Evaluation of asbestos composite separators in advanced water test electrolysers

E. MONTONERI

Dipartimento di Chimica Industriale e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Pz. L. da Vinci 32 — 20133 Milano, Italy

Work performed at Milan Politecnico under sponsorship by the Commission of European Communities and in cooperation with international institutions involved in hydrogen energy programs in the last decade is surveyed. The performance of composite separators made from various linear, cross-linked and sulphonated aromatic polymers and asbestos cardboards or cloth from various sources is reported in medium temperature (95–125° C) alkaline (40–50% KOH) water electrolysers having different configurations. The results are interpreted based on knowledge of the separator structures and properties.

1. Introduction

The energy efficiency [1] of the production of hydrogen from water electrolysis [2–8] improves, in principle, as the thermodynamic voltage associated with the water splitting reaction and the cell electrical resistance decrease. Experimentally this means raising the working temperature, operating in more concentrated alkaline or acid water, shortening the interelectrode gap and using electrodes and cell separators with lower ohmic drop. In practice, the development of advanced water electrolysers operating above 100° C is severely limited by the availability of cell materials. For this reason most research prototype units have been designed to work under the following conditions: electrolyte KOH % w/w = 40–50, T = 95–125° C, P = 1–30 bar, electrode-separator gap (ESG) = 0–2 mm, current density (CD) = 1 A cm^{-2}. Under these conditions the cell separator must fulfil the following requirements [9]: low electrical resistance, good separation between anodic and cathodic gas evolving compartments and long term chemical, mechanical and performance stability.

Crysotyle asbestos (ASB) is a material used as separator in conventional water electrolysis [10, 11] which is carried out well below 100° C. It is commercially available in a variety of mechanically flexible forms which differ in porosity, thickness, area density and mechanical strength; it exhibits the most desirable combination of properties. Working above 100° C, however, it deteriorates rapidly due to alkaline hydrolysis [12],

$$Mg_3Si_2O_5(OH)_4 + KOH(aq.)$$

$$= 3 Mg(OH)_2 + \text{soluble silicates(aq.)} \qquad (1)$$
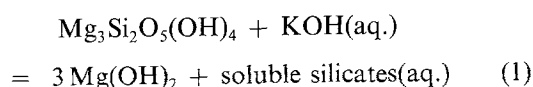
In the reaction asbestos converts to insoluble brucite which remains in the separator solid phase together with the unconverted material. Silicon leaches into the electrolyte. Because of the material loss the separator becomes more porous, mechanically weaker and, ultimately, may be reduced to fragments. The chemical composition of any left-over solid phase differs from that of the initial material. The weight loss (c.w.l. %) as derived by analysis of the change of chemical composition of the aged separators [12], corresponds to the weight loss by weight measurement (t.w.l. %). In advanced electrolysers, which operate with low ESG, mechanical erosion may occur before, or prevail over, chemical degradation. In this case, the high current density implies a fast rate of gas evolution over the surface and on the pore walls of the separator. Local mechanical stress may be high enough to cause loss of material fragments. Contrary to reaction (1), pure mechanical erosion causes no change of chemical composition in the left-over separator, regardless of its weight loss. When both chemical and mechanical erosion occur, determination of the specific contribution of each phenomenon to the overall material degradation [12] is achieved by comparing t.w.l. % and c.w.l. %.

Work on modified asbestos [12–22] has been performed with the intention of improving its stability provided that other desirable properties (i.e. mechanical flexibility and hydrophilicity) were not lost. The approach was to coat commercial asbestos with high temperature alkali resistant organic polymer layers, being aware that the behaviour of such composites would depend on the following parameters:

1. the nature of the organic polymer,
2. the morphological structure of the asbestos,
3. the average and local (i.e. bulk and surface) asbestos/polymer ratio and
4. the configuration of the electrolyser cell in which the separator is designed to work.

The lipophilic nature of organic materials is the key factor which allows protection of the asbestos fibres from hydrolysis by the alkali. Mechanical stability arises as a secondary effect due to the thickness of the coating layer and, consequently, to reduction of the

Table 1. Asbestos composite tested as separators of advanced water electrolysers*

Type of asbestos	Polymer	Polymer concentration % w/w	Thickness (TKN) mm	Area density (d) $g cm^{-2}$	Tensile strength (T_s) $kg cm^{-2}$	Water regain (W_R) $ml g^{-1}$
API CICAT (Milan)						
cardboard (ASBAC)	PPS	0.0	0.55	0.0528	30	0.44
cardboard (ASBAC)	PPS	10.0	0.55	0.0575	40	0.33
cardboard (ASBAC)	PPS	14.2	0.56	0.0618	59	0.19
cardboard (ASBAC)	PPS	17.9	0.56	0.0678	83	0.15
cardboard (ASBAC)	PPS	24.5	0.60	0.0754	115	0.10
cardboard (ASBAC)	PPS	45.8	0.76	0.0923	183	0.05
cardboard (ASBAC)	VP-DVB	4.0	0.55	0.0575	63	0.15
cardboard (ASBAC)	VP-DVB	10.0	0.53	0.0585	93	0.14
cardboard (ASBAC)	VP-DVB	13.5	0.54	0.0592	102	0.14
cardboard (ASBAC)	VP-DVB	14.5	0.54	0.0598	102	0.13
cardboard (ASBAC)	VP-DVB	16.6	0.55	0.0623	102	0.14
FERLAM VALEO						
(France) Ni wire reinforced cloth (ASBFV)	PPS	0.0	0.75	0.0693	193	0.58
(France) Ni wire reinforced cloth (ASBFV)	PPS	15.0	0.81	0.0791	126	0.43
(France) Ni wire reinforced cloth (ASBFV)	PPS	17.8	0.82	0.0809	142	0.50
(France) Ni wire reinforced cloth (ASBFV)	PPS	18.1	0.82	0.0824	141	0.51
John Manville						
(Milan) cardboard (ASBJM)	PPS	0.0	0.18	0.0170	nd	0.84
(Milan) cardboard (ASBJM)	PPS	0.0	0.40	0.0296	61	0.94
(Milan) cardboard (ASBJM)	PPS	39.4	0.22	0.0205	53	0.45
(Milan) cardboard (ASBJM)	PPS	36.2	0.45	0.0356	145	0.36
API CICAT						
(Milan) cardboard (ASBAC)	SPPS	19.0	0.56	0.0720	80	0.31

* All data referred to fresh materials, except values of ASBFV at PPS% > 0 which refer to the aged separators (Table 3); *nd* = not determined

void volume of the initial uncoated article. On the other hand as the asbestos/polymer ratio decreases, reduced wettability of the composite by the electrolyte and higher affinity for sorption of evolved electrolytic gases is to be expected. Therefore high electrical resistance of the separator may be caused either by low electrolyte concentration and/or by retainment of the gaseous film in the solid phase. These factors limit the minimum working asbestos/polymer ratio in the separator, particularly in electrolysers with low ESG configuration where the gas film effect is likely to be serious.

Composites made from asbestos and several high temperature alkali resistant aromatic polymers have been developed at Milan Politecnico within the EEC Hydrogen Energy Program [23] and tested by four engineering laboratories involved in electrolyser design and optimization. The polymers belong to two classes: polyphenylenes [15, 17], $-(-C_6H_4-X-)_n-$, (I) and polyphenyl- or polypyridyl-ethylenes (II) [14, 16]. Members of class I were polyphenylene (PP, X = 0) and polyphenylene sulfide (PPS, X = S); members of class II were polystyrene (S) and polyvinylpyridine (VP). VP was expected to show relatively higher hydrophilicity due to the highly polar pyridine nucleus. However, both class II polymers had to be used in cross-linked form (polystyrene-divinylbenzene, SDVB, and polyvinylpyridine-divinylbenzene, VP-DVB) in order to withstand the conditions to which they are

exposed in alkaline electrolysers. Irreversible chain entanglement in the cross-linked polymers occurred depending upon conditions of the synthesis. The polymers were therefore obtained in two morphological forms, i.e. the compact (C) or the macroporous (MP) form. The C form gave very non-reproducible results and serious problems connected with gas film retention. The MP form was much more hydrophilic. Sulphonated polymers, SPPS [18–20], SPP [15], SSDVB [14] were also made from PPS, PP and SDVB respectively to obtain more wettable separators. The asbestos articles which were used for the preparation of the composite separators were from various commercial sources and different sizes, mechanical strength and wettability. Table 1 lists these data for the base materials and the composite separators which have been tested under electrolysis. Table 2 summarizes the most significant features of the testing electrolysers. All of them operate at fixed electrode-separator gap, except the NRC electrolyser which had the facility [24] to move both electrodes simultaneously at the same rate towards, or away from, the separator. This feature permitted study of the dependence of the electrical behaviour of the separator on ESG.

It is concluded that the change of cell configuration, as indicated in Table 2, is not likely to influence strongly the behaviour of the separator and that PPS is the best choice.

Table 2. Electrolysers for the evaluation of the asbestos composites

Electrolyser						Tested separator
Name	Electrode -separator gap (ESG) mm	Electrolyte KOH concentration % w/w	T °C	P bar	Current density (CD) A cm²	
DTH	0.0	50	90	1	1	20 cm² ASBAC-(10–45.8%)PPS
DTH	0.0	50	100	1	1	20 cm² ASBAC-(11%)VP-DVB(C)
LDM	2.0	40	115	1	1	32.5 cm² ASBFV-(15–18.1%)PPS
LDM	2.0	40	125	30	1	20 cm² ASBAC-(10%)PPS
LDM	2.0	40	115	1	1	32.5 cm² ASBAC-(4–16.6%)VP-DVB(C)
NRC	−0.1 to 3.0	45	100	1	1	25 cm² ASBJM-(36.2–39.4%)PPS
NRC	−0.1 to 3.0	45	100	1	1	25 cm² ASBAC-(15%)VP-DVB(C)
Sodeteg	0.0	30	110	20	0.4	20 cm² ASBAC-(19%)PPS

2. Experimental details

Details have been given in recent work [12–22]. The composite separators were manufactured by soaking the asbestos (Table 1) with a solution of the polymer or, for class II polymers, with a solution of the monomers which were then polymerized into the asbestos phase. The *in situ* polymerization was carried out at 70° C, while the sorbed solvent (acetone) evaporated, to yield C-type materials. For MP-type polymer composites, the solvent was decaline or xylene and the reaction was carried out at room temperature to allow copolymerization in the presence of the sorbed solvent.

In this work PPS % w/w $= 100(w_f - w_i)/w_f$, where w_i and w_f are the weights of the asbestos commercial sample respectively before and after being coated with PPS. In previous work [12, 22] PPS$_{wg-ca}$ or PPS$_{Ir}$% $= 100(w_f - w_i)/(w_f - w_i + w_i^0)$, where $w_i^0 = 0.80w_i$ and represents the analytical weight of dry asbestos as $Mg_3Si_2O_5(OH)_4$ in the asbestos commercial sample before being coated.

3. Results

3.1. Polyphenylene sulfide composite separators

PPS separators have been manufactured over a wide polymer concentration range starting from three different asbestos types (Table 1). The ASBAC-PPS separators are made from the least porous asbestos (ASBAC $W_R = 0.44$ ml g⁻¹). In the composites the water take up capacity decreases as more PPS causes reduced porosity and change of the solid–liquid interaction due to increased lipophilicity of the solid phase [22]. Mechanical strength increases on increasing the PPS%. The performance of these materials reflects their physical and chemical nature.

The 10% PPS separator was a complete failure. High weight loss ($\sim 46\%$ w/w) occurred during electrolysis in the LDH electrolyser (Table 2). The Si concentration in the electrolyte increased as in Fig. 1, suggesting chemical degradation of the separator as in equation (1). Compositional analysis of the separator recovered from the cell confirmed that at least half

Table 3. Data* for ASBAC-PPS and ASBFV-PPS composite separators aged in DTH and LDM electrolysers

Composite	PPS in separator % w/w	Electrolyser	Electrolysis time (t) h	Water regain (W_R) ml g⁻¹	Tensile strength (T_S) kg cm⁻²	Total weight loss (t.w.l.) % w/w	Weight loss due to hydrolysis (c.w.l.) % w/w
ASBAC-PPS	10.0	LDM	660	0.75	18	46.0	23.0
ASBAC-PPS	14.2	DTH	1000	nd	nd	26.4	nd
ASBAC-PPS	14.2	DTH	1680	0.88	13	44.4	6.4
ASBAC-PPS	17.9	DTH	1000	nd	nd	19.8	nd
ASBAC-PPS	17.9	DTH	1440	0.66	33	28.5	9.8
ASBAC-PPS	24.5	DTH	1000	nd	nd	2.2	nd
ASBAC-PPS	24.5	DTH	1440	0.30	77	3.2	0.3
ASBAC-PPS	45.8	DTH	1000	nd	nd	0.6	nd
ASBAC-PPS	45.8	DTH	1440	0.29	125	0.9†	2.7†
ASBFV-PPS	15.0	LDM	1197	0.43	126	nil	nil
ASBFV-PPS	17.8	LDM	590	0.50	142	2.0	nil
ASBFV-PPS	18.1	LDM	864	0.51	141	2.0	nil

* All measurements referred to samples recovered from the cell, washed to neutral pH, dried and conditioned to 50% humidity; $W_R = H_2O$ ml dry separator g⁻¹; nd = not determined
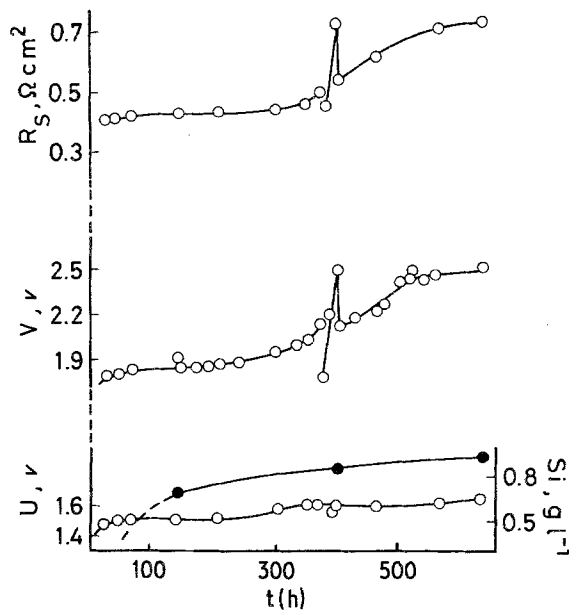† t.w.l.-c.w.l. difference within experimental error [12]

Fig. 1. Total (V, volts), net (U = V-iR, volts) cell voltages, separator resistance (R_S) and silicon (●) concentration in the electrolyte (Si) against electrolysis time for LDM electrolyser operated with ASBAC-(10%)PPS cardboard.

Fig. 3. Cell voltage (V, volts) and separator resistance (R_S, $\Omega\,cm^2$) against electrolysis time (h) for LDM electrolyser operated with ASBFV cloth coated with 15 (O); 17.8 (△) and 18.1 (■) % w/w PPS.

of the material loss (Table 3) was due to chemical hydrolysis of asbestos (i.e. ∼61% mol/mol conversion of initial asbestos to brucite). The cell voltage (V and U = V − iR) and the separator resistance (R_S) against time plots (Fig. 1) show that after 375 h, when the rate of degradation had slowed, V increased sharply due to the increase in R_S. Temporary improvement was obtained upon stopping the electrolysis for 7.5 h which allowed detachment of possible gas bubbles from the separator surface and rewetting by the electrolyte. On resuming operation, both V and R_S increased again. Another sample of the same separator caused short circuit after 600 h in the DTH electrolyser (Table 2); degradation left only a fragment of the separator between the electrodes.

More stable separators are obtained at higher PPS concentration. The tests, performed in the DTH electrolyser (Table 2), revealed that chemical stability of ASB is achieved with a 14% PPS coating, but sufficient mechanical strength requires over 25% PPS. Analysis of the chemical composition of samples of aged separators, which were taken after 1000 and 1440 h showed that (Table 3), for separators with 14 ≤ % w/w PPS < 24.5, the weight loss (c.w.l. %) due to the chemical reaction (1) accounts for only a minor fraction of the total weight loss (t.w.l. %). Therefore, most of the failure is mechanical. The composites with PPS% ≥ 24.5 have higher mechanical
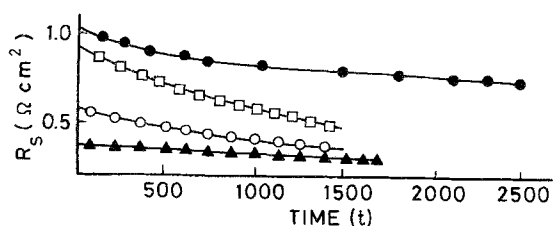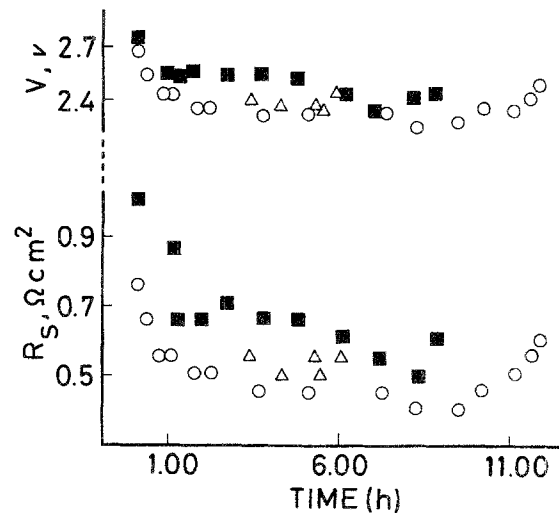

Fig. 2. Electrical resistance (R_S) of ASBAC cardboards containing 14.2 (▲); 17.9 (O); 24.5 (□) and 45.8 (●) % PPS in DTH electrolyser.

strength and are clearly the most stable. The initial electrical resistance (Fig. 2) varies from 0.36 to 0.97 $\Omega\,cm^2$ for the least and most PPS concentrated composites. During electrolysis R_S decreases continuously over the test time to final values of 0.38–0.58 $\Omega\,cm^2$. The weight loss (t.w.l. %) raises the initial porosity [12, 17]. Consequently, for each composite material, W_R increases and T_S decreases (Table 3) relative to the initial values (Table 1). The results indicate a minimum initial mechanical strength of over 100 kg cm^{-2} in order to withstand mechanical stress during electrolysis.

The solution to the problem of achieving chemical stability, high mechanical strength and low electrical resistance at the same time was sought by changing the base asbestos material to be coated.

The ASBFV–PPS composites (Table 1) are made from more porous (W_R = 0.58 ml g^{-1}), thicker (TKN = 0.75 mm) and stronger (T_S = 193 kg cm^{-2}) base material. High mechanical strength (T_S > 140 kg cm^{-2}) is therefore attained with considerably lower PPS load than that required for the ASBAC composites. The tests in the LDM electrolyser (Table 2) confirmed that for the ASBFV cloth 15% PPS was quite sufficient to secure stability. A comparison of ASBFV (Fig. 3) against ASBAC (Fig. 2) most stable materials (i.e. materials with t.w.l. < 4% in Table 3) shows a far superior electrical performance for the former both in level (0.5 ≤ R_S ≤ 0.7 after 100 h) and stability (no definite time effect). The apparent increase of R_S after 1000 h (Fig. 3) could just be part of a random fluctuation due to accumulation of gas bubbles over the separator surface and to consequent decrease of the electrolyte concentration in the separator phase [9].

The ASBJM–PPS composites (Table 1) are made from very thin (0.18–0.40 mm), but mostly porous (W_R = 0.84–0.94 ml g^{-1}) asbestos. With the 0.40 mm thick material, high mechanical strength (T_S = 145 kg cm^{-2}) was achieved at high PPS load level (36%) as well as in the case of ASBAC separators,
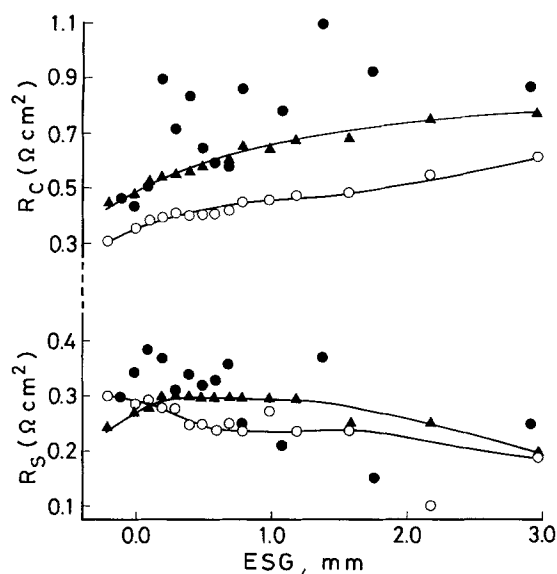
Fig. 4. Total cell (R$_C$) and separator (R$_S$) resistance upon changing the distance between the gas evolving electrodes and the separator (ESG, mm) in NRC electrolyser operated with ASBJM cardboards coated with 39.4 (●) and 36.2 (○) % PPS compared to values obtained for 2.5 mm thick electrolytic grade-woven asbestos cloth (▲).

but the former composite became much more porous (W$_R$ = 0.36 ml g^{-1}) by virtue of the higher initial porosity of the base article. The 0.18 mm thick material in cardboard form was too weak initially and the mechanical strength at 39% PPS level was still low (T$_S$ = 53 kg cm^{-2}). Tests performed in the NRC electrolyser (Table 2) permitted study of the dependence of the electrical behaviour of the ASBJM-PPS composites on changing the distance between the gas evolving electrodes and the separator [21]. For the PPS composites and, by comparison, for a sample of neat electrolytic grade woven asbestos, it was found that (Fig. 4), whereas the total cell resistance (R$_C$) is directly related to ESG as expected, the separator resistance (R$_S$) tends to increase on decreasing ESG, probably reflecting the accumulation of gas bubbles on the separator. The thinnest separator exhibits the highest scatter. The interelectrode voltage (IVD) against current density (CD) plots (from which R$_S$ was derived after correcting for the gas-free electrolyte contribution) were linear [21] for neat asbestos, but not for the ASBJM-PPS composites regardless of the operating ESG value in the whole range up to 3.0 mm. Further measurements at 11 mm ESG also yielded linear IVD-CD plots for the composites.

3.2. Polyvinylpyridine-divinylbenzene composite separators

The VP-DVB composites were all made from one type of asbestos (Table 1). Because of the presence of the polar pyridine nucleus, VP-DVB was expected to present less problems than PPS due to polymer lipophilicity. The morphological structure of the cross-linked polymer appeared to be an important parameter. All ageing tests in electrolysis were run with the first generation of these materials which

contained the polymer in composite form. Major problems were associated with gas film retention which occurred at low polymer loads. Table 1 shows that, against expectation, the ASBAC composites containing the C-type VP-DVB polymer do not have higher water retention than the equally concentrated ASBAC-PPS composites. Furthermore, there seems to be no W$_R$ change across the 4–17% VP-DVB range. The only advantage of VP-DVB over PPS seems to be in mechanical strength ($\simeq$ 100 kg cm^{-2} already at 13.5% VP-DVB). In the DTH electrolyser (Table 2) the 11% VP-DVB separator underwent degradation similarly to the PPS composite of lowest concentration. Although the mechanical strength of the former (T$_S$ = 92 kg cm^{-2}) was relatively higher, it was still not sufficient and 58.5% w/w weight loss occurred after 1200 h. The most striking difference, relative to the PPS composite (Table 3 and Figs 1, 2) was, however, the initial electrical resistance [16], which started at a very high value (> 1 Ω cm^2) and decreased to approaching that of the 14% PPS separator (0.30 Ω cm^2) over 1200 h. For a similar VP-DVB sample, which had previously been swollen for 1 h in EtOH, the initial resistance was much lower (0.68 Ω cm^2) and decreased continuously to the same final value of 0.30 Ω cm^2 over half of the time. The potential drop (V) against current density (0 < CD, A cm^{-2} ⩽ 1.5) plots, from which R$_S$ was determined, were linear in all cases (PPS and VP-DVB) in the 30–130°C range, except for that at 30°C of the unswollen VP-DVB composite, which deviated from the ohmic behaviour above 1 A cm^{-2}.

More extensive tests in the LDH electrolyser (Table 2), however, revealed no relationship between VP-DVB% and R$_S$, but high fluctuations of R$_S$ after 200–700 h operation for some separators (Table 4). In one case (the 14.5% VP-DVB sample) R$_S$ rose as high as to cause cell explosion. With the 4% VP-DVB separator, the electrolysis was stopped after 580 h, since R$_S$ was very unstable (reached 2.1 Ω cm^2) and caused instability of the cell voltage. The separator was reconditioned in the cell electrolyte in the absence of evolving gases. On resuming operation, V and R$_S$ fluctuated again to the end of the test. Weight losses were 39 and 25% w/w for 4 and 13.5% VP-DVB composites after 729 and 361 h respectively. Two samples (Fig. 5), at 10 and 16.6% VP-DVB level, performed with no problem up to 1300 h and with good R$_S$, which stabilized at 0.35–0.40 Ω cm^2 after 100 h. Weight losses at the end of the test time, 1314 h for 10% VP-DVB and 714 h for 16.6% VP-DVB, were 45% w/w and nil respectively. In the NRC electrolyser (Table 2), operated with 15% VP-DVB, both cell (R$_C$) and separator (R$_S$) resistances apparently decreased on decreasing ESG (Fig. 6). This is more likely a time effect, which masks any gas-bubble effect as otherwise evidenced with PPS and neat ASB (Fig. 4). The VP-DVB results were taken over a period of two weeks with the gap being progressively decreased; during this time electrolyte penetration into the polymer compact structure may take place and the polymer becomes

Table 4. Cell voltage (V, volts) and separator resistance (R_S, Ωcm^2) against electrolysis time (t, h) for LDM electrolyser operated with ASBAC cardboards coated with 4, 13.5 and 14.5% VP-DVB(C)

ASBAC-(4%)VP-DVB			ASBAC-(13.5%)VP-DVB			ASBAC-(14.5%)VP-DVB		
t	V	R_S	t	V	R_S	t	V	R_S
0.0	2.15	0.30	0.5	2.45	0.55	24	2.60	0.70
1.5	2.19	0.35	23	unst*	unst*	48	2.60	0.70
4	2.22	0.35	97	2.56	0.65	144	2.31	0.40
28	2.25	0.40	121	2.53	0.60	168	2.37	0.45
52	2.24	0.40	145	2.64	0.70	192	2.56	0.65
100	2.23	0.40	169	unst*	unst*	216†	2.70†	unst*
220	2.22	0.35	265	2.15	0.30	216†	3.60†	unst*
292	2.19	0.35	313	2.27	0.30	240§	unst*	unst*
388	2.20	0.35	337†	3.10†	unst*			
412	2.38	0.45	337†	3.60†	unst*			
436	2.17	0.30	361†	2.90†	unst*			
460	unst*	unst*	361†	3.50†	unst*			
484	unst*	unst*						
556	unst*	unst*						
580†‡	2.6†	0.7†						
580†‡	3.9†	2.1†						
650	unst*	unst*						
674	unst*	unst*						
729†	2.12†	0.3†						
729	3.35†	1.5†						

* Not determined because unstable; † minimum and maximum V and R_S values during fluctuation at a given time; ‡ current turned off and operation resumed after 70 h; § cell explosion

more hydrophilic. The IVD against CD plots were linear for the VP-DVB composite over the whole ESG range (Table 2).

The irreproducible performance of VP-DVB separators seems limited to the poorly wettable C-type polymer. Tables 5 and 6 report electrical resistance data which have been taken at ESG = 11 cm in the absence of any possible gas-bubble accumulation over the separator. For the C-type polymer (Table 5) it is observed that the samples preconditioned in EtOH give more reproducible and lower values than the untreated samples. Ethanol is likely to bring about some swelling of the lipophilic compact structure and

facilitate penetration of the aqueous electrolyte into the separator phase. By comparison, plain asbestos does not exhibit any ethanol effect. The macroporous VP-DVB composites (Table 6) show significantly improved behaviour over that of the C-type materials, even without pretreatment in EtOH.

Table 5. Electrical resistance (R_S) in cell [16] operated with 11 cm ESG and 30% KOH at 100° C for plain ASBAC cardboard and for ASBAC-(11%)VP-DVB(C) composite cardboard as a function of the material pretreatment

Separator	T (°C)	R_S (Ωcm^2)		% ΔR_S*
		u†	p††	
ASBAC-(11%)VP-DVB(C)§				
(e)	30	3.35	0.61	81.8
	50	2.34	0.57	75.6
	65	1.58	0.39	75.3
	80	1.16	0.35	69.8
	100	0.64	0.28	56.2
(ee)	30	8.73	0.73	91.6
	50	7.82	0.49	93.7
	65	6.35	0.43	93.2
	80	5.17	0.37	92.8
	100	3.67	0.27	92.6
ASBAC (plain)	30	0.18	0.20	−11.1
	50	0.14	0.12	11.1
	65	0.12	0.13	−8.3
	80	0.10	0.10	0.0
	100	0.08	0.09	12.5

Fig. 5. Cell voltage (V, volts) and separator resistance (R_S) against electrolysis time (h/100) for LDM electrolyser operated with ASBAC cardboard coated with 10 (O) and 16.6 (▲) % VP-DVB (C-type).

* % $\Delta R_S = -100 R_S(p) - R_S(u)/R_S(u)$; † measured after 1500 h ageing in boiling 30% KOH, washing with H_2O to neutral pH and drying at 120° C for 24 h; †† treated as above, then soaked in a 1:1 mixture of EtOH and 30% KOH(aq.) and mounted wet in the measuring cell; § (e) and (ee): two different 25 cm² samples taken from a 100 cm² cardboard
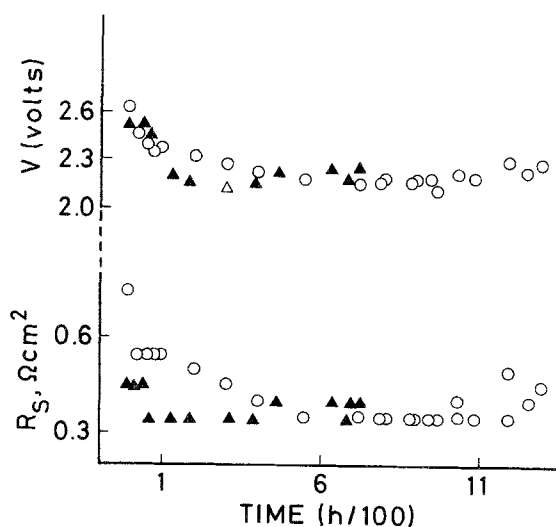
Table 6. Electrical resistance (R$_S$) measured in cell operated with 11 cm ESG and 30% KOH at 100° C for ASBAC cardboards coated with macroporous (MP) and compact (C) VP-DVB

VP-DVB		R$_S$	Swelling medium[†]
		Ω cm^2	
Concentration in separator % w/w	Type*		
11.5	MPD	0.17	none
11.7	MPD	0.14	none
12.3	MPD	0.16	none
10.4	MPX	0.14	none
6.5	C	0.37	EtOH
7.8	C	0.39	EtOH
7.8	C	0.27	EtOH
9.1	C	0.29	EtOH

* MPD and MPX stand for *in situ* synthesized macroporous polymer in presence of decaline and xylene respectively, C stands for bulk synthesized compact polymer in absence of monomers solvent; [†] medium in which sample is conditioned before R$_S$ measurement; EtOh stands for 5 h boiling ethanol

3.3. Sulphonated composite separators

Asbestos composites with sulphonated aromatic polymers were manufactured to yield more wettable and polar separators and to overcome any gas-bubble accumulation effect associated with parent polymers during electrolysis. The first reported members of this class were made of John Manville 0.25″ L/Fx36″ type base material in cardboard form (TKN = 0.65 mm and W$_R$ = 0.79 ml g^{-1}) and 11–35% SSDVB which had 0.16–0.10 –SO$_3$H mEq g^{-1} of separator [14]. W$_R$ decreased steadily on increasing SSDVB%, being ~0.6 and 0.04 ml g^{-1} at 11–12.4 and 36.5–41% SSDVB respectively. The cell voltage during electrolysis [14] depended strongly on the separator. The electrical resistance of the separator containing 12.4% SSDVB was 0.65 Ω cm^2 in 10% KOH and 0.40 Ω cm^2 in 20% KOH at 70° C. For the separators containing ~40% SSDVB the R$_S$ values were ~1.5 Ω cm^2 higher. By comparison for the VP-DVB composites having 6–14% and 41% polymer content R$_S$ changed by 8 Ω cm^2 from the least to the most concentrated separator. Although both SSDVB and VP-DVB had the same cross-linked compact morphological structure, the lower electrical resistance of the former is to be ascribed to the presence of sulphonic functions which make the separator more hydrophilic.

The sulphonated linear polymers (SPP and SPPS) yielded highly wettable composites, even if the base material (ASBAC, Table 1) was less porous than the John Manville type: SPP or SPPS% from 13 to 27 –SO$_3$H mEq g^{-1} of separator = 0.07–0.20, W$_R$ from 0.35 to 0.26 ml g^{-1}. Accordingly the changes of R$_S$ were from 0.20 to 0.56 Ω cm^2 in 100° C, 30% KOH. The behaviour of a separator containing 19% SPPS, 0.12 –SO$_3$H mEq g^{-1} of separator was tested in a Sodeteg electrolyser (Table 2). R$_S$ started at 0.375 Ω cm^2 and decreased continuously over the test period to reach a value of 0.25 Ω cm^2 after 1800 h.
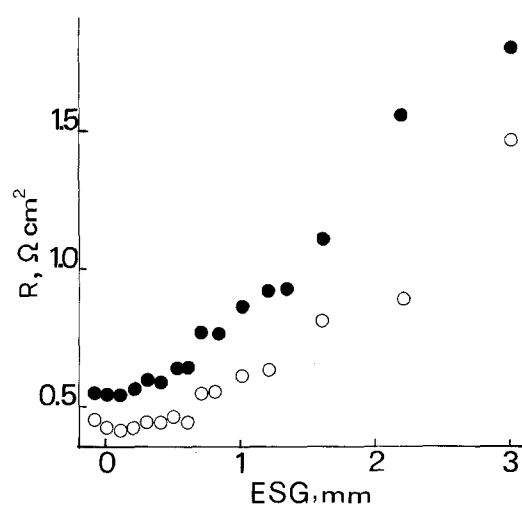

Fig. 6. Total (●) and separator (○) resistance (R) upon changing the distance (ESG) between the gas evolving electrodes and the separator in NRC electrolyser operated with ASBAC-(15%)VP-DVB(C) cardboard presoaked in EtOH-17% KOH 24 h, in 25% KOH 24 h and in 45% KOH 24 h.

The voltage drop against CD plots showed a linear ohmic behaviour of the separator.

4. Discussion

The results indicate that the separators, during electrolysis, are exposed to two different actions simultaneously: chemical hydrolysis by the alkali (1) and mechanical stress due to the electrolytic gases. For chemical stability the minimum concentration of organic polymer in the separator appears to be 14–15%; for mechanical stability the minimum material strength is > 100 kg cm^{-2}. Stable separators have been made in two ways: either loading a relatively weak article (i.e. ASBAC or ASBJM) with > 25% organic polymer or by charging a strong support (ASBFV) with nearly the minimum concentration of polymer. Among all these composite materials, the 0.45 mm thick ASBJM cardboard containing 36% PPS appears the best since, due to the high porosity of the plain support material from which it is made, it exhibits the lowest electrical resistance (~0.29 Ω cm^2) coupled with high mechanical strength (~145 kg cm^{-2}).

Contrary to expectations, the VP-DVB composites performed worse than PPS separators. Cross-linking introduces a further physical parameter in polyvinyl-pyridine, which results in masking the properties of the pyridine nucleus. During copolymerization of vinylpyridine and divinylbenzene into the asbestos phase in the absence of solvent [16], chain entanglement and irreversible collapse of the structure yield a hard and compact (C) material characterized by low swelling properties. Therefore, the composite materials in cardboard form which contain the C-type polymer have higher mechanical strength than the same PPS composites of comparable organic load (Table 1), but lower water wettability.

Absolute values of water take up capacity, however, are not sufficient alone to explain the electrical performance of the separators. In electrolysis, compe-

tition between sorption of evolved gases and of liquid electrolyte on the separator solid phase may occur. Sorption of the gas film is obviously favoured on lipophilic sites. SEM and Ir studies [12] have revealed that the distribution of the polymer in the separator phase is not homogeneous, the surface being more concentrated than the bulk phase and homogeneity decreasing as the polymer load in the separator increases. Also it has been found that the heavily charged thinnest separators (i.e. 0.22 mm thick ASBJM-PPS) are the least homogeneous [21]. Weight loss during electrolysis generally creates higher porosity and results in higher water sorption capacity by the separator (Table 3). Chemical hydrolysis (1) particularly leads to loss of inorganic material only, the extent of this phenomenon being higher over less coated asbestos fibres. Therefore, local changes of the inorganic/organic ratio (i.e. on the surface or the pore walls) may be very high and strong lipophilic sites may form where gas sorption concentrates. The potential for the appearance of the gas bubble effect on the electrical resistance grows, in spite of the higher overall wettability acquired by the separator. This effect may be so serious as to cause fragmentation of the separator, short circuit and cell explosion. PPS separators containing 10% polymer exhibited these phenomena. The VP-DVB(C) separators were however mostly affected, regardless of the polymer concentration. Separators coated with macroporous VP-DVB and sulphonated polymers have not been tested as much as the PPS and VP-DVB(C) composites. The former are expected to be less affected by gas-film retention problems due to the higher hydrophilicity and offer additional scope for improved performance.

Acknowledgment

References

[1] F. J. Salzano, G. Skaperda and A. Mezzina, *Int. J. Hydrogen Energy* 10 (1985) 801.

[2] M. Bonner, T. Botts, J. McBreen, A. Mezzina, F. Salzano and C. Yang, *Int. J. Hydrogen Energy* 9 (1984) 269.

[3] H. Vanderborre, R. Leysen, H. Nackaerts and Ph. Van Asbroeck, *Int. J. Hydrogen Energy* 9 (1984) 277.

[4] H. Wendt, H. Hofmann and V. Plzak, *Int. J. Hydrogen Energy* 9 (1984) 297.

[5] R. Aurelle and J. Pottier, *Int. J. Hydrogen Energy* 9 (1984) 18.

[6] R. LeRoy and F. Hufnagl, *Int. J. Hydrogen Energy* 8 (1983) 581.

[7] C. T. Bowen, H. J. Davis, B. F. Henshaw, R. Lachance, R. LeRoy and R. Renaud, *Int. J. Hydrogen Energy* 9 (1984) 59.

[8] T. N. Veziroglu and J. B. Taylor (eds.), Proceedings of the 5th World Hydrogen Energy Conference, Toronto, Canada, 15–20 July 1984, Vol. 2 (Pergamon Press, Oxford).

[9] P. Gallone, L. Giuffré and G. Modica, *Electrochim. Acta* 28 (1983) 1299.

[10] B. G. Mandelik, D. S. Newsome and P. Kellog, 'Encyclopedia of Chemical Technology', J. Wiley and Sons, New York, 12 (1982) 938.

[11] J. J. Leddy, I. C. Jones, Jr., B. S. Lowry, F. W. Spillers, R. E. Wing and C. D. Binger, 'Encyclopedia of Chemical Technology', J. Wiley and Sons, New York, 1 (1982) 799.

[12] E. Montoneri, G. Modica and S. Maffi, *J. Compos. Mater.* 20 (1986) 504.

[13] E. Montoneri, L. Giuffré, G. Mondica and E. Tempesti, *Int. J. Hydrogen Energy* 11 (1986) 233.

[14] G. Modica, L. Giuffré, E. Montoneri, V. Pozzi and E. Tempesti, *Int. J. Hydrogen Energy* 8 (1983) 419 and references therein.

[15] E. Montoneri, L. Giuffré, E. Tempesti, S. Maffi and G. Modica, *ibid.* 9 (1984) 571.

[16] G. Modica, L. Giuffré, E. Montoneri, H. Wendt and H. Hofmann, *Polymer* 25 (1984) 1513 and references therein.

[17] E. Montoneri, L. Giuffré, G. Modica and M. Gennuso, *J. Mater. Sci.* 18 (1983) 3311.

[18] L. Giuffré, E. Montoneri, G. Modica, B. M. Ho and E. Tempesti, *Int. J. Hydrogen Energy* 9 (1984) 179.

[19] E. Montoneri, G. Modica, L. Giuffré, L. Peraldo Bicelli and S. Maffi, *Int. J. Polymeric Materials* 11 (1987) 263.

[20] E. Montoneri, 'The products of the reaction of polyphenylene sulfide with sulphur trioxide and thionyl chloride' to be published.

[21] E. Montoneri, G. Modica, C. Bowen, D. Gauthier and R. Renaud, *Int. J. Hydrogen Energy* 12 (1987) 831.

[22] E. Montoneri, E. Ranzi and G. Mondica, *J. Compos. Mater.*, in press.

[23] G. Imarisio and A. S. Straub (eds), 'Hydrogen as an Energy Carrier', Proceedings of the 3rd International Seminar, Lyon, France, May 25–27, 1983 (D. Reidel Publ. Co., Dordrecht).

[24] R. L. LeRoy, M. B. I. Janujua, R. Renaud and U. Leuenberger, *J. Electrochem. Soc.* 126 (1979) 1674.