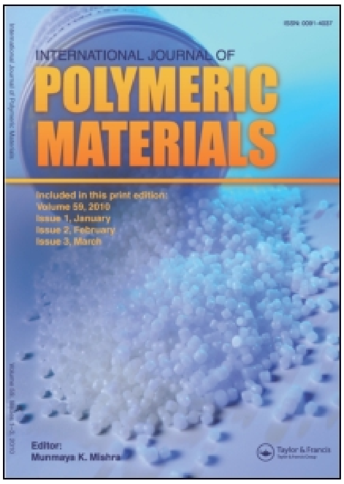

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Polyphenylene Sulfide Sulphonic Acid: Processing, Solid State Conductivity and Electrolyte Transport Properties

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Polyphenylene Sulfide Sulphonic Acid: Processing, Solid State Conductivity and Electrolyte Transport Properties

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Polyphenylene sulfide sulphonic acid is an amorphous, non melting solid which dissolves only in $SOCl_2$, dehydrates at 40–180°C and degrades with heavy weight loss starting from 270°C. The polymer has been tested as solid state component of electrochemical devices in the 20–160°C range with the following results: conductivity $(\text{ohm}^{-1}\,\text{cm}^{-1}) = 10^{-1}$ in 30% KOH aq., 10^{-2} in 5 atm steam pressure and 10^{-5} in air; transport number in KCl $(t^+) \sim 1$.

Possible applications are discussed in relation to the performance of other established material.

INTRODUCTION

Polyphenylenes, $(C_6H_4{-}X)_n$, have attracted the interest of modern industry[1,2] aiming to the development of conductive materials which are thermally and chemically stable, can sustain mechanical stress, may be shaped in various physical forms and/or used to coat fabricated articles. The polymers, depending on the phenyl spacing group (X = none, S, O and aliphatic chain), have variable[3] cristallinity, mechanical flexibility, thermal and chemical resistance.

Sulphonation[4,5] is known to provide polar materials to work in aqueous environment; it is a mean to tailor polymer properties (i.e. solubility, dyeability, ion exchange capacity) to specific performance demands.

The sulphonic acid of polyphenylene sulphide (SPPS) is not well known, but in one preliminary communication.[5] The polymer with equivalent weight (EW = polymer g/SO_3H eq.) ranging from 300 to 1600 is the product of the reaction of polyphenylene sulfide (PPS) with SO_3 at variable reagents concentration. The exceptional thermal properties which identify PPS as high temperature polymer (i.e. melting point at 280°C and no weight loss up to 400°C) degrade in the sulphonated derivative (i.e. weight loss starting at 270°C and no melting point). However, compared to other members of the polysulphonic acid class (i.e. polystyrene sulphonic acid), SPPS exhibits remarkable insolubility regardless of the equivalent weight. These properties have encouraged further investigation into the nature of sulphonated polyphenylene sulfide and into its behaviour as solid state component of electrochemical devices of industrial interest operating below 160°C.

EXPERIMENTAL

Materials preparation

The preparation of neat SPPS[5] and of PPS–ASB† composites[6] has been previously reported. The SPPS–ASB composites have been manufactured by soaking a 0.055 cm thick commerical crysotyle asbestos cardboard (5 cm dia specimen) in SPPS dissolved in $SOCl_2$ for 15 minutes, withdrawing the cardboard from the soaking bath, eliminating the sorbed solvent by standing in air under hood for 1 hour, washing with boiling water and drying at 120°C for 24 hours. The concentration of sorbed SPPS in the composite was obtained by

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† ASB = asbestos.

the cardboard weight gain at the end of the preparative cycle. The amount of SPPS sorbed onto asbestos (SPPS w/w% = C_1) was found to vary according to the SPPS concentration (C_2 w/w%) in the soaking bath: $C_1 = 0.57\,C_2$.

Solid state conductivity measurements

Solid state conductivity measurements have been performed as reported elsewhere.[7] The sample as compressed powder disc (for neat PPS and neat SPPS: $\phi = 5$ cm, thickness = 0.2 cm) or cardboard disc (for composites: $\phi = 5$ cm, thickness = 0.055 cm) was encapsulated in the measuring cell. The cell consisted of two gold plated SS flanges which are insulated from each other by means of compressed asbestos gasket suitable to hold 5 atm internal pressure. The flanges contained a groove for lodging the sample specimen. Sample to flange electrical contact was assured by means of carbon felt discs placed in between. The cell was tightened by means of four bolts which were insulated from the cell case with ceramic material. Each cell flange contained an inlet and outlet for steam to flow under pressure through the cell from a steam generator. The cell was placed in a thermostatic oven and connected to the steam generator and to the vent line through teflon tubing running through holes drilled in the oven back wall. The cell electrical resistance was measured by a.c. Philips 6301 RCL meter at 1 kHz. The instrument was connected to the outer surfaces of the cell flanges by gold plated copper wire (0.5 cm thick). The conductivity (χ, ohm^{-1} cm^{-1}) was calculated from the measured cell resistance (R) according to the relation,

$$\frac{1}{\chi} = (R - R_0)\frac{S}{L}$$

where R_0 is the resistance of the external circuit (~0.5 Ω) and S and L are the geometric area and thickness of the sample disk respectively. R_0 measurements were obtained by short circuiting the cell flanges through the C felts without the sample disc in between them. Insulation of cell flanges was checked by measuring the cell resistance of the empty cell, where the only contact between flanges occurred through the flanges and bolts insulating material.

Discharge experiments and cyclic voltammetry

The electrochemical cell for discharge experiments, Li/$LiClO_4$-PC/P, was made of lithium ribbon electrode (Alfa Ventron product, purity >99.9%), 1 M $LiClO_4$-propylene carbonate (PC) electrolyte and a working-electrode pellet (P) made of the lithium salt of SPPS (SPPSLi).

Dry $LiClO_4$ was obtained by melting under vacuum $LiClO_4 \cdot 3H_2O$ at 235°C. The PC solvent (Merck reagent grade) was purified by vacuum distillation in presence of lithium turning and collection of the intermediate fraction. The cell was prepared in a dry box by placing the lithium disk, three glass-wool separator disks soaked with the electrolytic solution and a pellet of 50 mg of polymer material into a teflon container having stainless steel terminals. The pellet about 12 mm in diameter was obtained by compressing the SPPSLi powder to be examined on Pt support at about 300 MPa. The cyclic voltammetry experiments were performed in a three electrode glass cell having three compartments separated by porous glass walls, 1 cm^2 Pt mesh-SPPSLi working electrode housed in the central cell compartment and the lithium ribbon counterelectrode and reference electrode (in contact with the solution) located in the two lateral compartments.

The stability of the $LiClO_4$-PC solution was tested in the same cell using the platinum mesh as the indicator electrode. All the measurements were carried out at room temperature, in a controlled-atmosphere drybox, by means of standard electrochemical instrumentation: Amel 549 potentiostat-galvanostat, Amel 567 function generator, Amel 862/D X–Y recorder, HP 240/2A voltmeter and Keithley 169 digital multimeter. Computer-aided acquisition and analysis of the experimental data were performed by an Apple Microcomputer.

Other details

BET measurements were performed with C. Erba Model 1800 porosimeter. All other experimental details have been reported previously.[4,6,8]

RESULTS AND DISCUSSION

Polyphenylene sulfide sulphonic acid, $-[(C_6H_4-S)_n-C_6H_3(SO_3H)-S]_m-$, contains an aromatic chain with pendant $-SO_3H$ functions; therefore a certain number of properties were suggested for this material. The sulphonic function was expected to provide water wettability and ion mobility. This coupled with the polymer insolubility suggested investigation of the material as solid state ion conductor and as separator for electrochemical cells. On the other hand the aromatic chain alone (such as in the parent polyphenylene sulfide polymer, PPS) is known to acquire electron conductivity upon chemical doping with oxidizing and reducing agents.[2] It was therefore interesting to ascertain if the same was true with SPPS. Experimental testing of the above properties was carried out at the light of further information on the chemical and morphological structure as reported below. Development of a technological procedure was also necessary in order to shape the polymer into articles which allowed the above tests to be carried out.

Polymer nature and processing technology

Contrary to PPS, polyphenylene sulfide sulphonic acid was always found amorphous by x-ray investigation. Scanning electron microscopy showed the SPPS powder to be formed by irregularly shaped grains. The specific surface area as obtained by BET measurements was $0.22\,m^2\,g^{-1}$ and the specific pore volume at the sensitivity limit of the determination method.

The pendant sulphonic function was always found associated with hydration water ($>2\,H_2O$ mole/SO_3H eq). The IR spectra of the sulphonic acids compared to that of the parent polymer showed distinctive features similar to those of the previously reported diphenylsulphide sulphonic acid containing $2.5\,H_2O$ moles per SO_3H function.[9]

These were: a medium broad OH stretching vibration band extending from 3600 to $2500\,cm^{-1}$ associated with H-bonded OH functions, a broad OH bending vibration band covering the 1800–$1600\,cm^{-1}$ range and associated with the H_3O^+ ion and strong broad bands in the 1000–1250 cm^{-1} range where the typical absorptions of free $S{=}O$ and H-bonded $S{-}O\cdots H$ functions fall. Extensive association of sulphonic functions via H-bonded polyhydronium ions, $\leftarrow\cdot[SO_3^-(P)H(H_2O)_n^+\leftarrow]_m\cdot$, P = polymer chain, $n > 2$, was therefore suggested in the solid state. TGA scans showed that destruction of the H-bonded system with temperature was found to occur at least in two stages. Up to 180°C only $n-1$ moles of H_2O per repeating unit are lost. The remaining water molecule is more stongly bound to the polymer chain, probably in the form of the $(H_3O)^+$ ion, and is eliminated while the material decomposition occurs at higher temperature (~280°C).

No solvent was found to dissolve SPPS either in free acid or salt form. The free acid ($—SO_3H$) however could easily be converted into the sulphonylchloride ($—SO_2Cl$) form by refluxing in $SOCl_2$ and the sulphonylchloride polymer was found soluble in excess $SOCl_2$. From this solution a though fragile polymer film could be obtained by slow evaporation of the $SOCl_2$ solvent. Boiling the film with water (acid or alkaline) to convert the $—SO_2Cl$ polymer pendant function in the sulphonic acid ($—SO_3H$) or sulphonate ($—SO_3^-$) form did not improve the mechanical performance of the film. The skeletal rigidity of the polyphenylene sulfide chain such as found in the parent polymer[3] appeared retained or higher in the sulphonated derivatives.

From the technological point of view the insolubility, non melting properties and mechanical rigidity of polyphenylene sulfide sulphonic acid is a severe limitation. The polymer as such cannot be processed and shaped in form of useful articles. Testing of the potential of this material in industrial applications as anticipated above was possible by exploiting the solubility of the $—SO_2Cl$ polymer in $SOCl_2$ to manufacture composite materials. At this purpose commercial crysotyle asbestos (ASB) cardboards (0.055 cm thick) having 44% porosity were soaked into a solution of the sulphonyl chloride polymer in $SOCl_2$, withdrawn from the soaking bath and then boiled in water to hydrolyze the sorbed polymer $—SO_2Cl$ function into $—SO_3H$. The product was an asbestos —SPPS composite material which retained most of the mechanical flexibility of the initial asbestos support article, but contained a surface coating layer of sulphonated polymer to provide the required chemical properties. This procedure was found very flexible in that it allows the manufacture of composite articles with a wide range of compositions depending on the concentration of the soaking bath (see Experimental).

SPPS as separator for electrochemical cells

Separators of cathodic and anodic compartments of electrochemical cells[10] have mainly two functions: i.e. (1) to avoid mixing of gaseous products developed at the electrodes and (2) to select electrolyte ions migrating to one of the two electrodes. Compliance with one or both requirements depends upon the electrochemical process taking place: i.e. for water electrolysis ion selectivity is not required, for brine electrolysis exclusion of Cl^- ions from the cathodic compartment is necessary. Depending upon the specific process the separator morphology may change from porous (i.e. in diaphragms) to compact (i.e. in membranes) structures. Main rating parameter for these articles are the electrical resistance (R_s, $\Omega\,cm^2$) across the separator phase[8] and the capacity to select ions migrating from one electrode compartment to the other as measured by the transport number (t_+).[4]

Figure 1 reports the electrical resistance measured across SPPS-

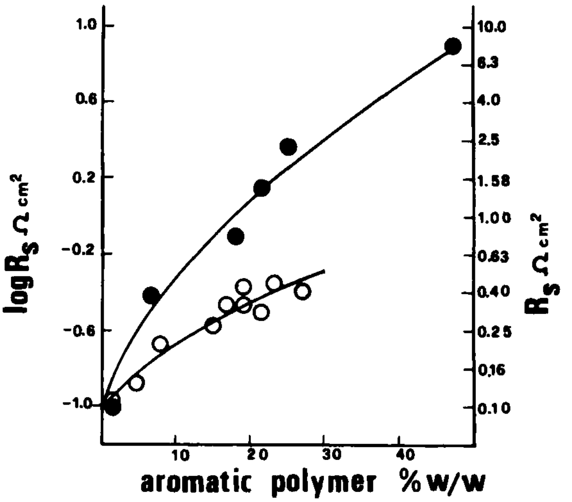

FIGURE 1 Electrical resistance (R_s) of 0.55 cm thick PPS (●) and SPPS (○) composite separators in 100°C 30% aq KOH.

asbestos separators in water electrolysis cell containing 30% w/w aqueous KOH. For comparison the values measured with composites containing the parent PPS polymer in the same concentration range are shown. The SPPS separators exhibit significantly lower ohmic drop than the PPS separators. Also the resistance difference between unsulphonated and sulphonated articles of equal aromatics load increases directly as the aromatics % load in the composite increases. Table I shows these resistance change as directly related to the concentration of sulphonic functions in the composite.

Interpretation of this behaviour is accomplished at the light of scanning electron microscopy results which showed that increasing the aromatics % load brings about a decrease of porosity and a change of the composite morphology from the porous one of diaphragms to that compact of membranes. The decrease of the void volume % in the composite structure as compared to that of neat asbestos appeared directly related to the % SPPS. The organic polymer provides a non porous (see preceding section) coating which deposits over the asbestos fibers and reduces the initial void fraction (44%) of the support article. Accordingly, a change in the charge transport mechanism must be accounted for. In porous structures the electrical charge is transported by the electrolyte mass flow through the pores, whereas in membranes mass flow is very limited and the charge is mainly transported by ion exchange over the structural functional groups of the separator solid phase. The contribution of the chemical nature of the composite surface coating to the transport of electricity across the separator phase becomes

TABLE I

PPS–SPPS resistance difference ($\Delta R\%$) vs. aromatics-SO_3H% in composites

Aromatics w/w%	—SO_3H meq/w%[a]	$\Delta R\%$[b]
10	7.0	53
20	13.5	62
30	21.5	80

[a] —SO_3H concentration in SPPS composites

[b] $\Delta R\% = 100\ (R_{PPS} - R_{SPPS})/R_{PPS}$, $R(\Omega\ cm^2)$ = electrical resistance of PPS or SPPS composites of equal aromatics % as measured in 100°C 30% aq. KOH

therefore heavier as the material porosity decreases. Obviously, in this situation the difference of performance between the apolar PPS separators and those containing ion-exchanging sites is enhanced.

Confirmation of this charge transport mechanism change was obtained by measurements of the transport number (t_+) in aqueous KCl. Figure 2 shows readily how the K^+ transport number increases significantly with the load of sulphonated polymer in the composite. At 20% load there is no ion selectivity yet; the charge is transported both by K^+ and the counterion, meaning that the separator porosity (~20%) is too high for the SO_3^- functions to interact with the electrolyte ions. At 43% load, the porosity (<1%) is low enough to allow almost total interaction between polymer fixed charge and electrolyte ions, thus excluding Cl^- transport through the polymer negative —SO_3^- fixed charge barrier.

Solid state conductivity

Materials with conductivity in the solid state find use in many different electrochemical and electronic devices depending upon the nature of conductivity (i.e. electronic or ionic). Fuel cells, batteries and electrochemical heat engines[11] for instance are devices which

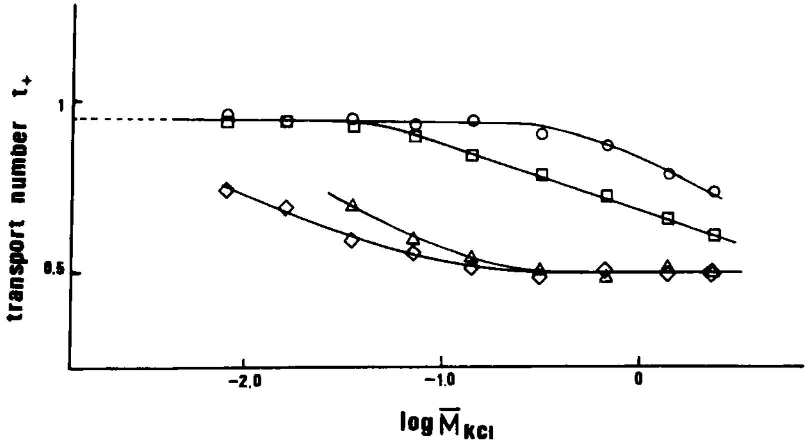

FIGURE 2 Potentiometric transport number (t_+) for the potassium ion through SPPS composite separators (◇ = 20, △ = 25, □ = 35, ○ 43% w/w of SPPS) as measured in KCl; M = molarity.

are currently undergoing technological development and require solid state ionic conductors.

The solid state conductivity of SPPS was tested in 1 kHz a.c. with the polymer in form of neat compressed powder and of porous composite cardboard. For comparison the neat PPS powder and the porous asbestos cardboard were also tested. Table II reports the electrical conductivity of these materials vs. temperature in air and in 5 atm steam.

In solid state electrical conductivity measurements it is hard from the use of one technique to establish whether the observed conductivity is electronic, ionic or both. Polyphenylene sulfide has been reported previously to be an insulator.[2] Electron injection into or abstraction from aromatic π systems performed chemically or electrochemically has been reported to enhance greatly the electronic contribution to conductivity. On the contrary many organic and inorganic solids containing mobile protons and extended H-bonded chains have been reported[7,12] to be mainly proton conductors. The

TABLE II

Conductivities (χ, ohm^{-1} cm^{-1}) under various experimental conditions

Environment	T(°C)	t(min)	χ_{SPPS}[a]	$\chi_{SPPS-ASB}$[b]	χ_{ASB}[c]	χ_{PPS}[d]
air[e]	20	00	1.1×10^{-5}	2.2×10^{-6}	5.0×10^{-7}	8.0×10^{-9}
	80	40	1.1×10^{-5}	5.8×10^{-6}	1.3×10^{-6}	1.0×10^{-8}
	130	45	1.2×10^{-5}	1.8×10^{-6}	1.5×10^{-6}	1.5×10^{-8}
	160	47	1.2×10^{-5}	2.3×10^{-5}	1.5×10^{-6}	8.0×10^{-8}
	160	80	1.0×10^{-5}	4.6×10^{-7}	6.2×10^{-9}	
5 atm steam[f]	160	95	6.2×10^{-2}	1.6×10^{-3}	1.1×10^{-5}	5.9×10^{-4}
	160	130	3.2×10^{-2}	1.1×10^{-3}	1.0×10^{-5}	3.9×10^{-4}
	160	150	3.0×10^{-2}	9.5×10^{-4}	1.1×10^{-5}	3.1×10^{-4}
30% aq. KOH[g]	30			6.1×10^{-2}	3.1×10^{-1}	
	50			9.2×10^{-2}	3.9×10^{-1}	
	65			1.0×10^{-1}	4.5×10^{-1}	
	80			1.2×10^{-1}	5.4×10^{-1}	
	100			1.2×10^{-1}	6.8×10^{-1}	

[a] Neat SPPS, EW = 344 polymer g/—SO_3H eq, 5 × 0.2 (dia. × thickness) cm^2 pellet.

[b] Composite, EW = 7170 composite g/—SO_3H eq, 5 × 0.55 (dia × thickness) cm^2 cardboard.

[c] Neat asbestos, 5 × 0.055 (dia. × thickness) cm^2 cardboard.

[d] Neat PPS, 5 × 0.2 (dia × thickness) cm^2 pellet.

[e,f] Sample tested as solid conductor in absence of liquid electrolyte.

[g] Sample tested as separator in electrochemical cell.

conductivity of SPPS and asbestos therefore is expected to be mainly ionic. Indeed the order of solid state conductivities in Table II seems to follow the expected order of acidity and H-bonding strength: neat SPPS and the SPPS composite are in the first two positions and contain respectively 2.9 and 0.14 milliequivalents of strong acid and H-bonded —SO_3H functions per gram of material; they are followed by neat asbestos with weaker —OH hydrogen-bonded chains[13] and by non H-bonded PPS.

The conductivities of SPPS and asbestos are not stable above 100°C; they tend to decrease rapidly in dry air at 160°C. This behaviour is common to all materials which have been reported to have conductive H-bonded system; loss of hydration water or condensation of structural OH functions result in reduced conductivity.[7,14] Weight loss of SPPS has been discussed above (see Polymer nature) to start already at low temperature and to involve mainly loss of water from polyhydronium ion with progressive destruction of the H-bonded system. The variation of SPPS conductivity in the 20–160°C range (Table II) results from the combination of parameters which depend upon temperature in opposite ways: i.e. decreasing water concentration and increasing mobility of left over protons on raising the temperature. However upon aging at constant temperature (160°C) the water loss effect on conductivity overcomes the initial benefit brought by increasing proton mobility at that temperature.

The attempt to stabilize the H-bonded system in steam under pressure is reported next in Table II. Compared to the conductivities in dry air, the experiments in 5 atm steam show a marked rise in conductivities but do not succeed to stop the downward tendency upon aging. The experimental equipment was not suitable to carry on further the steam pressure investigation.

Finally Table II contains a face to face comparison of electrical conductivities for the same materials when tested as solid conductors and separators respectively in the absence and presence of liquid electrolyte. The conductivity of the porous separators (porosity = 44% for ASB and 22% for SPPS-ASB) is in reality that of the liquid electrolyte taken up by the separator phase. The charge across the separator phase is carried by the sorbed electrolyte ions. The conductivities of the separators are therefore the highest of Table II. The conductivity order (ASB vs. SPPS–ASB) is directly related to the order of porosity. The inverse order is true for the solid state conductivities. In this case the charge is carried through the material by the structural protons. The conductivity is related directly to acidity, rather than to porosity. Indeed neat SPPS, the least porous, has the highest conductivity.

These straightforward comparisons are not often found in literature and may be very helpful hints to the interpretation of phenomena and the design of materials.

Electrochemical doping experiments

Electrochemical doping by either electron injection (*n*-charge injection) or abstraction (*p*-charge injection) is a mean to raise the electrical conductivity of polymers which have potentially conducting conjugated π electrons system but behave as insulators in the ground state. Polyacetylene has been the most widely studied material by this technique; the pristine polymer is considered[15] as a semiconductor having the Fermi level (electrons electrochemical potential) situated at mid-gap in the valence to conduction band energy interval. When the polymer (P) is mounted as electrode in an electrochemical device such as Li/$LiClO_4$-propylene carbonate/P the difference in Fermi energy of Li and P may be counterbalanced by the applied potential difference (V). Thus, depending on the sign of V, n- or p-charges may be injected into the available states of the polymer.

We have carried out a similar experiment with the lithium salt of polyphenylene sulphide sulphonic acid (SPPSLi) of 349 g repeating unit molecular weight.

The open-circuit voltage of a fresh Li/$LiClO_4$-propylene carbonate/SPPSLi cell was 3.1 V. By closing the circuit a sudden voltage rise or drop was observed depending on the circulating current if anodic or cathodic. This "floating" voltage was nearly 0.5 V in both directions, at a current density of $20\,\mu A\,cm^{-2}$. For such very small current ($\sim 0.4\,\mu A$ per mg of material) all nonequilibrium effects, e.g. ohmic loss and over-potential, are unimportant. Hence, the above 0.5 V voltage change may well represent half of the band gap energy for charge injection into the material valence or conduction band[15] to occur.

Discharge experiments were then carried out by controlling the

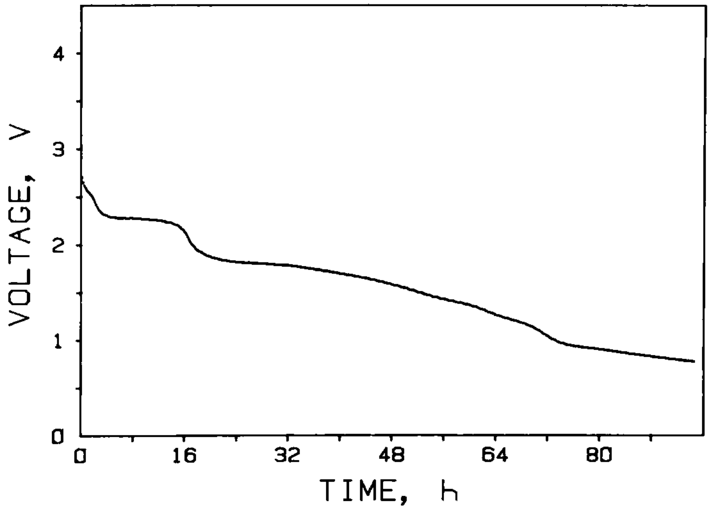

FIGURE 3 Discharge curve with 50 mg SPPSLi (EW = 349) cathode in 1 M $LiClO_4$-PC electrolyte at 20 μA cm^{-2} and at room temperature.

current density and following the cell voltage as a function of time.

Figure 3 reports a typical discharge curve at 20 μA cm^{-2} current density for the above cell assembled with the SPPSLi cathode. The maximum quantity of discharged cation calculated from the curve up to the cut-off voltage of 1 V where the electrolyte decomposes corresponds to ~0.36 Li equivalents per polymer repeating unit. At higher current densities the 1 V cut-off voltage was reached with less cathodic lithium take up (e.g. 0.2 Li equivalents per polymer repeating unit at 50 μA cm^{-2}). Also visual lithium deposition on the polymer pellet surface was more and more evident as the current density was increased. It appears therefore that with SPPS *n*-type doping of and simultaneous introduction of cations into the bulk polymer to balance negative charges are possible only at very low current density. At higher rates, due to slow diffusion of the cations through the polymer electrode, most of lithium deposits on the surface and the voltage goes down to 1 V with much less total Li take up.

Further information on the reduction and oxidation processes as occurring upon doping have been sought also by cyclic voltammetry, where the working electrode potential is linearly swept back and forth over the same region and the flowing current measured. Typical scans of the 2.0 to 3.8 V vs Li/Li$^+$ region are reported in Figure 4. A cathodic shoulder (downward peak at 2.4 V) is observed only during the first scan and indicates a permanent modification of the material. The very strong downward peak starting at 2.3 V is associated with the cation discharge and thus with the *n*-doping step of the SPPSLi cathode. The weak upward peak at 2.2 V is to correspond with electron withdrawal from the cathode and restoration of the polymer in the undoped form.

Both strong cathodic peak and weak anodic peak at potential <2.3 V were observed during all consecutive runs. The lack of coincidence of the peaks voltage has been observed also with other doped π systems and attributed to diffusion phenomena.[16] Similar cycles starting from the zero current potential were also performed in the anodic (increasing voltage) direction. Owing to the high oxidation potential of SPPSLi, the stability range of propylene carbonate (<3.5 V) was exceeded. The solvent was therefore not adequate to explore the polymer *p*-doping stage.

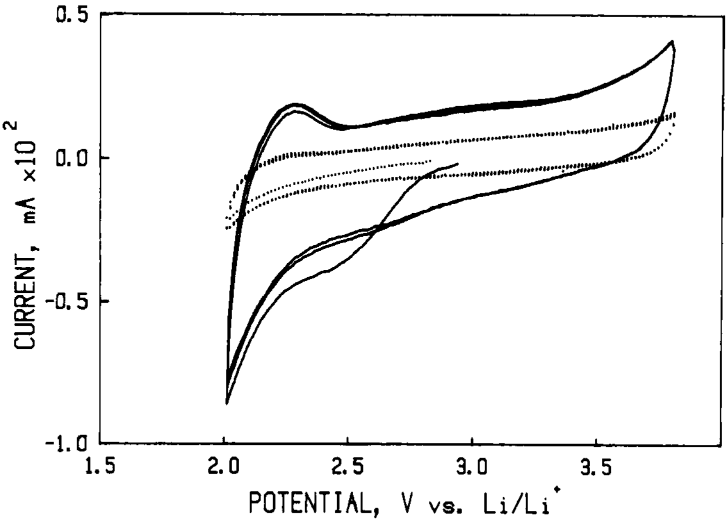

FIGURE 4 Cyclic voltammograms with SPPSLi (EW = 349) on Pt mesh electrode (continuous line) and blank Pt mesh electrode (dashed line) in 1 M $LiClO_4$-PC elecctrolyte at 10 mV sec^{-1} sweep rate. Starting potential = potential of zero current.

CONCLUSIVE REMARKS

The class of polymeric sulphonic acids is not large: long known polystyrene sulphonic acid and more recent Nafion® are so far the dominant members.[4] Polystyrene sulphonic acid has an aliphatic chain containing pendant phenyl sulphonic rings (—C_6H_4—SO_3H), is soluble in water and used mostly as polyelectrolyte. Chain cross-linking with divinylbenzene affords insoluble, rigid materials. Nafion® has a fluorinated hydrophobic aliphatic chain containing pendant —SO_3H functions. It affords flexible free standing films and is very expensive. For industry therefore the search for alternative materials is still an up-todate issue. The new polyphenylene sulphide sulphonic acid has a whole different structure (the aromatic rings being part of the polymer chain) and can afford strongly acid insoluble materials (containing up to 3 —SO_3H meq/g) without need of cross-linking agents or of expensive fluoride substituents. The highest limitation of this material is mechanical: no free standing flexible films can be obtained due to the rigidity of the aromatic chain. The prospects to bypass this defect may lie in substituting the SPPS chain sulphur atom with other phenyl spacing groups. Notwithstanding mechanical aspects, evaluation of the performance of SPPS in electrochemical devices of industrial interest has been done through the manufacture of composites and comparison of its behaviour with other known materials is possible.

As composite material with asbestos, polyphenylene sulphide sulphonic acid may have potential in industrial electrolysis. The range of compositions is such that these products vary from diaphragm type materials with low electrical resistance to ion exchange membranes. The former are currently items of interest for advanced water electrolyzers:[1] $BaTiO_3$, NiO and electrolytic-grade woven asbestos have been reported very recently[17] as best candidates for their low electrical resistance (0.18–$0.25\ \Omega\,cm^2$ in 100°C conc. alkali). The 10–15% SPPS composites do exhibit ohmic drop in the competitive range (Figure 1). The more concentrated composites have higher resistence; however, due to its ion-exchange capacity 43% SPPS–ASB becomes interesting again in relation to industrial brine electrolysis. Figure 5 shows how the K^+ transport number in KCl for the SPPS composite approaches that of nowadays established Nafion® membranes.

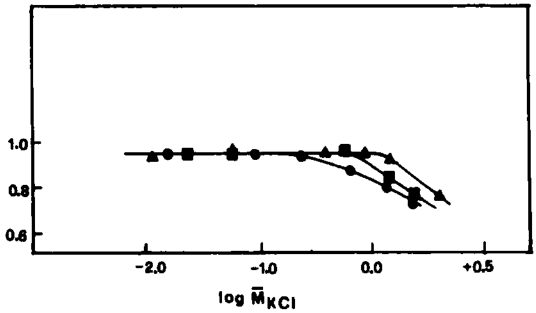

FIGURE 5 Potentiometric transport number (t_+) for the potassium ion through 43% SPPS composite (●), Nafion® 427 (■) and Nafion® 120 (▲) membranes as measured in KCl: M = molarity.

The solid state conductivity of SPPS (10^{-5} ohm^{-1} cm^{-1} in Table II) is of the order of that reported for polystyrene sulphonic acid.[18] The strong conductivity rise (to 10^{-2} ohm^{-1} cm^{-1}) which has been observed for SPPS under steam pressure is also in agreement with the dependence of conductivity on polymer water content as reported for the proton conducting polystyrene sulphonic acid.[19] The conductivities of these sulphonic polymers are not exceptional. Many inorganic acids[7] of P, As, U, Al exhibit even higher conductivities, from 10^{-4} up to 10^{-1} ohm^{-1} cm^{-1} range. It could be that polymers with higher content of sulphonic functions (e.g. SPPS with EW < 340) had higher conductivity. However, standing the above known mechanical limitation, the issue is of low interest.

Electrochemical doping of SPPS has been qualitatively suggested, however both cell discharge (Figure 3) and cyclic voltametry (Figure 4) curves imply that the morphological and structural parameters (i.e. porosity and polymer-current collector contact) of the polymer electrode assembly have to be optimized.

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