing graft copolymers. There was little difference in performance between cells containing copolymers made by either the organic or the aqueous process and no obvious dependence on the choice of separator base film.

Cells containing P-2291 maintained a fractionally better capacity at the higher number of cycles and this may have been related to the pre-crosslinking of the base film of the separator [10].

The superior behaviour of the cellulosic was attributed, in part, to the tight cell packing resulting from large thickness changes associated with this type of material in electrolyte. Attempts to mimic this swelling pressure by

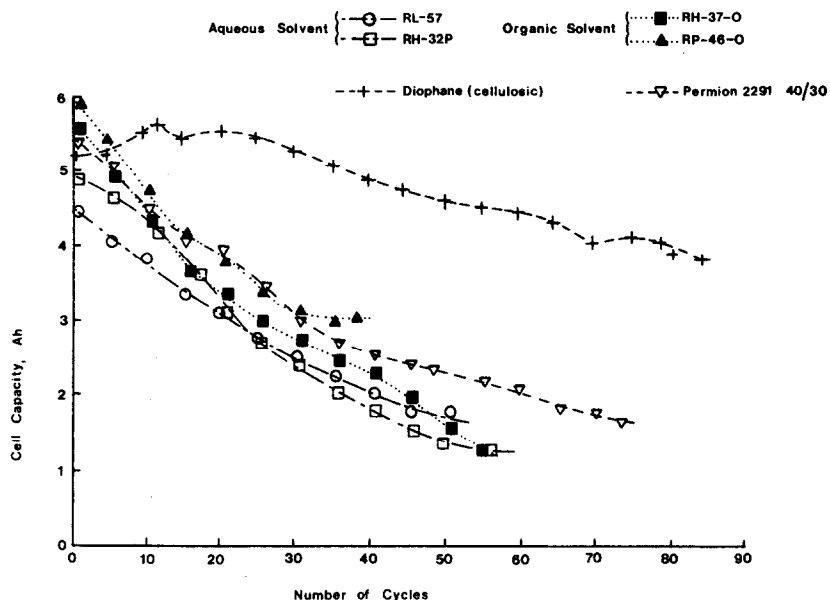


Fig. 13. Cycle life of medium-rate silver-zinc cells containing RMCS separators.

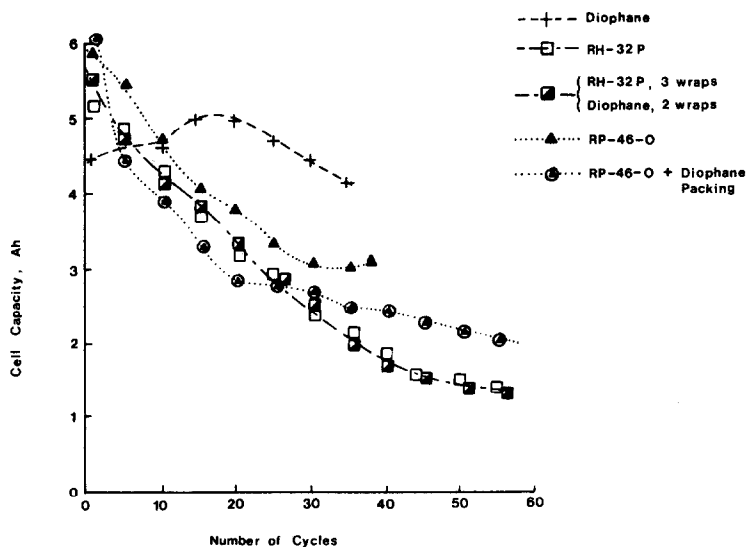


Fig. 14. Cycle life of medium-rate silver-zinc cells containing RMCS separator/cellophane combinations.

using cellophane as packing pieces were not conclusive however, since cells without cellophane packing gave the better capacity retention (Fig. 14). A composite separator system of 3 layers of copolymer and 2 layers of cellulosic also failed to improve on the performance of the copolymer alone.

TABLE 9

Cycle life of medium rate silver-zinc cells rebuilt with new electrodes

Separator	Total number of cycles		
	Initial	First rebuild	Second rebuild
RL-30-0	63	129	213
RH-33-0	94	118	—
PUDO 134	106	132	—

Examination of cycled cells revealed that most of those with cellulosic separators had failed because of separator degradation, whereas cells containing graft copolymer materials tended to lose capacity because of densification and shape change of the zinc electrode. The copolymer separators themselves remained intact and functional. The retention of separator properties is demonstrated in Table 9 which shows some results obtained by rebuilding cells with new electrodes but using the same separators. One copolymer material, RL-30-0, though giving low initial cycle life, withstood rebuilding twice and, thereby, more than tripled its original life.

High rate. Table 10 summarises some basic separator properties, cycle lives, and methods of cell failure for cells containing 18 different copolymer separators and 2 control cellulosic materials. In these high rate cells, apart from those which failed to discharge properly because of high separator resistance, a significant number of cells failed because of dendrite shorting although all cells were also found to have suffered from slumping of the zinc electrode.

The use of graft copolymers in these cells to replace a cellulosic material could not be effected directly without making allowance for the differences in thickness between the two types of material when swollen in electrolyte, and inert plastic spacers were used as packing in the cell assembly; the number of pieces was critical, too few resulted in no improvement in cell performance and too many resulted in cell rupture.

The cycling results achieved are illustrated in Figs. 15 and 16. Figure 15 shows the discharge profiles obtained for a number of separator combinations on the 7th cycle. The addition of one layer of a graft copolymer, RL-35P, next to the silver electrode, together with 3 layers of cellophane to make a composite separator, though slightly reducing the cell voltage gave the greatest capacity. Multiple layers of cellophanes were found to have suffered progressive oxidative degradation starting with the layer adjacent to the silver electrode. The introduction of the one layer of graft copolymer next to the silver electrode was sufficient to restrict silver migration and protect the cellophane layers from degradation.

Figure 16 shows some typical cycle life performances where the capacities plotted are the average of 3 cells. The control material, C19 (a proprietary silver loaded cellophane), had good high rate output over the first few

TABLE 10
Properties of graft copolymer separators tested in high rate silver-zinc cells

Separator	Dry thickness (μm)	Electrolytic resistance* ($\Omega \text{ cm}^2$)	Electrolyte permeability** (mmoles KOH $\text{cm}^{-2} \text{ min}^{-1}$)	Zincate diffusion (nmole $\text{cm}^{-2} \text{ min}^{-1}$)	Zinc penetration time*** (min)	Average number of cycles	Cell failure mode †
RL-33P	16	0.06	0.42	280	49	4	ZP
RL-40	18	0.38	0.25	9	159	> 13	—
RL-32	20	1.45	0.21	3	> 300	3	CL
RL-35	25	0.14	0.32	70	44	8	CL
RL-35P	25	0.07	0.45	310	33	6	ZP
RL-35	26	1.35	0.20	—	> 300	3	CL
RL-42P	29	0.07	0.46	270	45	7	ZP
RL-34P	34	0.14	0.28	—	74	5	CL
RL-35P	52	0.17	0.24	—	117	7	CL
RL-45	52	0.72	0.25	—	> 300	3	CL
RH-29	10	0.97	0.24	3	> 300	11	ZP
RH-30	10	0.06	0.30	—	80	5	ZP
RH-55	35	0.19	0.45	—	226	3	CL
RH-55P	28	0.04	0.57	320	27	8	ZP
RP-41	25	0.18	0.28	70	68	8	CL
RP-59P	38	0.06	0.48	250	58	7	ZP
RF-20P	15	0.12	0.36	340	60	7	ZP
RF-26P	32	0.13	0.31	120	41	10	ZP
PUDO 193	25	0.07	0.39	390	128	—	—
C19	29	0.08	0.30	290	153	> 13	—

*9.8M KOH, 25 °C.

**10M KOH concentration gradient.

***Average of 5 measurements.

†ZP signifies zinc penetration.

CL signifies capacity loss.

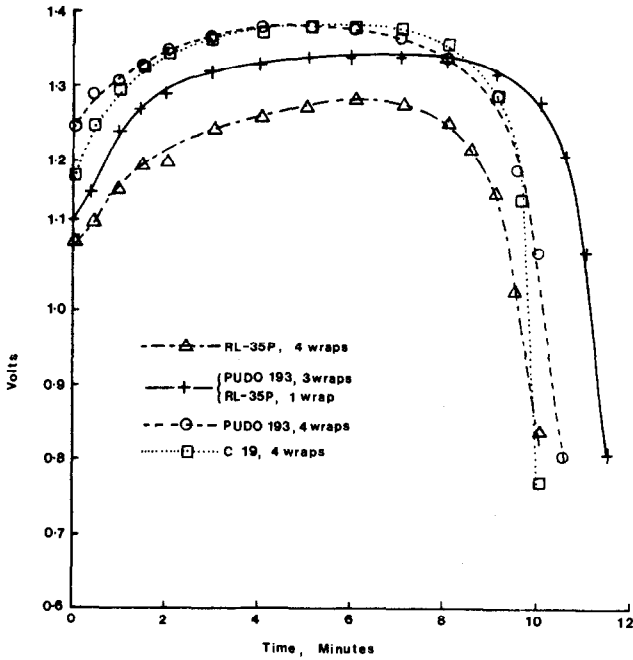


Fig. 15. Discharge characteristics of high rate silver-zinc cells (cycle no. 7, 27 A).

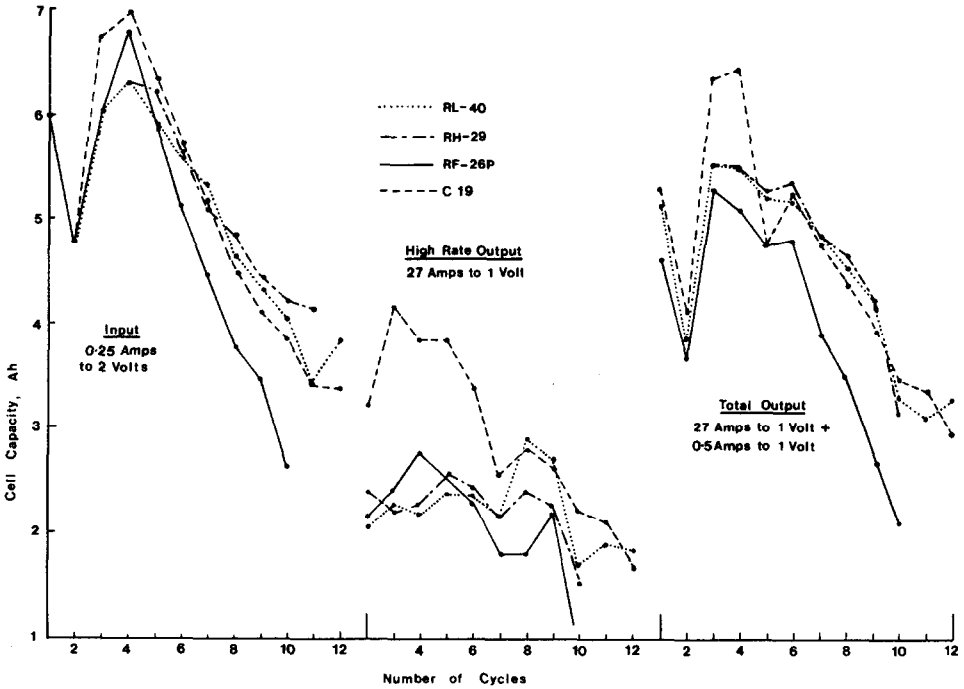


Fig. 16. Cycle life of high-rate silver-zinc cells containing RMCS separators.

TABLE 11

Charge/discharge efficiencies of high rate silver-zinc cells

Cycle number	Cell efficiency (%)							
	C19		RL-40		RH-29		RF-20P	
Separator	High rate	Total	High rate	Total	High rate	Total	High rate	Total
1	—	88	—	85	—	77	—	77
2	67	84	42	80	51	87	45	77
3	62	95	38	92	37	92	39	87
4	55	92	34	87	36	87	40	75
5	60	74	39	87	40	84	42	80
6	59	91	41	92	43	94	44	94
7	50	93	42	92	41	92	40	87
8	61	96	62	97	50	97	48	93
9	63	96	63	98	51	97	64	84
10	56	90	42	81	38	74	31	81
11	62	100	54	89	—	—	—	—
12	50	87	49	86	—	—	—	—

$$\text{Efficiency} = \frac{\text{Ampere hour output}}{\text{Ampere hour input}} \times 100.$$

Cycles 1, 2; forming cycles.

Cycle 3 onwards; charge at 10 A m^{-2} discharge at 10^3 A m^{-2} , drain at 10 A m^{-2} .

cycles but the capacity gradually falls and the material RL-40, though initially worse, has, at the end of cycling, a performance comparable with the control. The high rate performance of RL-40 may well have been limited by its relatively high electrolytic resistance ($0.38 \Omega \text{ cm}^2$) compared with C19 ($0.08 \Omega \text{ cm}^2$), though it was chemically more stable and well able to prevent dendrite failure of the cell. The individual cycle efficiencies for the cells are given in Table 11, and these results indicate that both the total and high rate efficiencies for the best graft copolymer are similar to those of the best cellulosic material evaluated.

In those cells where zinc penetration was the primary mode of failure the penetration occurred near the electrode edges. It was also observed that separators with low zinc dendrite resistance in screening tests allowed premature cell failure by zinc penetration. The screening tests further indicated that there were differences in the method of dendrite damage between cellulose and graft copolymers. In cellulose, zinc appeared to be deposited in layers over the whole exposed surface prior to penetration, whereas in graft copolymers the dendrite penetrated at isolated points around the periphery of the zinc stud.

4.2.2. Nickel-zinc

Cell construction and test procedures

Test cells (nominally 10 A h) comprised 1 zinc and 2 nickel electrodes with the separator and a standard felt absorber, Viledon FT 2119, formed into a pocket surrounding the zinc electrode. The electrode dimensions were 15 × 9 cm and the electrolyte was 30% KOH saturated with zinc oxide (6 - 8%) and contained 1% lithium hydroxide.

Cells were charged at 2.5 A for 2 h and discharged at 5 A to a 1.0 V cut-off, representing approximately 50% depth of discharge for the nickel electrode and 20% for the zinc electrode. Cycling tests were normally considered to be terminated when a cell failed to give 90% efficiency, where efficiency is defined as the charge delivered divided by the charge input per cycle, although, in some cases, cycling was carried out to ~ 80% efficiency.

Results

Table 12 summarises the properties of the range of materials tested. Initially the copolymers were chosen for good dendristatic properties as indicated by the long zinc penetration times, and an electrolytic resistance low enough to permit the required current drain from the cell. Subsequent materials were chosen for high electrolyte permeability.

Figure 17 shows some typical cycling performance data. The graft copolymers were initially tested in a 2 layer wrap to accommodate the range of material thicknesses supplied. In discharge tests most of the cell efficiencies were better than 95% and, after several forming cycles, normal cycling pro-

TABLE 12

Properties of separators tested in nickel-zinc cells

Separator	Dry thickness (μm)	Electrolytic resistance* ($\Omega \text{ cm}^2$)	Electrolyte permeability** (mmoles KOH $\text{cm}^{-2} \text{ min}^{-1}$)	Zinc penetration time (min)	Average number of cycles***
RP-34	32	0.11	0.25	> 400	200
RP-16	25	0.015	0.20	117	300
RH-29	22	0.13	0.14	225	75
RL-35-305	20	0.07	0.23	> 400	55
RP-35Ni	32	0.24	0.12	300	65
RP-32Ni	32	0.18	0.15	170	140
RL-33	40	0.16	0.21	58	145
RL-33Ca	40	0.15	0.17	—	115
RL-35-241	28	0.08	0.40	46	140
RL-42	28	0.03	0.55	19	> 200
RL-37	15	0.02	0.60	49	85
Celgard 3401	25	0.05	0.19	42	190

*5.8M KOH, 25 °C.

**10M KOH concentration gradient.

***2 separator wraps, except Celgard 3401 with 3 wraps.

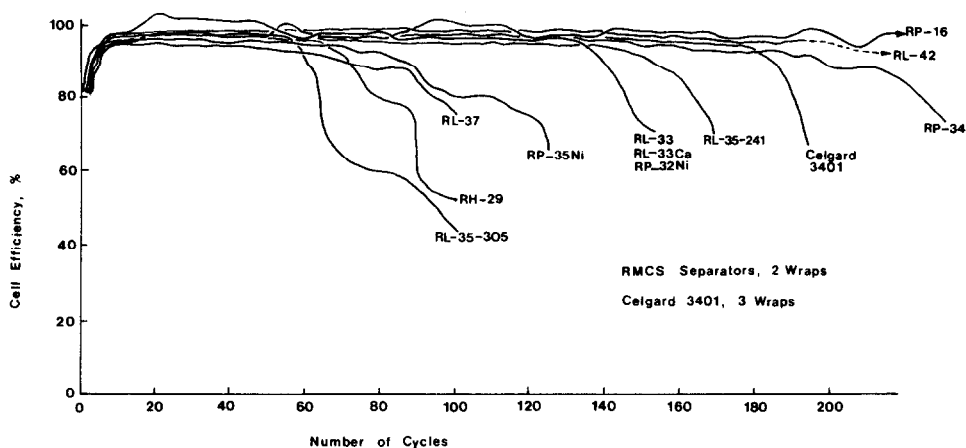


Fig. 17. Cycle life of nickel-zinc cells containing RMCS separators.

gressed until cells failed by capacity loss. Overall cycle lives ranged from 60 to 400 cycles according to the separator type and combination.

The number of separator wraps around the zinc electrode was shown to influence the cycle life markedly. In some cases reducing the separator to a single thickness resulted in a 50% reduction in cycle life, as shown in Fig. 18, though this was not the general case for graft copolymers and Fig. 19 shows the cell performance for single, double, and triple wraps, where the single wrap gave the best life, albeit quite low at 80 cycles.

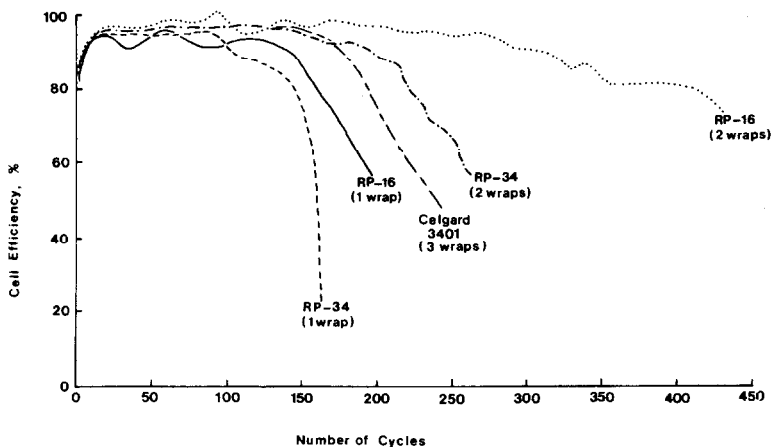


Fig. 18. Effect of number of separator wraps on cycle life of nickel-zinc cells containing RMCS separators.

The material used throughout for comparison was Celgard 3401, a microporous polypropylene, in a 3 layer wrap, chosen as a commercially available, uniform, and reproducible separator. It consistently gave 190 cycles.

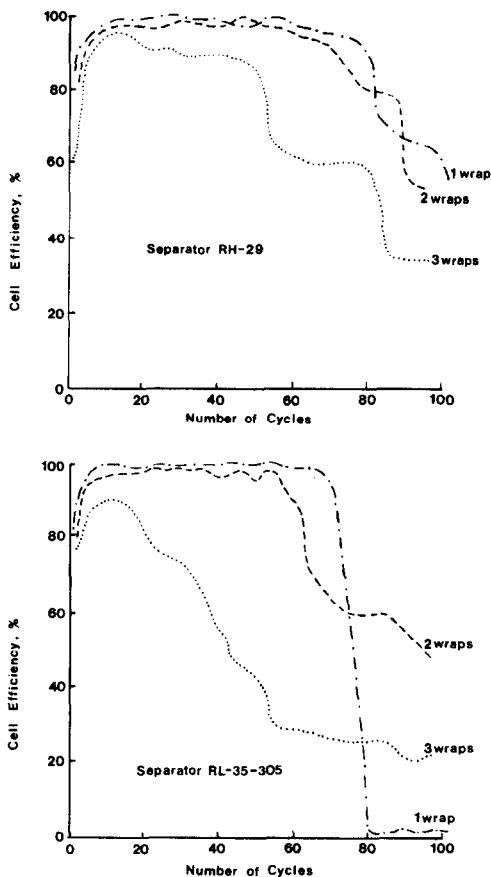


Fig. 19. Effect of number of separator wraps on cycle life of nickel-zinc cells containing RMCS separators.

There was an indication that the separators, or combinations, which gave the best initial efficiencies eventually produced the longest cycle lives and those with lower efficiencies failed early. This implies that poor zinc utilisation and deposition control started very early and consequently caused premature failure.

Examination of failed cells revealed that the cause of failure was invariably irregular and irreversible shape change of the zinc electrode. Dendrite formation and shorting was apparently not a significant problem with any of the graft copolymers, especially when multiple wraps were used. In some tests, using a single separator thickness, a sudden loss of capacity was noted which may have been due to dendritic growth (RP-34 in Fig. 18 and RL-35-305 in Fig. 19). No visual evidence of dendrites was found, however, and since these failures usually occurred at about the same number of cycles as significant shape change was expected, the cause may have been physical damage to the separator resulting from the electrode deformation.

Although a number of copolymer separators with good cycle life in this system have been identified, specific correlations of in-cell performance with separator properties such as electrolytic resistance, zinc dendrite stopping power, and electrolyte permeability, have not been found.

4.2.3. Nickel-cadmium

Cell construction and test procedure

Graft copolymer separators were tested in conjunction with 2 layers of a non-woven nylon felt absorber, with the copolymer adjacent to the negative electrode, in 16 A h and 40 A h capacity cells. Sintered plate electrodes were used with the separator combination wrapped around the plates in a zig-zag conformation. The electrolyte was 30% KOH. Test cells were discharged at the 10 C rate at various temperatures. Metal migration analysis was undertaken on cells that had been subjected to controlled cycling.

Results

Some basic characteristics of the copolymer materials tested are given in Table 13 and typical discharge profiles for 2 materials and cellulosic controls are shown in Figs. 20 and 21.

From Fig. 20 it can be seen that, at ambient temperature, cells containing a relatively thick material, RL-34P (53 μm), with a moderately high resistance and a low electrolyte permeability, performed reasonably well in comparison with control cells containing a cellulosic separator. At -30°C , however, cells with RL-34P had a poor overall capacity and suffered an unacceptable voltage drop at the start of discharge. Results for a thinner material, RL-33P2 (18 μm), which had a similar resistance and a higher electrolyte permeability than cellophane are shown in Fig. 21. A much improved capacity at low temperature was observed and the voltage dip at -30°C experienced by cellulosic containing cells was virtually eliminated.

TABLE 13

Properties of graft copolymer separators tested in vented nickel-cadmium cells

Separator	Dry thickness (μm)	Electrolytic resistance* ($\Omega\text{ cm}^2$)	Electrolyte permeability** (mmoles KOH $\text{cm}^{-2}\text{ min}^{-1}$)	Dimensional stability*			
				l	b	t	w
RL-34P	53	0.12	0.23	8	10	10	40
RL-33	18	0.08	0.24	2	6	1	25
RL-33P1	18	0.04	0.33	6	4	1	45
RL-33P2	18	0.03	0.46	9	11	1	30
RH-29	9	0.06	0.28	3	0	0	35
Cellulosic	20	0.03	0.32	-4	12	265	280

*7M KOH, 25°C .

**10M KOH concentration gradient.

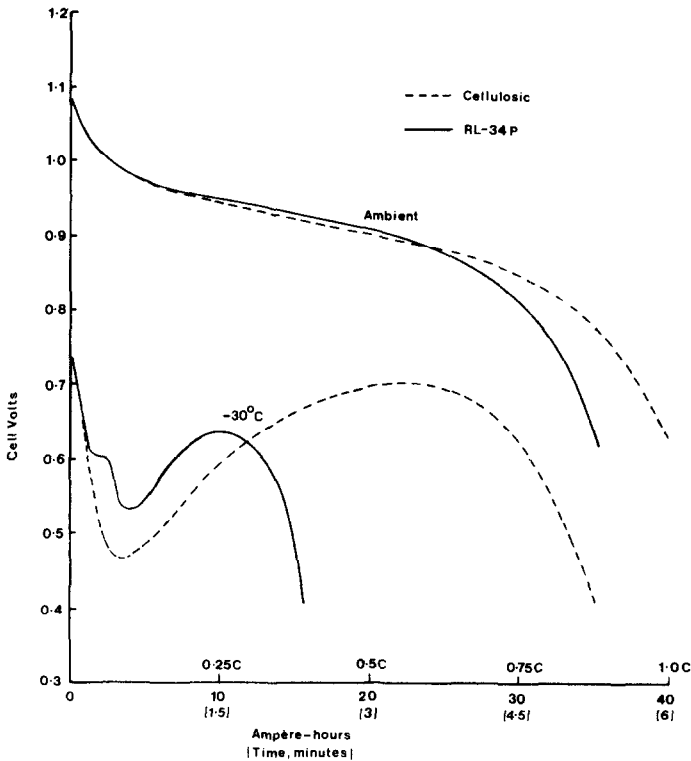


Fig. 20. Discharge characteristics of 40 A h vented nickel-cadmium cells containing RMCS separators (at 10 C rate).

The influence of some basic separator properties given in Table 13 on the in-cell performance of the materials was also particularly well demonstrated in this application. For example, RL-33, RL-33P1 and RL-33P2 were made from the same basic graft copolymer, differing only in post graft treatment to change its resistance and electrolyte permeability. At ambient temperature cells containing these materials had similar discharge characteristics comparable with the cellulosic control. But at -30°C only cells containing RL-33P2 were better or comparable with the performance of cells with the control cellophane.

The resistance to oxidation and degradation of graft copolymers has been shown to be far superior to cellulose in laboratory tests [2], and battery tests have confirmed these findings. For example, in cells subjected to a C/10 overcharge at 55°C , graft copolymers gave lifetimes 2 - 3 times longer than cellulose as monitored by the water consumption of the cells [6]. Examination of used cells has also revealed that, whereas graft copolymer separators were always intact, cellulosic materials were either very fragile or had disintegrated into a sludge on the electrode surface.

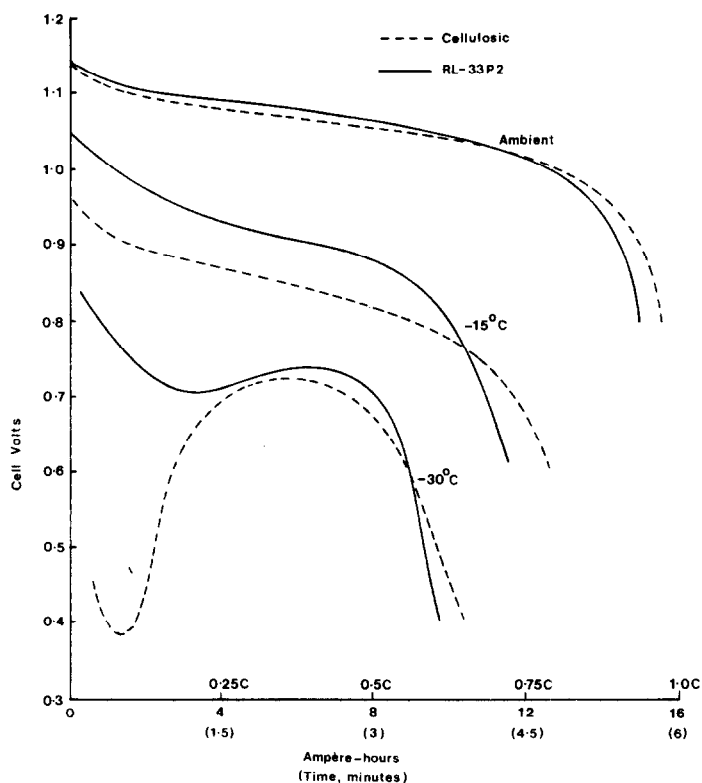


Fig. 21. Discharge characteristics of 16 Ah vented nickel-cadmium cells containing RMCS separators (at 10 C rate).

Metal contents of separators from selected 40 Ah test cells were measured after subjecting the cells to the following cycle regime: a prolonged overcharge at the $C/10$ rate for 60 h with up to twice the recommended water loss, topping-up with water followed by a C rate discharge to 0.5 V and a stand in the discharged state for a few hours before recharging. After 25 cycles the cells were dismantled and the separator layers from at least 2 positions in the cell were examined for metal content by X-ray fluorescence spectroscopy.

In cells where the copolymer or cellophane separator was adjacent to the cadmium electrode, the maximum amount of nickel found in any layer was $15 \mu\text{g cm}^{-2}$ and cadmium levels in any layer did not exceed $18 \mu\text{g cm}^{-2}$.

In another type of cell where the copolymer or cellophane separator was sandwiched between the two felt layers, the maximum amounts of nickel found were again $15 \mu\text{g cm}^{-2}$. Cadmium levels were higher with up to $60 \mu\text{g cm}^{-2}$ in cellophane layers and up to $230 \mu\text{g cm}^{-2}$ in copolymers, although levels in felt layers did not exceed $20 \mu\text{g cm}^{-2}$.

Some cells after cycling were deliberately driven into thermal runaway situations. For cells with cellophane separators, nickel and cadmium levels

were higher in all layers, including felts; in the vicinity of hard shorts that developed at the base of the cells, cadmium levels up to $60 \mu\text{g cm}^{-2}$ were measured in the felt layers.

Cells containing graft copolymers were more difficult to drive into thermal runaway and only one cell, which had developed a hard short, again at the base of the cell, was analysed. Nickel levels of approximately $8 \mu\text{g cm}^{-2}$ were found in all the separator layers except in the vicinity of the short where a felt next to the nickel electrode contained $40 \mu\text{g cm}^{-2}$. Cadmium levels in the vicinity of the short were higher than elsewhere, with levels up to $400 \mu\text{g cm}^{-2}$ being found in the copolymer.

In summary, nickel and cadmium levels in copolymer and cellophane separators and felts were generally about $20 \mu\text{g cm}^{-2}$. If cells were put into thermal runaway conditions higher levels were found, with a maximum level of cadmium of $400 \mu\text{g cm}^{-2}$ in the vicinity of the short. Even so, the latter value of metal uptake is much lower than those associated with separators from other systems studied such as primary silver-zinc cells.

5. Discussion of results

5.1. Primary cells

The test results on silver-zinc button cells clearly illustrate the effects of graft copolymer separator resistance on cell performance. In general, freshly made cells containing low resistance materials performed best, especially when high current pulses were required. For low current drain applications the effect of separator resistance was marginal. After long storage periods, however, particularly at elevated temperatures, cells containing low resistance separators often gave low capacity retention, probably because of silver migration, since low resistance separators have been shown to have inferior properties as a metal barrier.

A compromise must therefore be sought between resistance and barrier properties unless some means of improving metal stopping power of low resistance separators can be found. Cross-linking of the base polymer by irradiation before grafting seems to be reasonably effective, as shown by the pulsed current data where an improvement in cell life of the pre-irradiated separators is believed to have resulted from better barrier properties. Improved metal stopping power may also be obtained by the lamination of graft copolymers to cellophane. Laminates were originally produced to aid the handling properties of graft copolymers during cell assembly; they are often difficult to machine punch, and have a tendency to curl on contact with electrolyte. The cellophane was being used essentially as a sacrificial layer. Some workers [9] have established that such materials have better barrier properties than expected, and the so-called synergistic effect is now an important part of silver-zinc button cell technology [14]. The superior in-cell performance of the laminate P-2190 reported in this work is in agreement with these findings.

The results indicate that, overall, there are major problems in predicting separator/cell behaviour for different applications. In particular, storage at elevated temperatures, often used in accelerated ageing tests, can lead to enhanced metal migration not found under normal usage. Ideally, therefore, comparisons of separator performance should be made as near as possible to the environment in which the cell is to be used.

Results from mercury-zinc cells lead to similar conclusions. Low resistance separators produced superior high current drain performance on fresh cells but much reduced cell capacities at lower current drain rates after long periods of storage at elevated temperature. The reduced capacity here was probably a result of mercury migration, and the large quantities of metal which were found to have migrated to the anode compartment of the mercury-cadmium cells substantiate this theory. The most efficient separators in the prevention of mercury diffusion, however, produced inferior electrical performances, particularly on low temperature discharges.

It appears, therefore, that a compromise must be made again or an alternative method of preventing mercury migration found. Griffin [12] measured mercury transport to the anode in a standard mercury-zinc cell for various types of absorbers and membrane separators and his results indicated that cross-linked separators were more effective (100% reduction in mercury transport) than non-crosslinked materials (70% reduction) either in a single layer or as a laminate. A cellulosic material (dialysis paper) was among the least effective metal barriers and a synergistic effect for prevention of mercury migration was not indicated. The present results indicated that, on mercury-cadmium cells, even multiple layers of graft copolymer separators tended not to reduce mercury migration substantially, though it was noted that overall cell performance was better for a multilayer than for an equivalent thickness, lower resistance, single layer separator.

5.2. Secondary cells

For convenience the discussion of separator performance in rechargeable cells has been subdivided into two parts, zinc-containing and non-zinc-containing couples.

The major problems in any zinc-containing couple arise from the zinc electrode and are concerned with dendritic growth during charging and shape change during cycling. It is outside the scope of this paper to discuss these phenomena but the comprehensive review on zinc battery technology by Bobker [5] is among many which cover these topics in depth. The discussion here is, of necessity, limited to the influence of graft copolymer separators on the zinc couples reported on, namely, silver-zinc and nickel-zinc, and the aim has been to find common factors in separator properties and performance for each system.

It has previously been reported [1] that the use of graft copolymer separators in silver-zinc cells promoted shape change in the zinc electrode and this was the primary cause of cell failure, whereas cells containing cellu-

losic separators generally suffered less from shape change and failed because of separator degradation. The results in this paper confirm that shape change is again the major problem though the reasons for this are still not clear. In general, graft copolymers have higher electrolytic resistances than cellulosics of comparable thickness, possess lower electrolyte uptakes, swell less and, although of similar electrolyte permeability, tend to have lower zincate diffusion rates. The effects of these separator properties on the zinc electrode behaviour are not understood however and there remains the possibility that the presence of separator degradation products in cellophane-containing cells influences the re-formation of the zinc electrode during charging and thus minimizes shape change.

Graft copolymers are, however, chemically very stable, and permit good capacity retention in cells on activated charged stand tests at normal and elevated temperatures. For the medium rate silver-zinc cells stored at 40 °C the best material, RL-57, had a high acrylic acid content and abnormally low electrolytic resistance considering its thickness. It did not, however, perform well in subsequent cycling tests and better results were obtained from other materials, RL-46-0, P-2291 and a cellulosic (Diophane). Zinc slumping was the main cause of failure in all cells containing graft copolymers.

In the higher rated silver-zinc cells the regime was so severe as to limit cycle lives. All separators tested, including cellulosics, quickly lost capacity because of shape change, although some materials, especially those with low zinc penetration times, eventually failed because of dendritic shorts. The best graft copolymer tested in this system was RL-40 but others such as RH-29 and RF-26P produced reasonable performances. All these materials again had high acrylic acid contents (for their respective base polymers) and fairly high equilibrium electrolyte retention. Their electrolytic resistances were, however, substantially higher than the cellulosic control C19, and although cell efficiency was affected, the cycle life was comparable.

The zinc electrodes in the nickel-zinc cell were never more than 20% utilised in the cycle regime adopted and this factor was probably responsible for the relatively high number of cycles attained; electrode shape change again being the main cause of cell failure. Several graft copolymers were capable of giving a greater number of cycles than the control material, Celgard 3401. One of the best graft copolymers, RL-42, had a high acrylic acid content and, like the two other successful separators, RP-34 and RP-16, had a low electrolytic resistance. Their resistance to zinc dendrite growth, as measured by laboratory penetration tests, was poor and, seemingly, not an important parameter in this system, especially if the separator was used in multiple thicknesses.

RP-16 was prepared from a microporous base film similar to the Celgard control, and judging from previous experience in secondary zinc systems the high number of cycles obtained without zinc penetration was surprising, even when allowance is made for the cycle regime. Recent work [15] however, has shown that multilayers of this type of material, in particular a nickel coated variant, can produce a satisfactory cell cycle life.

The type of absorber material used in conjunction with the separator in the nickel-zinc system was found to have a pronounced effect on the cell performance, and cycle lives in excess of those reported here were achieved using optimised separator/absorber combinations. No such improvements were observed using multiple separator wraps, since the optimum number of layers varied for different separators. Multilayer wraps have traditionally been used in secondary zinc technology to prevent direct shorts through film defects such as pinholes and, though this precaution may not be so important nowadays because of improved film quality, it is possibly still useful since the extra surfaces of multilayers may retard dendritic growth. Multilayer separators, however, cannot be used without penalty and increases in resistance, for example, are to be expected and may be unacceptable unless ultra-thin separators are used. Recent work at RMCS on multilayers of RL-33P and PUDO 193 has shown that electrolytic resistances are additive and electrolyte permeability is approximately inversely proportional to separator thickness.

It is clear from the above that the preparation of a suitable graft copolymer for zinc-containing secondary batteries remains a problem, although cell test results on separators with high acrylic acid content, low resistance, and possibly used in multilayers, were most encouraging. It is also evident that the best separator/absorber combination will only be satisfactorily evolved as a result of studies in conjunction with all other cell parameters.

The only non-zinc-containing couple to be studied was vented nickel-cadmium. For this cell the choice of separator is not so restrictive except that chemical stability remains a prime requirement, and low resistance and high electrolyte permeability are necessary for high rate, low temperature applications.

The merits of replacing cellophane by a specially developed graft copolymer have been discussed [6], and improvements in cell performance resulting from separator behaviour and changes in other cell parameters were reported. The importance of separator stability in the cell environment was stressed and premature cell failure was ascribed principally to oxygen barrier breakdown.

The need for studies on other possible causes of cell breakdown such as cadmium metal migration has been identified [11, 13]. The latter workers showed that soft shorts caused by cadmium ingrowth into separators were more likely to cause cell malfunction than oxygen barrier breakdown. Work at RMCS has confirmed the importance of cadmium metal migration since heavy loadings of cadmium were found in separators from failed cells, particularly near the region of a hard short. The erratic behaviour on overcharge of nickel-cadmium cells operated without separators may also be more readily explained by the repeated formation and destruction of soft shorts rather than oxygen transport and recombination behaviour within the cell; observed currents of 40 A on overcharge are not easily accounted for solely in terms of oxygen recombination phenomena.

6. Conclusions

The production of graft copolymer separators by aqueous grafting techniques is simpler and more economical than the usual organic processes and the copolymers are uniform and reproducible.

Comparisons of these separators with battery grade cellophanes have shown that many of the separator properties of cellophanes may be emulated, except thickness change in electrolyte, although a single graft copolymer cannot be made which reproduces all the properties of cellophane. Graft copolymers are, however, more stable in alkaline cell environments than cellulose. Battery tests in primary and secondary alkaline systems have shown that there is no universal graft copolymer separator which combines all of the necessary requirements for different cells.

In primary cells needing long storage life at elevated temperatures the most successful graft copolymer separators are those with the highest resistances because they have the best metal barrier properties, although limiting the cell discharge current. For higher current drain rates, either pulsed or continuous, lower resistance separators are necessary and other methods of reducing metal migration must be employed. Crosslinking of the copolymer base film and/or lamination to cellophane is often effective for silver cells but is not as successful in mercury cells. Even multilayers of graft copolymers are inefficient barriers to mercury, although cell performance with a multilayer separator is generally better than that of a single layer of equivalent thickness.

In secondary zinc systems, the major causes of cell failure are shape change of the zinc electrode and the growth of dendritic shorts. Graft copolymers can be produced which have excellent resistance to dendrites, but cells with these materials suffer more from shape change than those containing cellulosic separators. For the vented nickel-cadmium secondary cell, a copolymer separator has been developed which meets all the separator requirements of the system over a wide range of operating conditions and, because of its superior chemical stability in the cell environment, it is an attractive alternative to the commonly used cellulosic materials.

In summary, graft copolymer separators are available which will function efficiently in most alkaline systems, but for optimum performance, in addition to intrinsic separator properties, other aspects of cell technology, including separator/electrolyte interaction and the behaviour of absorber/separator combinations, must be considered. Ultimately the final selection will depend on tests carried out under user conditions; accelerated storage tests, for example, at elevated temperatures may produce misleading results.

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