THE ELECTROLYTE CHALLENGE FOR A DIRECT METHANOL-AIR POLYMER ELECTROLYTE FUEL CELL OPERATING AT TEMPERATURES UP TO 200 °C

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ABSTRACT

Novel polymer electrolytes are being evaluated for use in a direct methanol-air fuel cell operating at temperatures in excess of 100 °C. The evaluation includes tests of thermal stability, ionic conductivity and vapor transport characteristics. The preliminary results obtained to date indicate that a high temperature polymer electrolyte fuel cell is feasible. For example, Nafion 117 when equilibrated with phosphoric acid has a conductivity of at least 0.4 $\Omega^{-1}cm^{-1}$ at temperatures up to 200 °C in the presence of 400 torr of water vapor and methanol vapor cross over equivalent to 1 mA/cm^2 under a one atmosphere methanol pressure differential at 135 °C. Novel polymers are also showing similar encouraging results. The flexibility to modify and optimize the properties by custom synthesis of these novel polymers presents an exciting opportunity to develop an efficient and compact methanol fuel cell.

INTRODUCTION

The direct methanol-air fuel cell is a very promising system for a wide spectrum of applications where high efficiency and light weight are required. Methanol is attractive for fuel cell use for a number of reasons; it is more convenient to store and handle than hydrogen or ammonia, and it offers a relatively high energy density. The direct methanol fuel cell is favored over the indirect (reformed methanol) system since the direct oxidation of methanol offers the promise of greater efficiency and simplicity with lower weight and lower cost resulting from the elimination of the fuel reformer. Present direct methanol-air fuel cell configurations are severely limited by the lack of sufficiently active catalysts for the methanol anode, and to a lesser extent, the oxygen cathode. In addition, current methanol-air fuel cells are hindered by the cross-over of methanol from the anode to the cathode, which results in a loss of efficiency via chemical reaction of the fuel with oxygen and depolarization of the cathode.

The use of solid polymer electrolytes offers new opportunities to overcome the catalyst stability and activity problems, provided the polymers are stable and retain reasonable ionic conductivity at temperatures approaching 200 °C. The use of a polymer electrolyte membrane (PEM) at 200 °C should allow for the identification of effective catalysts which lack sufficient activity at the lower temperatures typical of conventional PEM fuel cells or that are significantly deactivated by the adsorption of phosphate in high temperature phosphoric acid fuel cells. The higher temperatures will increase the catalytic activity substantially, while depressing the self-poisoning effects associated with strongly adsorbed intermediates. The polymer should have other properties such as high oxygen solubility and low electrolyte adsorption which will promote better electrode performance. In addition, the use of a polymer electrolyte as opposed to a liquid electrolyte should result in extended fuel cell life due to the elimination of electrolyte movement within the electrodes, i.e. electrode flooding. A DARPA sponsored project is in progress at CWRU with the objective of developing highly efficient methanol-air polymer electrolyte fuel cells. This research is focused on 1) developing new ion-conducting polymers capable of operation at 200 °C, 2) more active and stable electrocatalysts for methanol oxidation, 3) high performance electrocatalysts for oxygen reduction that are tolerant of methanol and its oxidation products, 4) optimized electrode structures and 5) new high area electrocatalyst supports with greater oxidative stability than the traditional carbon.

This paper will focus on recent results obtained with several promising solid polymer electrolytes. In particular, the electrolytes are being evaluated with respect to three criteria; 1) thermal stability, 2) proton conductivity, and 3) transport of methanol, oxygen, water and carbon dioxide. These evaluations are being carried out under temperatures and environments (humidity level, oxidizing or reducing conditions) that are indicative of the anode and cathode conditions in an operating fuel cell.

RATIONALE OF APPROACH

The present commercially available sulfonic acid ionomers (e.g. Nafion 117, Dow 560, see Figure 1) depend on water to solvate the protons generated by the ionization of the sulfonic acid groups. When the polymers are subjected to temperatures above 100 °C at one atmosphere pressure, water is lost, including the water solvating the hydronium ions. The membrane shrinks and conductivity is lost. The use of a pressurized system can extend the useful temperature range, but at the expense of overall system efficiency. For an operating temperature of 200 °C, the pressure required is too high to be practical. It has been shown that the ionization of trifluoro methane sulfonic acid (CF_3SO_3H) can be produced by the addition of phosphoric acid to yield $P(OH)_4^+$ and $CF_3SO_3^-$ [1]. A similar effect occurs with the equilibration of sulfonic acid ionomers in concentrated phosphoric acid. The phosphoric acid acts as a Bronsted base, ionizing the strong sulfonic acid groups and solvating the proton in the same manner as water. However, due to the relatively low vapor pressure/high boiling point of phosphoric acid, it would not be expected that ionization and solvation would be lost at temperature above 100 °C. The use of phosphoric acid has the disadvantage that H_3PO_4 or its dissociation products are strongly adsorbed on Pt based catalysts, resulting in a loss of catalytic efficiency.

The equilibration of Nafion with phosphoric acid is one example of the focus of the polymer synthesis effort within the DARPA direct methanol fuel cell project. The goal of the synthesis effort is to produce a polymer that is stable at high temperatures, with a superacid functionality for conductivity and enhanced catalytic activity, also containing an immobilized Bronsted base. One possibility is that the immobilization of the base could be accomplished by bonding the base onto the polymer backbone. It may also be possible to synthesize a polymer in which water is strongly hydrogen bonded, which would reduce the activity of the water and allow water to be retained at temperatures above 100 °C.

Researchers at Clemson University are currently developing perfluorosulfonimide polymers analogous to Nafion. Examples of some of the polymers currently under study are given in Figure 1a,b. One of the advantages of the sulfonimide functionality is that much greater flexibility in the design of the polymer is possible. For example, the side chain length can be varied and one or more functional groups can be included in the side chain. In this manner a wide range of ion exchange capacities can be obtained, and the domain structure of the polymer can be varied to provide optimized conductivity and vapor barrier properties. In addition, preliminary samples of these materials have been shown to be soluble in dimethylformamide (DMF) and are readily cast into films. This behavior is in distinct contrast to Nafion, which is only solublized with considerable effort.

Researchers at University of Iowa are currently developing perfluorophosphonic acid polymers as shown in Figure 1c. It is expected that these polymers will have excellent thermal stability, will be melt formable and will have good conductivity resulting from the two ionizable protons on each side chain. In addition, it is expected that this material will strongly hydrogen bond to water to provide high temperature conductivity without the need for a low vapor pressure solvent such as phosphoric acid. Since the functional groups are part of the polymer chain, they should be sufficiently sterically hindered to prevent adsorption onto active catalyst sites. In addition, it may be possible to make co- or ter- polymers of these materials with the perfluorosulfonimide polymers described above.

A third synthesis effort is underway at CWRU to produce films of polybenzimidazole (PBI) which have been doped with a strong acid such as sulfuric acid and then reacted at high temperature to produce a polymer with the acid anion bound to the phenyl ring on the polybenzimidazole. The protons are ionized by the basic nitrogen atoms in the benzimidazole rings as shown in Figure 1d. Polybenzimidazoles are known to have excellent oxidative and thermal stability, and should be further stabilized by the reaction with acid. Proton hopping between basic sites should provide ionic conductivity

and the barrier properties of these films should be better than that of Nafion since the benzimidazoles will be a single phase material, unlike the nonpolar fluorocarbon/polar ionic biphasic nature of Nafion.

EXPERIMENTAL

Preparation of Polymer Electrolytes

Nafion 117 (acid form) membranes were obtained from duPont and hydrated by immersion in boiling water for four hours. Following hydration, the samples were either left in distilled water until use or were equilibrated with phosphoric acid. The phosphoric acid equilibration consisted of immersion in 85% H_3PO_4 at 150 ^{0}C for 12 hours. Following equilibration the samples were left in phosphoric acid until use.

Polybenzimidazole was purchased from Celanese. Films were cast from a solution of the polymer in dimethylacetamide using a Gardner knife. The films were then doped by immersion in 8M sulfuric acid for 16 hours.

The perfluorosulfonimide membranes were prepared by Dr. D. DesMarteau and co-workers at Clemson University. The details of the polymer synthesis have been given elsewhere [2]. These membranes were hydrated and equilibrated with phosphoric acid using the same procedure as was used for the Nafion 117 samples. The results discussed below are for the difunctional polymer (acid form) shown in Figure 1b. The ion exchange capacity of this material was 0.66 mg H/g.

Four Probe Conductivity Measurements

The conductivity measurements were made with a four probe apparatus constructed at CWRU. In this apparatus two Pt foil electrodes are clamped to the ends of a 3 cm (L) x 0.5 cm(W) sample. These electrodes are used to pass current through the sample. The magnitude and frequency of the applied current were controlled using a PAR 173 potentiostat/galvanostat and a Wavetek 186 signal generator. Two platinum wires (0.5 mm dia.) spaced 1 cm apart, were used to measure the voltage drop in the center of the sample. Voltage measurements were made at three or more current levels to ensure that the (i,v) behavior was ohmic. The current was applied at two different frequencies, 100 and 1000 Hz. No frequency dependence was observed. The entire apparatus was contained within a sealed stainless steel vessel, which was placed inside an oven and connected to a gas manifold system so that the temperature, pressure and composition of the gas phase in contact with the sample could be controlled. Measurements as a function of water partial pressure above 100 ^{0}C were performed by partially evacuating the cell and then injecting sufficient liquid water via a septum to yield the desired water partial pressure.

Vapor Permeability Measurements

The vapor permeability measurements were made using a technique based on ASTM D-1434. In this experiment the membrane separates two thermostated chambers. In one chamber (the retentate) a constant partial pressure (typically 15 psi) of the gas of interest is maintained. As the gas permeates across the membrane the pressure in the second chamber (the permeate) is monitored. Both chambers contain an equal background pressure of an inert gas. Assuming that the pressure in the second chamber is small compared to that in the first chamber, the pressure rise is linear with respect to time and can be directly related to a pseudo-steady-state flux of gas across the membrane. In our apparatus the membrane area was π cm^2, and the volume of the second chamber, including the internal volume of the pressure gauge, was 10 cm^3. A stainless steel screen was used to support the membrane on the low pressure side. An MKS Baratron pressure gauge was used to measure the pressure independent of gas composition to within one torr. A Hewlett Packard 7090A recording plotter was used to record the pressure as a function of time. The same apparatus was also used to measure methanol fluxes in pervaporation. In the pervaporation experiment, one side of the membrane was contacted with pure, liquid methanol, while the

permeate cell on the other side of the membrane was initially evacuated. Following evacuation, the permeate cell volume was sealed. As methanol permeates across the membrane, it evaporates upon reaching the permeate volume. By measuring the pressure rise in the permeate volume, the methanol flux can be determined as in the vapor phase permeability experiments. In order to prevent methanol from condensing, the pressure in the permeate volume was never allowed to exceed the vapor pressure of methanol at the temperature used.

RESULTS AND DISCUSSION

Conductivity

The conductivity as a function of temperature for phosphoric acid equilibrated Nafion 117 (Nafion/H_3PO_4) in three different environments is shown in Figure 2. The curves labeled 'Dry' (pure N_2) and '370 torr H_2O/400 torr N_2' are self explanatory. The third curve, labeled 'H2O/MeOH/N2' is for a vapor phase with a water partial pressure of 350 torr, a methanol partial pressure of 350 torr and a nitrogen partial pressure of 100 torr, i.e., conditions similar to what might be found at the anode of the fuel cell. From these curves it can be seen that the presence of water in the atmosphere significantly increases the conductivity, and that the presence of water and methanol together increases the conductivity still further. These results suggest that even above 100 °C, the conductivity is dependent on the solubility of water in the membrane. Since the water solubility in Nafion is enhanced by the presence of methanol [3], if the conductivity depends on the water content of the membrane, a higher conductivity would be expected with methanol present, which is what was observed. The decrease in conductivity at higher temperatures suggests that the water content decreases with increasing temperature.

The conductivity results for the Clemson sulfonimide polymer 'B' (shown in Figure 1b) equilibrated with phosphoric acid are presented in Figure 3 (Vs. temperature at 400 torr water partial pressure) and Figure 4 (Vs. water partial pressure at 125 °C). For comparison purposes the conductivity of Nafion /H_3PO_4 under similar conditions is also shown. Although the reproducibility of the data for the sulfonimide samples is not good, the results are promising with conductivities significantly higher than Nafion being observed in some samples. The poor reproducibility may be the result of the sample equilibration procedure, which was the same as that used for the Nafion samples and resulted in highly swollen films. It may be possible to optimize the equilibration procedure for the sulfonimide material, to yield more reproducible results.

The conductivity results for the highly doped polybenzimidazole material are shown in Figure 5, as a function of temperature with a water partial pressure of 400 torr. The Nafion 117/H_3PO_4 results under the same conditions are again given for comparison. This sample contained approximately 250 mol% H_2SO_4, i.e., about 2.5 H_2SO_4 molecules to each repeat unit. With this doping level, the conductivity approaches that of Nafion, being about 50% lower at temperatures above 160 °C.

The best conductivity results to date are summarized in Table 1 for films at 170 °C and ca. 400 torr water partial pressure in terms of conductivity and voltage drop for a fuel cell operating at 100 mA/cm². For comparison literature values are given for 96% phosphoric acid at 170 °C and water equilibrated Nafion at 80 °C. While the conductivities obtained in this work are far below that of liquid phosphoric acid, they are very comparable to that of Nafion under traditional low temperature conditions.

Permeability

The permeability of oxygen through a Nafion 117 film equilibrated with phosphoric acid, Nafion equilibrated with water, a sulfonimide 'B' film equilibrated with water, and a PBI film doped with H_2SO_4 was measured using the closed volume technique. The results are summarized in Table 2a. The current density column represents the current density equivalent to the flux across the membrane with a one atmosphere pressure differential as a driving force. The equivalent current density was calculated as i = nFN where n = 4 for the oxygen reduction reaction, F is Faraday's constant and N is the flux. For comparison, literature values for oxygen permeation in phosphoric acid and in Nafion (water equilibrated

and dry) are also given. There is reasonably good agreement between our result for water equilibrated Nafion and the literature value shown, indicating that our apparatus appears to be functioning properly. The permeability of oxygen in the phosphoric acid equilibrated Nafion at temperatures above 100 °C is similar to that in water equilibrated Nafion at 80 °C. This result indicates that the performance of the cathode should not be hindered by poor oxygen transport to the electrode surface, which, as shown in the table, is a limitation of liquid phosphoric acid. The sulfonimide 'B' material is orders of magnitude more permeable to oxygen, most likely due to the fact that it was swelled greatly by the equilibration process. As indicated above, a different swelling procedure may be necessary to obtain optimal results with the sulfonimide polymers. The lowest oxygen permeability was obtained with the polybenzimidazole material, which was expected to show good barrier properties.

The permeability of methanol vapor through Nafion 117 films equilibrated with phosphoric acid and equilibrated with water was also measured. These results are summarized in Table 2b. The equivalent current density was calculated as shown above, but taking n = 6 for methanol oxidation. The results show that the permeability of methanol through the phosphoric acid equilibrated Nafion films at temperatures above 100 °C is significantly lower than through water equilibrated Nafion at 85 °C. From this preliminary result it appears that methanol crossover to the cathode will be less of a problem for a fuel cell operating at the higher temperatures under consideration. Since the diffusion coefficient might be expected to rise with temperature, the lower permeability is probably the result of a lower solubility for methanol in Nafion at the higher temperatures. A lower rate of methanol crossover should result in higher efficiency and a lower probability of cathode depolarization by methanol.

The results from the pervaporation experiments are given in Table 2c in terms of equivalent current density. A literature value for methanol pervaporation through Nafion 125 is also given for comparison. The pervaporation results are in relatively good agreement with the literature value cited. The agreement gives added confidence to our beliefs that our permeation apparatus and experimental procedures are producing valid results. These results show much higher permeation fluxes for the case where the membrane is contacted by liquid methanol as opposed to the permeation when methanol vapor is in contact with the membrane. Thus the methanol crossover through phosphoric acid equilibrated Nafion at temperatures above 100 °C may be considerably smaller than would be expected based on conditions where liquid methanol is in contact with a Nafion membrane.

Thermal Stability

The thermal stability of the sulfonimide 'B' polymer was investigated using Differential Scanning Calorimetry (DSC) as shown in Figure 6. An endothermic process starting at about 150 °C can be seen, corresponding to the loss of water from the membrane. The thermal decomposition of the polymer can be seen at temperatures above 320 °C. This result shows that under these conditions (N_2 atmosphere, heating at 10 °C/min) the polymer is stable in the temperature range of interest.

Thermogravimetric Analysis (TGA) has been used to study the thermal stability of polybenzimidazole and to follow the reaction between PBI film and sulfuric acid. In Figure 7a the TGA scan for an undoped PBI film in nitrogen is shown. The heating rate was 10 °C/min. The PBI film lost water at about 80 °C and underwent thermal degradation at 550 °C. The TGA of PBI doped with approximately 20 mol% sulfuric acid is shown in Figure 7b. This result shows a loss of water at 100 °C and also showed two further weight losses starting at 330 °C and 415 °C. The first loss at 330 °C is attributed to the reaction of the acid with PBI to generate sulfonic acid groups while the second loss is probably due to loss of SO_2 or SO_3 from the polymer. The weight loss due to thermal degradation has been shifted to 600 °C, which indicates that the reaction with the sorbed acid improved the thermal stability of the film.

CONCLUDING REMARKS

A research program is in progress at CWRU/Clemson University/University of Iowa aimed at developing a highly efficient methanol-air polymer electrolyte fuel cell capable of operation at temperatures up to 200 °C. Preliminary results obtained to date indicate that the electrolyte requirements needed to realize this goal can be met. In particular, three novel polymer electrolytes have shown stability and sufficient ionic conductivity at the elevated temperatures envisioned.

ACKNOWLEDGMENTS

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Table 1
MEMBRANE CONDUCTIVITY

Membrane / Electrolyte	Conditions	Conductivity / $ohm^{-1}cm^{-1}$	Voltage loss at 100 mA/cm^2	Reference
Nafion 117 / H_2O	80 °C, Saturated H_2O Vapor	0.08	25 mV	4
96 % H_3PO_4	170 °C	0.64	< 5 mV	5
Nafion 117 / H_3PO_4	170 °C, 400 torr H_2O	0.04	50 mV	this work
Clemson U. B / H_3PO_4	170 °C, 400 torr H_2O	0.05 - 0.10	20 - 40 mV	this work
PBI / H_2SO_4	170 °C, 400 torr H_2O	0.02	100 mV	this work

Table 2a
OXYGEN PERMEABILITY

Membrane/Electrolyte	Temperature / °C	Current Density / mA/cm^2	Reference
95% H_3PO_4	120	0.04	6
95% H_3PO_4	150	0.08	6
Nafion 117 /35 % H_2O	80	0.46	7
Nafion 117 / dry	80	0.06	7
PBI / H_2SO_4	80	0.08	this work
Nafion 117 / H_2O	80	0.6 - 0.8	this work
Clemson B / H_2O	76	20 - 47	this work
Nafion 117 / H_3PO_4	123	0.35 - 0.45	this work
Nafion 117 / H_3PO_4	150	0.25 - 0.67	this work

Table 2b
METHANOL PERMEABILITY

Membrane	Temperature / ^{0}C	Current Density / mA/cm^2
Nafion 117 / H_2O	85	2.9 - 3.3
PBI / H_2SO_4	85	3.1
Nafion 117 / H_3PO_4	135	0.5, 0.5, 0.4 (3 samples)
Nafion 117 / H_3PO_4	140	0.9
Nafion 117 / H_3PO_4	155	1.1

Table 2c
METHANOL PERVAPORATION

Membrane	Temperature / ^{0}C	Current Density / mA/cm^2	Reference
Nafion 117 / H_2O	25	10 - 18 27 - 30 16 (3 samples)	this work
Nafion 117 / H_2O	50	52 388 (2 samples)	this work
Nafion 125 / H_2O / $(CH_3)_3NH^+$	50	290	3

Figure 1
Example Structures of Polymer Electrolytes

a. Perfluorosulfonimide (monofunctional)

$[(CF_2 - CF_2)_m - CFCF_2]_n$
|
$OCF_2CFOCF_2CF_2SO_2NSO_2CF_3$
| |
CF_3 H
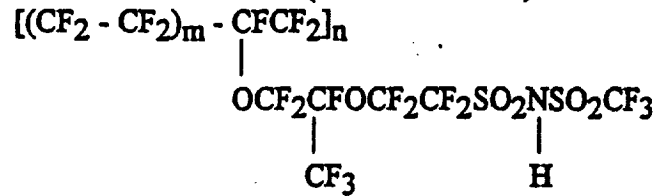
b. Perfluorosulfonimide (difunctional)

$[(CF_2 - CF_2)_m - CFCF_2]_n$
|
$OCF_2CFOCF_2CF_2SO_2NSO_2(CF_2)_4SO_2NSO_2CF_3$
| | |
CF_3 H H

c. Perfluorophosphonic acid

$[(CF_2 - CF_2)_m - CFCF_2]_n$
|
$O(CF_2)_xPO(OH)_2$
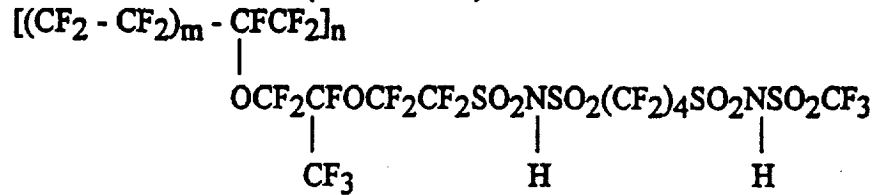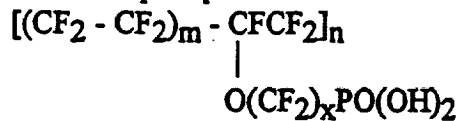
d. Polybenizimidazole (reacted with sulfuric acid)

e. duPont Nafion

$[(CF_2 - CF_2)_m - CFCF_2]_n$
|
$[OCF_2CF]_xOCF_2CF_2SO_3H$
|
CF_3

f. Dow

$[(CF_2 - CF_2)_m - CFCF_2]_n$
|
$OCF_2CF_2SO_3H$
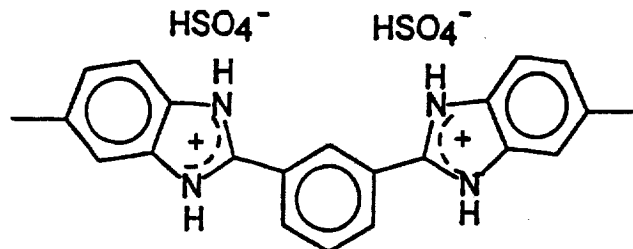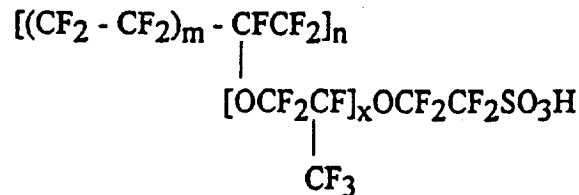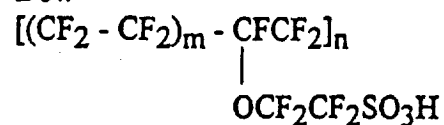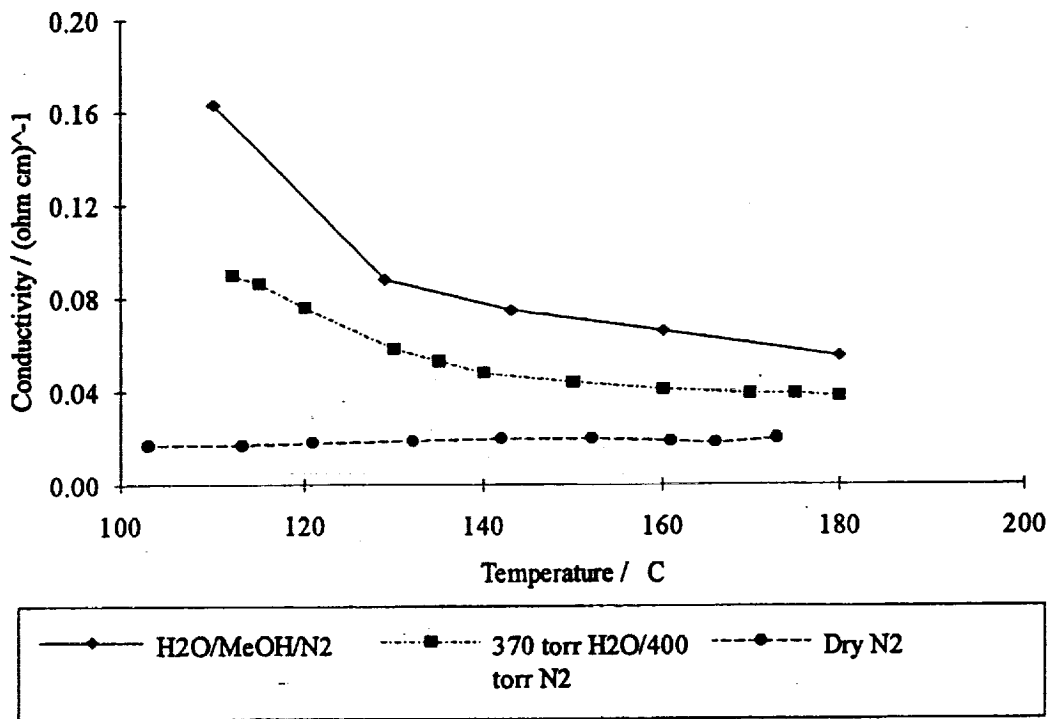
Figure 2   Nafion 117/H_3PO_4 Conductivity in different environments.
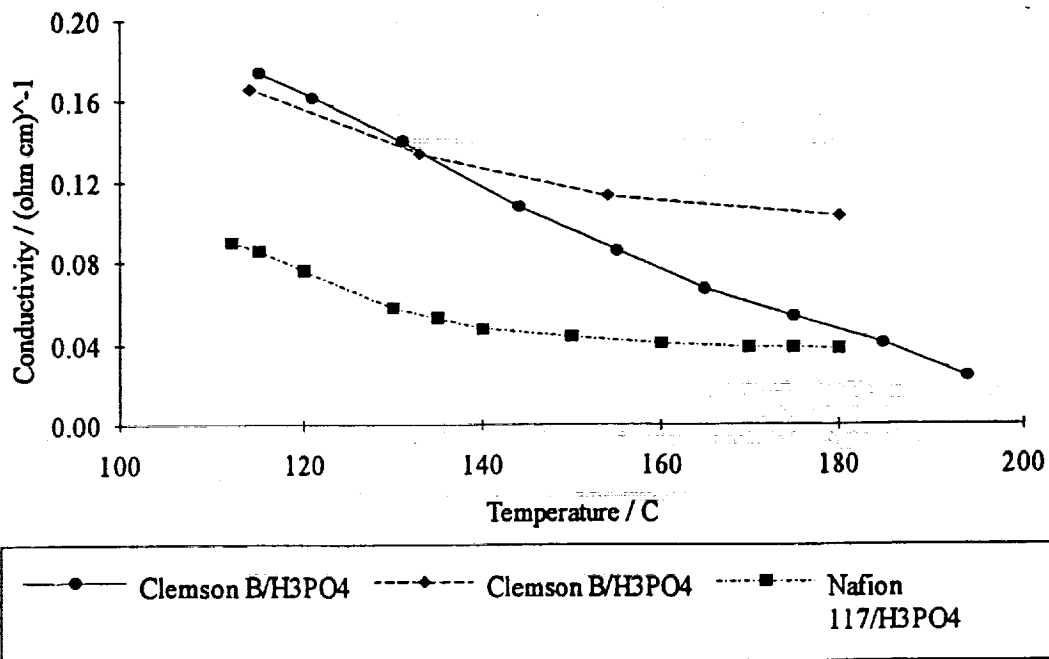
Figure 3   Conductivity vs Temperature at 400 torr water partial pressure.
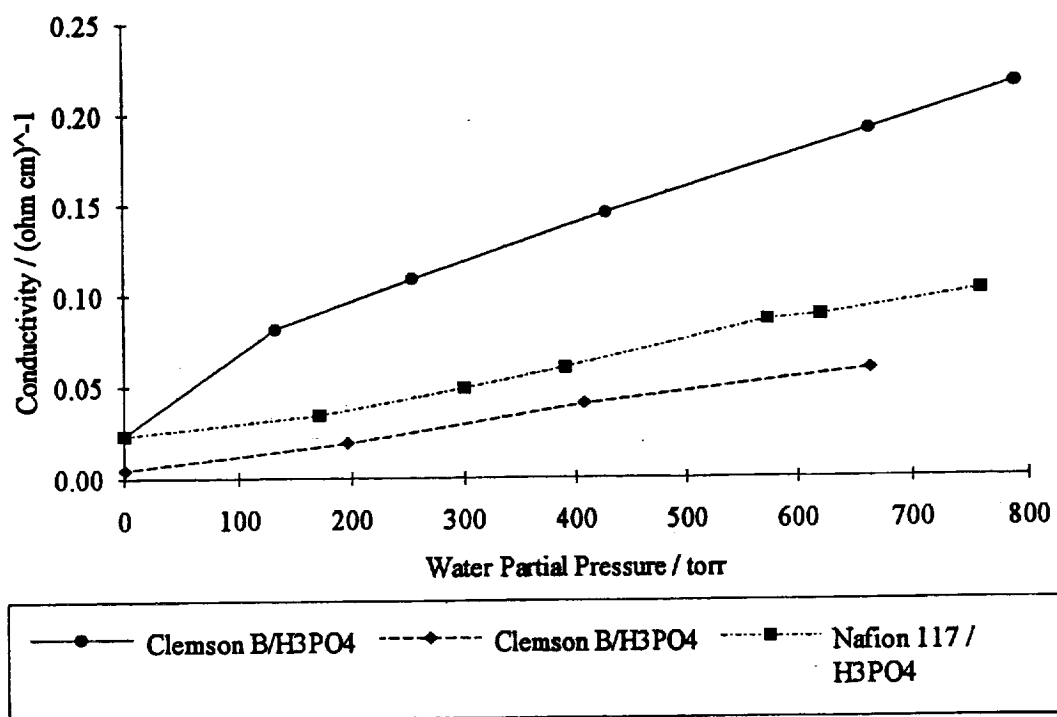
Figure 4   Conductivity vs Water Partial Pressure at ca . 125 °C.
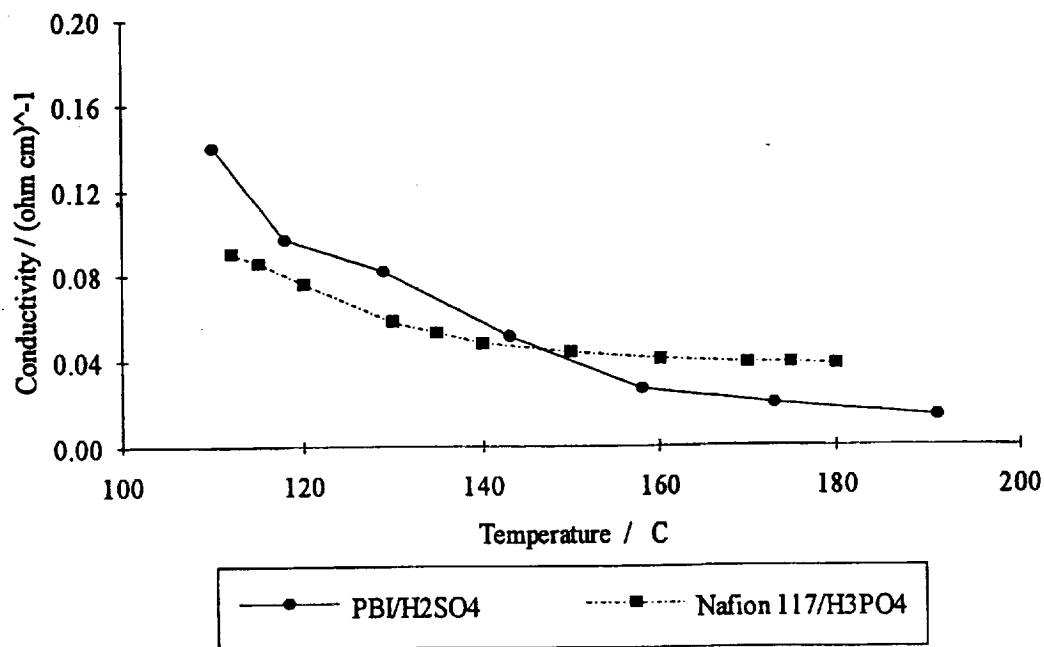

Figure 5   Polybenzimidazole Conductivity, 400 torr water partial pressure.
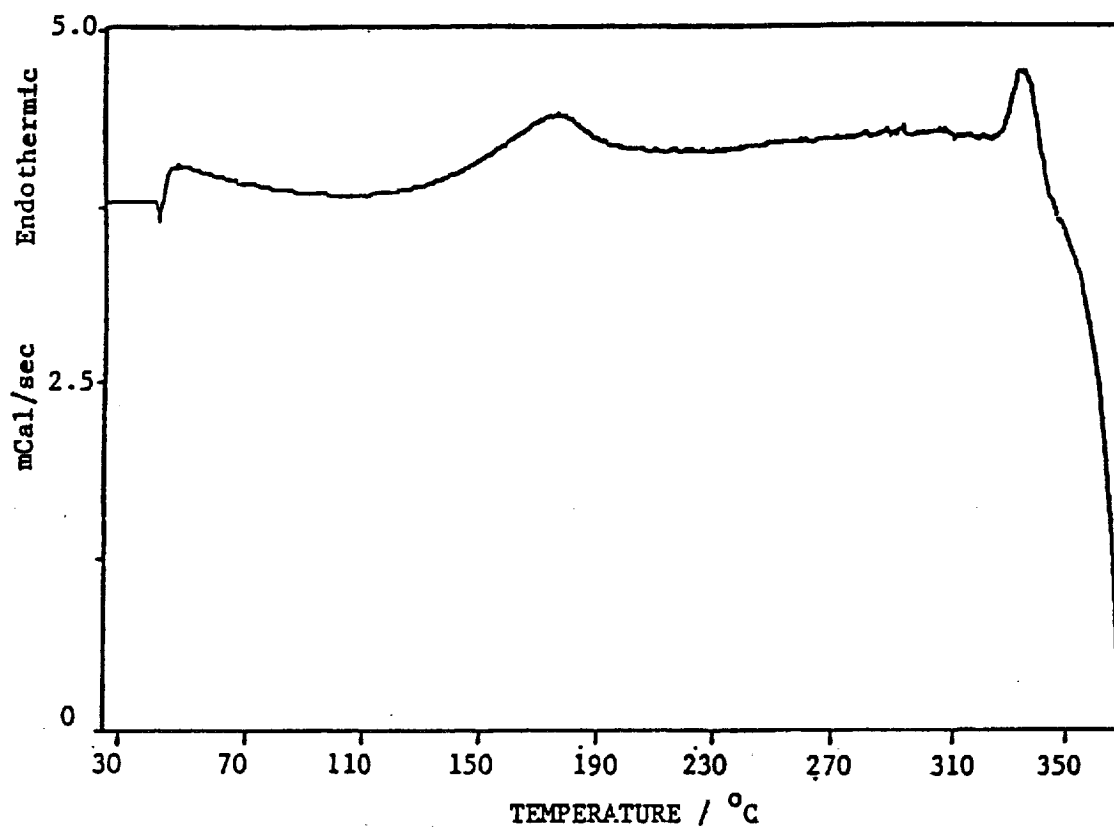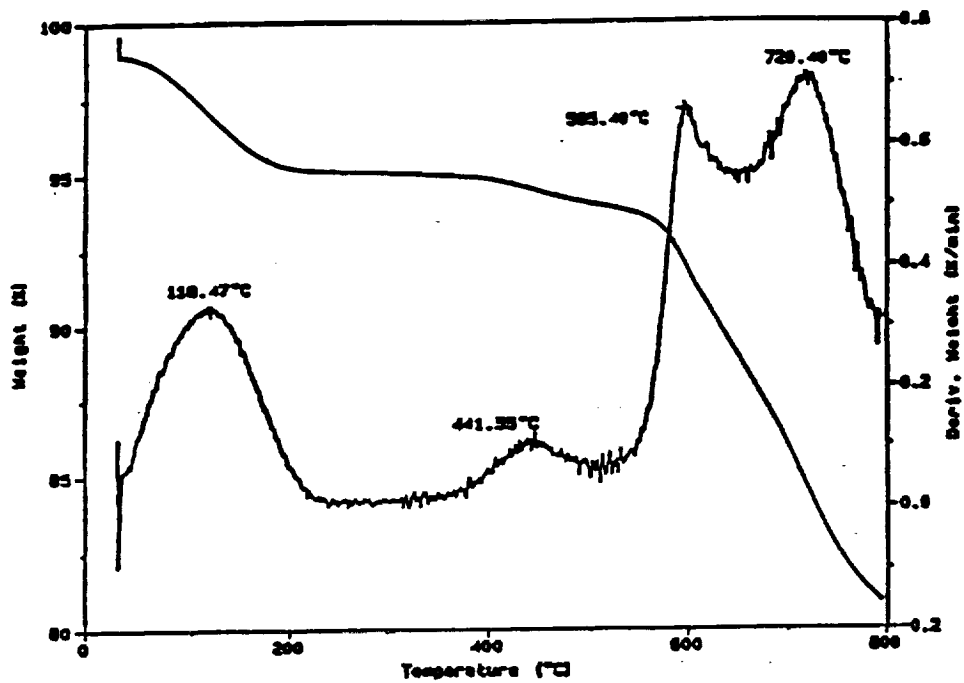
Figure 6   DSC of sulfonimide polymer 'B'.
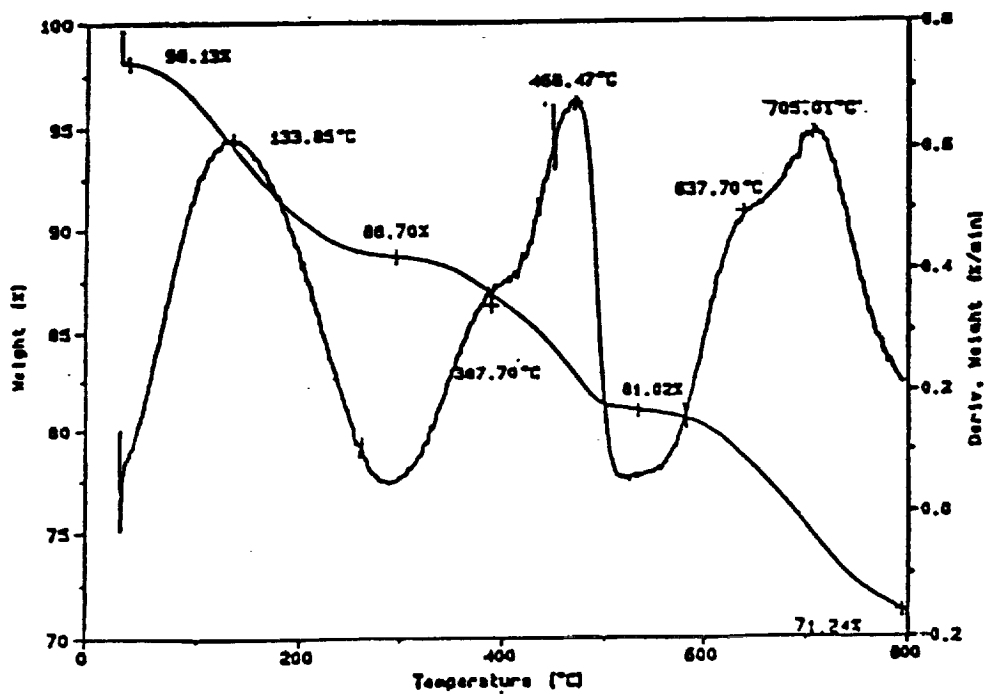
Figure 7a   TGA of undoped PBI polymer.

Figure 7b   TGA of Sulfuric acid doped PBI polymer.