Task 3 Report

Development of Solid Electrolytes for Water Electrolysis at Intermediate Temperatures

DOE/AL/85802--T2-P4.3

Annual Report

FSEC-CR-857-95

DOE Contract #DE-FG04-94AL85802

December 1995

Submitted to:
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PREFACE

This report describes the Sustainable Hydrogen Production research conducted at the Florida Solar Energy Center (FSEC) for the past year. The report presents the work done on the following four tasks:

- Task 1. Production of Hydrogen by Photovoltaic-Powered Electrolysis - This task represents the final effort of a cooperative project between the U.S. Department of Energy, NASA/Kennedy Space Center, FSEC and the Florida Energy Office. The activities covered five years of effort at a total funding of \$216,809. These results represent a successful coordination of two state agencies and two federal agencies.
- Task 2. Solar Photocatalytic Hydrogen Production from Water Using a Dual-Bed Photosystem - This task established the basis of the dual-bed concept by selectively evolving hydrogen or oxygen. A number of redox mediators were found to facilitate hydrogen production.
- Task 3. Development of Solid Electrolytes for Water Electrolysis at Intermediate Temperatures - Several ionomers were synthesized and fabricated into proton exchange membranes. Laboratory testing in an electrolysis cell gave comparable performance to the commercial product.
- Task 4. Production of Hydrogen by Thermocatalytic Cracking of Natural Gas - The experimental unit was constructed and a number of catalysts for methane cracking reactions were tested. Laboratory experiments established catalyst activity and identified stability problems.

This report was prepared by the Florida Solar Energy Center/University of Central Florida as an account of work sponsored by the U.S. Department of Energy (Contract #DE-FG04-94AL85802)). The work reported in this document does not imply endorsement by U.S. Department of Energy.

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DEVELOPMENT OF SOLID ELECTROLYTES

FOR WATER ELECTROLYSIS AT

INTERMEDIATE TEMPERATURES

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1.0 SUMMARY

This project is an attempt to synthesize and fabricate proton exchange membranes for hydrogen production via water electrolysis that can take advantage of the better kinetic and thermodynamic conditions that exist at higher temperatures. Current PEM technology is limited to the 125-150° C range. Based on previous work evaluating thermohydrolytic stability, some 5 families of polymers were chosen as viable candidates: polyether ketones, polyether sulfones, fluorinated polyimides, polybenzimidazoles, and polyphenyl quinoxalines. Several of these have been converted into ionomers via sulfonation and fashioned into membranes for evaluation. In particular, the sulfonated polyetheretherketone, or SPEEK, was tested for water uptake, thermo-conductimetric analysis, and performance as the solid electrolyte material in an electrolysis cell. Results comparable to commercial perfluorocarbon sulfonates were obtained.

2.0 BACKGROUND

2.1 Advantages in Performing Water Electrolysis at Elevated Temperature

If an electrolyzer could operate at higher temperatures, several benefits would accrue. The first is that the thermodynamic electrical energy requirement to drive the reaction would be reduced. As shown in Figure 1, supplying the total enthalpy of reaction at any temperature involves a combination of electrical and thermal energy inputs. Because of the positive entropy associated with water decomposition, the thermal contribution increases as temperature rises, allowing the free energy requirement to decrease.

Thus the open circuit voltage, V_{∞} , for water splitting drops as temperature rises. At room temperature, V_{∞} for water decomposition is 1.229 V. At 400° C, voltage requirement has

Figure 1. Energy relationships in water electrolysis

dropped to 1.1 V; at 1000° C, it is only 0.92 V. Since electricity is a more expensive form of energy on a btu basis, the more energy taken from the thermal surroundings the better. Moreover, this thermal energy content could be solar-derived. While the cost of solar thermal energy varies in the range of \$360-900/peak kilowatt, the installed cost of photovoltaic electricity is in the range of \$4,000-5,000/peak kilowatt. Thus if one is compelled to erect an array of photovoltaic panels to generate the e.m.f. necessary to split water, substituting as much area with thermal collectors as possible represents a substantial cost savings.

A second benefit is that activation barriers for the various electrode surface chemical reactions are more easily surmounted as temperature increases. As it stands now, expensive noble metals are frequently required in electrolyzers to keep cell voltages acceptably close to the thermodynamic value. For a unit operating at higher temperature one may be able to substitute cheaper, less catalytic metals with higher intrinsic activation energies toward O_2 and H_2 evolution.

This same consideration may likely be applicable to the electrolyte itself. Ionic motion in solids is frequently modeled as a hopping process, where the mobile ionic species, in our case H^+ or H_3O^+ , makes activation-limited jumps from one binding site to an adjacent one. Thus one could anticipate reduced ohmic overpotential loss from the electrolyte as well.

2.2 Current Proton Exchange Membrane Technology

In principle, this type of electrolyzer would include any electrolyte consisting of a polymeric material that could be fabricated into a gas impermeable membrane that could transport ions necessary to support water electrolysis. A number of other polymeric proton exchange membranes have been reported in recent years. Doping polyethyleneoxides with various salts results in proton conducting membranes with conductivities on the order of 10^{-5} - 10^{-4} S/cm at room temperature and greater than 10^{-3} S/cm at 100° C (1). Polymers doped with inorganic acids have been prepared and resulted in conductivities as high as 1.4×10^{-2} S/cm at 100° C for a polyacrylamide doped with sulfuric acid (2). A final example, poly(benzyl sulfonic acid) siloxane showed conductivities ranging from 2×10^{-3} to 10^{-2} S/cm at room temperature (3).

In practice, proton exchange membrane technology, or PEM, has come to mean those cells employing a perfluorinated hydrocarbon sulfonate ionomer, such as Du Pont's Nafion™. Originally developed as a substitute for other types of cell separators utilized in the chlor-alkali industry, it has come to occupy a place of prominence in the search for more efficient, less expensive ways to electrolytically produce H₂.

To exhibit protonic conductivity, Nafion must be pre-swelled with water, usually by boiling it. In this state it has a conductivity on order of 0.01 (ohm-cm)⁻¹. In comparison to a 1 M HCl solution (0.1 (ohm-cm)⁻¹), it is a factor of 10 too resistive, but can be fabricated and mounted in a cell with much closer tolerances, so that the absolute resistance is comparable. The uptake of water can amount to 28% by weight (4).

The water uptaken into Nafion is for the most part free and unbound, since it is quickly lost once temperature exceeds 100° C. By pressurizing the system, one can increase operating temperature; however, by the time temperature has been raised to 150° C, the thermal stability of the perfluorinated ionomer itself is brought into question. The normally light brown or clear membrane irreversibly becomes dark and brittle. Thus currently one cannot operate PEM electrolysis cells at temperatures above 150° C.

The sulfonated ionomer is acidic in nature, and so other components, especially the anode and its external electrical contacts, must have some corrosion resistance. To date this has required that the anode be either a noble metal such as Pt or a transition metal alloy based on Ir or Ru (5).

2.3 Development of Intermediate Temperature Solid Electrolytes

At the current level of water electrolysis technology, there exists an 800-900 degree gap, between zirconia-based ceramic membranes at the high end and PEM cells at the low end, in which there are no electrolytic systems suitable for water electrolysis. Even if one includes all of the fuel cell technologies that could possibly be run in reverse, such as phosphoric acid at up to 200° C and molten carbonate as low as 600° C, there still exists a 400 degree gap. In terms of striking a balance between faster kinetics and lower open circuit voltage by raising

temperature, and reducing corrosion and materials compatibility problems by lowering it, operation in the 200-400° C range appears to be desirable.

Most efforts to develop high temperature proton conductors have involved hydrated inorganic oxides (6,7). A less explored avenue would be to consider engineering polymers, those specialized polymers whose structures allow them to be used in applications requiring extremes of temperature and corrosivity. However, since they were developed for other applications such as flame retardant materials, seals for electronic components in hostile environments, and autoclavable medical supplies (8), their behavior in an electrolytic situation at elevated temperature has not been well characterized.

2.4 Previous Work on Engineering Polymers

A less tried route that could allow for higher operating temperatures is to use engineering polymers. These polymers are designed for use at temperatures in excess of 300° C and can be modified to yield ion conducting materials. For example, a polyimide containing quaternary copolymer was found to have a conductivity of 10^{-6} at 250° C (4). Aromatic polyethersulfones have been sulfonated and used as experimental water electrolysis membranes although no conductivity data for this system was reported (10). The derivatization of the aromatic polyetheretherketone (PEEK) to its sulfonic acid ionomer and the characterization of this ion containing polymer have been extensively studied (11-15), although its ion conducting properties have not been reported.

In previous work, over 40 different polymeric materials, each known for their thermal and chemical resistance, were examined under steam/O₂ and steam/H₂ conditions. This was done to simulate conditions that would be observed in the anode and cathode compartments of a steam electrolysis cell (16). Of these, several polymer families showed good stability: liquid crystal aromatic polyesters, polybenzimidazoles, and some of the polyimides were stable at 200° C. The polyphenylene sulfides, polysulfones, polyethersulfones, the various polyketones, and some of the polyimides were stable at 300° C. None of the polymers tested could withstand the combination of steam and O₂ at 400° C; however, some of the polyketones did survive at 400° C under the reducing environment.

The above list of polymers makes a fair representation of those families that are most likely to succeed as high temperature solid electrolytes. Some of the polymers of interest consisted of 1,4-disubstituted phenyl groups separated by any of a number of linkages:

where X,Y,Z = -O-, -C(O)-, -C(CH₃)₂-, -SO₂-, -S-, etc.

for PEEK, X = Y = -O-, Z = -C(O)-;

for PES, X = -SO₂-, Y = -O-, etc.

In the present work, our task has been to sulfonate these materials, converting them to ionomers, and then characterize their thermohydrolytic and proton-conducting behavior.

3.0 EXPERIMENTAL

3.1 Sulfonation Reaction

Electrophilic aromatic sulfonation of the PEEK was done following established literature methods (14). A typical reaction is as follows: 10 g of oven dried PEEK was dissolved in 100 ml of 96% H₂SO₄. The tan PEEK dissolved within 2 hours to give a deep red, viscous solution. The time and the temperature of the reaction were varied in order to achieve the desired level of sulfonation. The reaction was quenched by slowly pouring the acidic solution into one liter of distilled water. The polymer precipitated instantly, forming a continuous white string. The polymer was extensively washed to remove the excess acid, dried in a vac-oven at 100° C, and titrated to determine the level of sulfonation.

The above sulfonation technique was attempted on each of the polymer candidates. As it turned out, more often than not the results were unsatisfactory: sometimes the polymers was so

heavily sulfonated it was completely water soluble and thus unsuitable for membrane fabrication and testing, and in others the polymer would simply dissolve and reprecipitate unreacted. Therefore, a number of other sulfonation procedures were adopted that will be described in the Results section.

3.2 Membrane Formation

Initially, four levels of sulfonation were selected for testing: 20%, 30%, 45% and 65%. Thin films were made by solvent casting 10% wt:wt solutions of the polymers in dimethylformamide (DMF) onto either a glass plate or into a beaker. The solvent was removed by gentle heating until the film could be peeled off the substrate. The films used for the water electrolysis studies were cast onto glass onto which had been spread 4 mg/cm² of iridium black powder. These membranes, once dried, were coated on one side only with the iridium catalyst. All of the membranes were hydrated before use by heating them in distilled water. The temperature and duration of heating varied with the membranes' resistance to dissolution in the water.

3.3 Water Uptake

H₂O uptake by the ionomer membranes was determined by soaking the films in distilled water for one hour. It is uncertain whether the degree of water uptake so obtained truly constituted saturation - certainly the recommended procedure for swelling Nafion is more severe, involving boiling for several hours. Many of the test membranes, however, were not stable under boiling conditions, and so milder water uptake conditions had to be used.

The water uptake of the S-PEEK samples was determined as follows: the membranes were dried in a vacuum oven, weighed, soaked in distilled water overnight at room temperature, blotted dry to remove any surface moisture and reweighed. The water uptake is reported as the weight percentage of the membrane.

3.4 Degree of Sulfonation

Degree of sulfonation was determined via a combination of acid/base titrimetry and gravimetry. A dry sample of the test material would be weighed and then thoroughly soaked in 1 M HCl(aq) to completely protonate all of the sulfonic acid moieties contained within. It would then be rinsed with distilled water to remove excess acid and placed in a 3 M NaCl solution. This action would displace all of the labile protons and release them to the surrounding salt solution. The acidified salt solution would then be titrated with standardized NaOH solution. The results were used to calculate either degree of sulfonation (%), with 100% meaning 1 sulfonic acid group per repeating unit, or acid density (milliequivalents/g).

3.5 Thermo-Conductimetric Analysis

Resistance measurements were made using an a.c. bridge at 1000 Hz. The membrane conductivity cell was patterned after the work done at Los Alamos (17). Sample membranes were suspended in a holder and clamped with platinum contacts at opposite edges. The conductivity cell was immersed in deionized water within a Parr reactor equipped with electrical feedthroughs and ramped at 0.5° C/min. Resistance values so obtained would be corrected by the dimensions of the sample membrane to yield conductivity.

It was decided that since conductivity was a valid parameter in assessing the viability of a candidate membrane, we could use the conductivity bridge in a type of thermal analysis. To perform the "thermoconductimetric" analysis, the conductivity cell was suspended inside a Parr reactor that was equipped with electrical feedthroughs to enable connection with the a.c. bridge. Temperature was slowly ramped while measuring conductivity. In each case, temperature was raised until failure of the membrane occurred. This would be noted by a precipitous drop in conductivity.

3.6 Electrolysis Performance

The test cell, as shown in Figure 2, consisted of two graphite blocks bored out to allow the evolved gases to escape from the cell. The iridium coated polymer was sandwiched between two

pieces of carbon cloth, one of which was electrolytically imbedded with platinum. This current distributor was placed at the cathode, positioned on the side of the polymer not coated with iridium. The carbon cloth provided acceptable electrical conductivity as well as gas and water permeability. The membrane assembly was centered between the graphite blocks and the entire cell was bolted together. Poppet check valves were placed in the exiting gas lines to pressurize the cell during higher temperature testing. Feed water was contained in a vertical column connected to the inlet port of the cathode.

Once completely assembled, the current versus voltage curves were generated. The power to the cell was controlled with a variable direct current power supply. A temperature controller connected to heat tape adhered to the test cell walls maintained the operating temperature during testing.

Figure 2. Proton exchange membrane electrolysis test cell.

4.0 RESULTS AND DISCUSSION

4.1 Ionomer Synthesis and Membrane Fabrication

PEEK

PEEK was sulfonated at various levels between 20%-75% by varying either reaction time or temperature. The sulfonation was performed by dissolving a sample (10g) of PEEK in concentrated sulfuric acid. Once the reaction time was completed, the reaction was quenched by adding the viscous acid solution dropwise to cold, rapidly stirring water.

Once the polymer had been sulfonated and obtained as solid white strands and droplets, it was usually necessary to convert it into thin sheets for characterization. Films were cast by dissolving the polymer in DMF, casting the solutions in a crystallizing dish, and evaporating the solvent to dryness. Films were hot-pressed to uniform thickness at 100° C and several thousand psi.

PES

Sulfonated PES was prepared using the concentrated sulfuric acid method. The levels of sulfonation obtained were 7%, 17.5% and 29.5%. All attempts to cast films from solvent resulted in cracked films. The suspicion was that the concentrated sulfuric acid used in the reaction was causing some decomposition of the polymer and resulting in shorter chain length. Attempts to sulfonate at greater than 29.5% resulted in H₂O soluble polymers (actually the 29.5% sample was soluble in hot water).

Blends of SPES with commercial PES were made to try and form a non-brittle film. A 1:1 blend of 29.5% SPES and PES gave a film that did not crack. This obviously limits the degree of sulfonation.

Higher degrees of sulfonation were finally achieved using a literature procedure with dissolved sulfur trioxide, SO_3 , as the sulfonating agent (18,10). By varying the molar ratio of SO_3 to base polymer, 10% and 70% sulfonation levels were obtained.

PBI

Sulfonation of PBI was attempted using the concentrated sulfuric acid method, but was not successful. The polymer simply dissolved and re-precipitated after water dilution without reaction. Sulfonation was subsequently accomplished by soaking membranes, which were cast from a DMF solution doped with LiCl, in a 10% H_2SO_4 solution and then heating the swollen membrane at 300° C. This was based on a procedure obtained from Hoechst-Celanese (19). Initially, the swollen membranes were heated for one hour; this gave very brittle films that were not useful. Shortening the heating period to 1-2 minutes seems to improve the characteristics of these membranes. Attempts to make a membrane pliable enough for trials in the Parr reactor are still underway.

PPQ

Sulfonation of PPQ was also unsuccessful using the sulfuric acid method, but the soak and bake method using 35% H_2SO_4 has produced flexible membranes. The PPQ membranes used in this procedure are obtained from Cemota (Centre d'Études des Matériaux Organiques pour Technologies Avancées). The percent sulfonation (as determined by weight) can be controlled by varying the soaking period.

FPI

EYMYD films were cast from the supplied resin from the Ethyl Corporation and cured according to the prescribed procedure to give the polyimide film. Curing of a free film (not coated on any substrate) caused a crumpling of the membrane.

Attempts to sulfonate the polyimide were made using concentrated H_2SO_4 , concentrated H_2SO_4 at elevated temperature, and 30% oleum. In all cases some discoloring of the solution occurred,

but no significant dissolution or reaction was observed. The problem seemed to be the resistance of these films to any moisture uptake.

Attempts to sulfonate the diamine portion of the monomer were made using simple dissolution in concentrated H_2SO_4 . The diamine dissolved readily and was apparently sulfonated based on ^1H NMR at almost 200% after overnight reaction (one SO_3H group on each of the amine bearing aromatic rings). This sulfonated material would not dissolve in NMP (N-methyl pyrrolidone), however, when an attempt was made to do the polymerization reaction. Reducing the sulfonation reaction time from overnight to 6 hours gave a solid that was soluble in NMP. However, the polymerization reaction run under the hood with dry solvent and dry materials resulted in a brittle film when the reaction mixture was solvent cast. The assumption is that the polymerization reaction is producing low molecular weight polymer which forms a brittle film.

The polymerization reaction was performed using non-sulfonated diamine as a test of the polymerization reaction procedure. Attempts made in both the glove box and in the fume hood did not result in a usable film. Further consultation with the literature will be made before continuing this particular synthetic effort.

4.2 H_2O Uptake

It was anticipated that sulfonation of the base polymers would render them hygroscopic and capable of substantial water uptake. This effect can have a direct bearing on how well the ionomer conducts protons. Since most of our synthetic effort had been directed toward SPEEK, we were able to look at its water uptake ability in some detail.

In Table I, water uptake by SPEEK membranes as a function of degree of sulfonation is shown.

Table I. SPEEK Water Uptake Data

<u>% sulfonation</u>	<u>% water uptake</u>	<u># H₂O's / SO₃H</u>
20	19	23
30	25	22
45	41	33
65	60	49

As can be seen, substantial amounts of water were indeed sorbed into the membranes, and was directly related to the degree of sulfonation. Of particular interest is the number of water molecules per sulfonic acid group. Waters of hydration alone could only account for possibly 6 H₂O's per acid group. The size of the numbers shown above indicate swelling and separation of the polymer strands. Indeed, samples with higher degrees of sulfonation would expand in their lateral dimensions and were quite weak mechanically. Thus either cross-linking groups must be introduced or the degree of sulfonation must be kept low. This latter solution would unfortunately work against high protonic conductivity.

4.3 Thermoconductimetric Results

As was mentioned in the previous section, SPEEK showed substantial water uptake, which at first glance this would be considered a positive attribute, but the moisture uptake also brought on the loss of mechanical properties. At 80° C in the Parr reactor, a 32% degree of sulfonation SPEEK sample showed a resistance of 75 k Ω at 81° C. At saturation its H₂O uptake was 47% by weight of the original dried film. This corresponds to 25.6 H₂O molecules/sulfonic acid. Upon examination, the membrane had swollen into a gel-like state, and was unusable for further testing. H₂O absorbance was also tested on 20% SPEEK at 80° C to see if it possessed the rigidity to act as a good membrane; this too swelled to a gel-like state and was unusable.

After much trial and error, we were able to produce membranes with as high as 65% degree of sulfonation that were mechanically strong enough to perform a thermoconductimetric

examination. An exponential rise in conductivity versus temperature was obtained, consistent with Arrhenius-type behavior, as shown for in Figure 3. This was also generally the case with the other polymer candidates.

Figure 3. SPEEK conductivity vs reciprocal temperature.

A thick film cast with 10% SPES showed only 3% H₂O uptake and was highly non-conductive (> 1100 kΩ). Films using 70% SPES gave measurable results.

A resistance experiment was done with an SPPQ sample (% sulfonation unknown) which had an H₂O uptake of 23.2%. At 80° C the resistance was in the range of 30-35 kΩ. A second piece of SPPQ (no H₂O uptake information-but it had a longer soaking period) gave a resistance of 1.3 kΩ at 80° C. At elevated temperatures the membrane gave a minimum resistance of 525 Ω at 119° C. The membrane subjected to the higher temperatures (up to 165° C) had completely dissolved (or decomposed) when the reactor was opened up.

A resistance experiment was performed using SPPQ sulfonated at 100% degree of sulfonation (one SO_3H unit/monomer). The H_2O absorbence at this level of sulfonation is 13.8%. This is a rather resistive system, since at 80°C the resistance is $200\text{ k}\Omega$.

A resistance experiment on Nafion 117 was run using the Parr reactor setup; it gave a value of $850\ \Omega$ at 81°C and a minimum of $400\ \Omega$ at 167°C . The stability of the Nafion in high temperature steam was better than the other sulfonic acid polymers. The temperature reached a maximum of 270°C , and after cooling the reactor down, the membrane remained intact, although discoloration of the membrane had occurred.

A summary of the performance data for the ionomer membranes is shown in Table 2. As was discussed in the synthetic section above, degrees of sulfonation well in excess of the commercial product were achieved. In terms of thermal stability, only the SPPQ compared favorably with Nafion. Activation energies, as determined from the slope of their respective $\ln(\sigma_{\text{H}^+})$ vs T^{-1} plots, were decidedly higher than that for Nafion, indicating some difficulty in the proton transfer process.

Table 2. Thermoconductimetric Data for Candidate Polymers

Sample	% SO_3H	n (meq/g)	T_{max}	E_{act} (kcal/mol)	σ_{H^+} ($\Omega\text{-cm}$) ⁻¹
					100° C
Nafion	13	0.83	150	0.9	0.18
SPEEK	32,xl	1.02	98	8.1	0.025
SPES	70	2.42	121	6.2	0.022
SPPQ	107	1.87	153	3.9	0.005

Proton conductivities were compared at 100° C. Since the SPEEK membranes were typically unstable at that temperature, a cross-linking reaction using 1,1'-carbonyl diimidazole followed by reaction with bis-(4-aminophenyl) sulfone (18) was performed on a 32% sulfonated sample. Nevertheless, conductivities were below that of Nafion.

The combination of high degree of sulfonation and low conductivity with respect to Nafion points to a difference in conductivity mechanism. Water uptake measurements, while not given for all the samples, were generally quite substantial, commensurate with the high degree of sulfonation. Nafion is a perfluorinated hydrocarbon sulfonic acid ether; the acid is attached to the end of a 6-atom (on average) side chain. The aryl sulfonic acid polymers prepared in this work have sulfonic acid groups attached directly to the phenylene backbone, thus removing that degree of freedom. The base polymers typically have large glass transition temperatures, a good attribute as far as mechanical stability is concerned, but possibly detrimental with respect to proton conduction. Tertiary structure, i.e., how the polymer strands bind to one another, is another attribute that may be important to ionic conduction.

4.4 SPEEK Electrolysis Testing

The main variation in all the SPEEK samples prepared was the degree of sulfonation. While directly measuring water uptake and conductivity was informative, it was nevertheless interesting to see the aggregate effect of how well they performed in an electrolysis cell. Figure 3 represents the results of the conductivity testing, while the results of the electrolysis testing are presented in figures 4 through 8. The testing consisted of electrolyzing water at increasing cell temperatures in 10° C increments. Each membrane's testing continued until its performance declined.

The effect of temperature is quite evident: a general 3-4 fold increase in current density was obtained by increasing temperature from 60 to 100° C. Higher degrees of sulfonation enabled

modest improvements in current density: by doubling the density of ionic groups from 20 to 46.5% sulfonation the current density at 2.00 V increased from 50 to 70 mA/cm².

In Figure 7, a comparison between SPEEK at 65% sulfonation and the commercially available Nafion 117 is shown. The operating temperature for this comparison was only 60°C, because at this level of sulfonation the water uptake was substantial, so that at higher temperature the SPEEK was prone to creep. At low voltages, where activation overvoltages are at play, the two membranes perform essentially the same; however, at higher voltages and current densities, the SPEEK membrane performance actually exceeded the commercial material. While mechanically very fragile, the membrane was quite conductive, and so was less limiting at the higher applied voltages.

One other aspect of cell performance is the coulombic or current efficiency. While high current density at low voltage is a worthwhile objective, it constitutes wasted effort if the amount of charge going to generate H₂ remains the same. Coulombic efficiency was determined by dividing the integrated steady state current into the volume of H₂ produced. Figure 8 reveals the electrolysis current density of 20% SPEEK with the corresponding coulombic efficiency versus the cell voltage. While some losses are seen at the highest voltages, coulombic efficiency remains above 90%.

Figure 4. Water electrolysis curve for SPEEK membrane as a function of temperature;
20% degree of sulfonation.

Figure 5. Water electrolysis curve for SPEEK membrane as a function of temperature;
30% degree of sulfonation.

Figure 6. Water electrolysis curve for SPEEK membrane as a function of temperature; 46.5% degree of sulfonation.

Figure 7. Performance comparison between Nafion 117 and 65% SPEEK.

Figure 8. Correlation between current density and coulombic efficiency for 20% SPEEK.

5.0 CONCLUSION

Representative compounds from five engineering polymer families have been evaluated for utilization as a proton exchange membrane in a high temperature electrolyzer. Each was sulfonated with varying degrees of success. The SPEEK polymer was the most thoroughly studied, because it could easily be sulfonated and could be produced at a wide range of sulfonic acid content. Preliminary testing in an electrolysis cell showed performance comparable to existing commercial ionomer membranes.

6.0 ACKNOWLEDGMENTS

The authors would like to thank Dr. Gordon Nelson of the Florida Institute of Technology Chemistry Department for his guidance on this work. Financial support from the U.S. Department of Energy, Office of Advanced Utility Concepts is gratefully acknowledged.

7.0 REFERENCES

1. Z. Florjanczyk, W. Krawiec, W. Wieczorek and M. Siekierski, *J. Poly. Sci. Part B: Poly. Phys.*, **33**, 629 (1995).
2. J.C. Lassegues, B. Desbat, O. Trinquet, F. Cruège and C. Poinsignon, *Solid State Ionics*, **35**, 17 (1989).
3. J.Y. Sanchez, A. Denoyelle and C. Poinsignon, *Poly. Adv. Technol.*, **4**, 99 (1993).
4. P.W.T. Lu, and S. Srinivasan, *J. Appl. Electrochem.*, **9**, 269 (1979).
5. International Energy Agency Program of Cooperative Research and Development. 1987. *Task IV. Electrolytic Hydrogen Production*, 1986 Annual Progress Report, U.S. Department of Energy.
6. L. Glasser, *Chem. Rev.*, **75**, 21 (1975).
7. K. Kreuer, *J. Molecular Structure*, **177**, 265 (1988).
8. M.S. Reisch, *Chem. and Eng. News*, **67**, 21 (1989).
9. J. Bradshaw, S.B. Tian and G. Xu, *Solid State Ionics*, **73**, 147 (1994).
10. R. Nolte, K Ledjeff, M. Bauer and R. Mulhaupt, *J. Memb. Sci.*, **33**, 211 (1993).
11. X. Jin, M.T. Bishop, T.S. Ellis and F.E. Karasz, *Brit. Poly J.*, **17**, 4 (1985).
12. M.T. Bishop, F.E. Karasz, P.S. Russo and K.H. Langley, *Macromolecules*, **18**, 86 (1985).
13. J. Devaux, D. Delimoy, D. Daoust, R. Legras, J.P. Mercier, C. Strazielle and E. Nield, *Polymer*, **26**, 1994 (1985).
14. C. Bailly, D. J. Williams, F.E. Karasz and W.J. MacKnight, *Polymer*, **28**, 1009 (1987).
15. L. Leung, C. Bailly, J.F. O'Gara, D.J. Williams, F.E. Karasz and W.J. MacKnight, *Polym. Comm.*, **28**, 20 (1987).

16. C.A. Linkous, "Development of solid electrolytes for water electrolysis at intermediate temperatures," in vol I of *Hydrogen Energy Progress IX. Proceedings of the 9th World Hydrogen Energy Conference*, 419-427. T.N. Veziroglu, et al, eds., Paris, France, June 22-25, 1992, M.C.I., Paris.
17. T.A. Zawodzinski, Jr., M. Neeman, L.O. Sillerud and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040 (1991).
18. B.C. Johnson, I. Yidor, C. Trans, M. Iqbal, J.P. Wightman, D.R. Lloyd, and J.E. McGrath, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 721 (1984).
19. E.J. Powers and G.A. Serad, "History and Development of Polybenzimidazoles." In *High Performance Polymers: Their Origin and Development*, 355-373. R.B. Seymour and G.S. Kirshenbaum, eds., 1986, New York.