Contract Report

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Submitted to:
U.S. Department of Energy
Mr. Douglas Hooker
1617 Cole Boulevard
Golden, CO 80401

Submitted by:
Clovis Linkous
Darlene Slattery
Robert Kopitzke
Nazim Muradov

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Florida Solar Energy Center
1679 Clearlake Road
Cocoa, FL 32922-5703

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PREFACE

This is the final report on DOE contract #DEFC3695GO10062, entitled "Sustainable Hydrogen Production." Three tasks were performed under this contract:

- Task 1 .Solar Photocatalytic H₂ Production from Water Using a Dual Bed Photosystem - This task involved using semiconductors in powdered form to perform water-splitting when subjected to solar irradiation. Two different photocatalysts, immobilized in their own modules, or beds, and using a redox mediator to flow between them, enabled separate evolution of H₂ and O₂. The initial system consisted of TiO₂ for O₂ evolution and InP for H₂ evolution. The possibility of using organic pigments as photocatalysts was also investigated.

Two subtasks involving photocatalytic research were also performed. The first was participation in the Hydrogen Annex 10 agreement of the International Energy Agency on photoproduction of H₂. Because this work was closely related to the dual bed work described above, the results were integrated into the dual bed section. The other subtask involved providing assistance to Solar Reactor Technologies on their effort to develop a water decomposition cycle based on a high temperature, photochemical reaction between water and bromine gas, coupled with the electrolysis of HBr.

- Task 2. Development of Solid Electrolytes for Water Electrolysis at Elevated Temperatures - A number of wholly aromatic engineering polymers were acquired or synthesized, and then sulfonated, to produce proton-conducting materials. These ionomers were characterized as to water uptake, conductivity, and particularly resistance to hydrolysis under conditions of saturated steam pressure at high temperature (150-250° C). Degradation analyses were also performed.
- Task 3. Production of Hydrogen by Thermocatalytic Cracking of Natural Gas - The main goal of this project was to develop a technologically simple process for hydrogen production from natural gas and other hydrocarbon fuels via single-step decomposition of hydrocarbons. This approach eliminates or significantly reduces CO₂ emission. Our approach was based on the use of special catalysts that reduce the maximum temperature of the process from 1400-1500°C (thermal non-catalytic decomposition of methane) to 500-900°C. Transition metal-based catalysts and various forms of carbon were among the candidate catalysts for the process. This task was funded for only the first of three fiscal years covered by the contract.

Clovis A. Linkous
Darlene K. Slattery
Robert W. Kopitzke
Nazim Muradov

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Task 1 Report

Development of New Materials and Approaches to Photocatalytic Systems

Final Report

**FSEC-CR-1093-99
DOE Contract #DE-FC36-95GO100062**

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U.S. Department of Energy
Mr. Douglas Hooker
1617 Cole Boulevard
Golden, CO 80401

Submitted by:
Clovis A. Linkous
Darlene Slattery

Florida Solar Energy
1617 Clearlake Road
Cocoa, FL 32922-5703

DEVELOPMENT OF NEW MATERIALS AND APPROACHES TO PHOTOCATALYTIC SYSTEMS

Prepared by:

Clovis A. Linkous
Darlene K. Slattery
Florida Solar Energy Center
1679 Clearlake Road
Cocoa, FL 32922-5703

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1.0 SUMMARY

Our objective in this work was to develop an efficient, affordable, direct photoconversion scheme for generating H_2 from water using sunlight. We sought to find an alternative to the traditional photoelectrochemical cell configuration, with the idea of maintaining low module construction costs. Our approach was to use semiconductor powders in a dual bed configuration, breaking down the energy requirement for water splitting into a 2-photon process, and enabling separate production of H_2 and O_2 . The photocatalytic system would employ two modules, each consisting of a shallow, flat, sealed container, in which micron-sized photocatalytic particles are immobilized. An aqueous solution containing a redox mediator is pumped between the two chambers. Different photoparticles and catalysts are chosen for their respective modules so as to effect oxidative water-splitting in one vessel to evolve oxygen gas, and reductive water-splitting in the other to evolve hydrogen.

We initially investigated TiO_2 as the O_2 -evolution photocatalyst, and InP as the H_2 -evolution photocatalyst. $\text{Br}^-/\text{BrO}_3^-$ and I^-/IO_3^- were identified as compatible redox mediators. Several potential improvements were investigated: the use of carbonate ion in facilitating the O_2 evolution process; the use of NiO_x as a substitute for Ir on TiO_2 ; the use of WO_3 as a substitute for TiO_2 ; and a study of various classes of organic pigments for photocatalytic application. Using the PM3 semiempirical molecular orbital program, we determined that several classes of organic pigments should be energetically capable of oxidative water splitting. These calculations were verified through voltammetry and UV-visible spectroscopy. Some prototype designs for future dual photocatalyst systems that should enable higher efficiencies were also generated. Finally, assistance was provided to Solar Reactor Technologies on their effort to develop a water decomposition cycle based on a high temperature, photochemical reaction between water and bromine gas, coupled with the electrolysis of HBr .

2.0 INTRODUCTION

In 1972 Fujishima and Honda pointed out that irradiation of wide band gap semiconductors such as TiO_2 could supply much of the energy required to electrolytically decompose water, evolving O_2 and generating protons that could be reduced at a dark electrode to produce hydrogen.¹ This introduced photoelectrochemistry as a new approach to solar energy conversion. A flurry of activity began to develop semiconductor electrodes for use in photoelectrochemical cells.²⁻⁵

Despite continuing effort for over 25 years on photoelectrochemical production of H_2 from water, a number of major obstacles remain to be surmounted before the technology can make a significant impact in the overall energy economy:

- 1) the original wide band gap semiconductors, such as TiO_2 and SnO_2 , required light energy well into the ultraviolet, making poor utilization of the solar spectrum;
- 2) only highly crystalline, highly pure semiconductor specimens gave large photocurrents and quantum efficiencies, because of the limited lifetimes of the photogenerated charge carriers in the solid state;
- 3) semiconductors whose band gaps were better matched to the solar spectrum, such as Si , Ge , etc, were subject to photoanodic corrosion, where the photogenerated hole could decay by dissolving a surface metal atom into the electrolyte; and
- 4) the cost of manufacturing the module - much of the inherent cost is related to fabrication of the semiconductor photoelectrode, which involved much the same process technology as is utilized for photovoltaic cell manufacture. With the incident radiant power of sunlight only in the 1.0 kW/m^2 range, and practical efficiencies lying in the 10-30% range, the module cost of the photoconversion system, regardless of the technology, must lie in the $\$100/\text{m}^2$ range or less.

It was also realized that the classic electrochemical configuration of two planar electrodes standing parallel to one another did not lend itself well to efficient use of the incoming solar photons. One either had to use an optically transparent counter electrode so that light could pass through it and the

electrolyte to reach the semiconductor electrode, or deposit a thin film of semiconductor on glass and irradiate from the backside.

Thus our objective in this work is to develop an efficient, affordable, direct photoconversion scheme for generating H_2 from water using sunlight. We have sought to find an alternative to photoelectrochemical cell configuration, where wafers of single crystal or polycrystalline semiconductors are cut to fashion electrodes. Since the essential feature of photoelectrochemical energy conversion was development of a barrier voltage at the semiconductor/electrolyte interface, it was realized that this could just as well be accomplished with the semiconductor in powder form. Conceptually this was a much simpler way to perform solar photoelectrolysis: just pour the semiconductor powder into water, expose the system to light, and H_2 and O_2 would bubble out.

New problems arose, however. The main one was separation of products. In an electrochemical cell, chemistry is performed by the occurrence of two half-cell reactions, each reaction proceeding at its own respective electrode. In the case of electrolyte-soluble products, an ion-conductive separator can also be included to ensure that the two chemical product streams do not mix with one another and back react. For the semiconductor particle system, the microscopic nature of the half-cell reaction surfaces causes H_2 and O_2 to be evolved essentially together. The gas stream released from the photoparticle slurry would be 66% H_2 by volume, the balance mostly O_2 , well within the combustible range.

Our work to date has been geared toward understanding how photoparticle systems operate, and how a large scale reactor system might be configured. We have found that fixed bed arrays of particulates would make the most economic use of the solar energy-converting material. Furthermore, the loss in conversion efficiency compared to loose colloidal systems is compensated by the technical advantages of having a flow system that moves the dissolved products of reaction out the photoreactor, lessening the extent of back reaction.

2.1 Basic Concept

Our approach then has been to use semiconductor powders in a dual bed configuration, breaking down the energy requirement for water splitting into a 2-photon process, and enabling separate production of H_2 and O_2 .

A schematic showing how such a system would work is shown in the first row of Figure 1. In this approach, the photocatalytic system would employ two modules, each consisting of a shallow, flat, sealed container, in which micron-sized photocatalytic particles are immobilized. An aqueous solution containing a redox mediator is pumped between the two chambers. Different photoparticles and catalysts are chosen for their respective modules so as to effect oxidative water-splitting in one vessel to evolve oxygen gas, and reductive water-splitting in the other to evolve hydrogen.

Figure 1. Schematic of a dual bed photocatalytic water-splitting reactor

The general chemical mechanism for a dual bed concept photosystem would be as follows:

M is a "redox mediator", or charge-carrying agent, that shuttles electron equivalents from O_2 -evolving photomodule to the H_2 module.

2.2 Energy Level Relationships

On the microscopic level, there are many ways to configure the arrangement of catalyst and photoparticle. Certainly they must be in close proximity to each other, so that the photogenerated charge can flow from semiconductor to catalyst phase without recombination or other loss mechanisms. One normally thinks of a catalyst as precious material, dispersed as fine particles on an inert support. In our case, the catalyst would be deposited on a semiconductor powder, which is certainly not inert. The optimum size of a catalyst deposit, both in terms of its absolute size and size relative to the semiconductor particle that supports it, needs to be determined. Also, the proximity of one catalyst island to another is important, because too much catalyst could block the incoming light that is to be absorbed by the semiconductor.

If the catalyst is not too expensive, one could just as well consider depositing the semiconductor on the catalyst, or better still, deposit both semiconductor and catalyst on an inexpensive, but

conductive, substrate. That way, islands of semiconductor and catalyst could be placed side by side. This would cause some segregation of the respective oxidation and reduction reactions in each module, and would enable maximum light absorption by the photoparticle.

As was mentioned above, the photocatalysts must be selective for either H_2 or O_2 evolution. This is determined by the position of the photocatalyst band edges with respect to the redox levels for O_2/H_2O and H_2O/H_2 . In order for the H_2 -evolving, or water-reducing photocatalyst (PC-R) to function, the PC-R conduction band edge must be higher (or more negative on the redox scale) than the H_2 formal potential. Correspondingly, for the O_2 -evolving, or water-oxidizing photocatalyst (PC-O) to function, the PC-O valence band edge must be lower (or more positive on the redox scale) than the O_2 formal potential.

Furthermore, the band characteristics of PC-R and PC-O will limit what redox agents could possibly serve as mediator in the dual particle bed system. As shown in Figure 2, the positive limit of redox potential is determined by the valence band edge of the p-type, H_2 -evolving photocatalyst, while the negative limit is determined by the conduction band edge of the n-type, O_2 -evolving photocatalyst. As band edges are difficult to determine, researchers frequently approximate them by measuring the flat band potential, V_{fb} .

Figure 2. Energy Band Diagram Showing the Relationship between redox mediator and photocatalyst band edges.

To give an example, let PC-O be n-TiO₂. At pH 9, V_{fb} is calculated to be -0.375 V vs NHE, based on -0.7 V at pH 13.⁶ The previously mentioned approximation for n-type semiconductors is that $E_{cb} = V_{fb}$, and so -0.375 is the negative limit. Also let PC-R be p-InP. At the same pH, $V_{fb} = +0.7$ V, which approximates the InP valence band position. That enables a $0.7 - (-0.375) = 1.07$ volt range to work with.

In summary, the advantages of the dual bed concept are:

- separate evolution of H₂ and O₂
- potentially higher utilization of the solar spectrum, since the two light-absorbing modules will be able to use more abundant, lower energy photons; and
- cheap reagents, photocatalysts, and construction materials, plus minimal processing result in a low cost module.

In fact, a recent study by Block compared the dual bed photosystem approach to other types of renewable processes, such as electrolytic multi-layer thin film photoelectrochemistry, electrolytic concentrating high efficiency photovoltaics, and photovoltaic driven high temperature electrolysis.⁷ Using PV-electrolysis as the base case, he found that the dual bed approach could eventually net a 48-58% reduction in the cost of H₂.

Possible disadvantages of a dual bed system are:

- more complex than a single bed system
- for prototypes with circulating electrolyte, additional energy for pumping the reagents is consumed; and
- the two photoredox modules are competing for the same photons (this aspect motivates development of a photovoltaic tandem cell equivalent of the photoparticle bed-see subsequent section on tandemization).

3.0 Experimental

Our experimental approach has been to look at each of the photosystems separately, first identifying materials and condition that were satisfactory for either H₂ or O₂ evolution, and then comparing the results to identify any overlap. The first task was to identify the semiconductor materials that could be used for either H₂ or O₂ evolution, and devise ways to immobilize them on a surface. We decided to use TiO₂ as PC-O and InP as PC-R. Much of the work done over the years in photoelectrochemistry suggested that these were most successful as photoanodes and photocathodes, respectively, so they represented functional materials that required the least amount of developmental work. Even though a narrower band gap material than TiO₂ and a more chemically stable material than InP would be desirable, we nevertheless wanted to get to proof-of-concept stage in the near term, so as to validate this approach to water splitting.

3.1 General

Reagents used were purchased from Fisher Scientific unless otherwise noted and all were used as received, with no further purification. Water splitting experiments were run batch-wise in a sealed 50 mL glass reaction vessel. The vessel was purged thoroughly to remove air and placed in front of a xenon lamp, with stirring, for six hours. A 1.0 mL sample of the gas over the sample was removed and injected into a gas chromatograph (GC) equipped with a thermal conductivity detector. The carrier gas for samples expected to contain H₂ was argon and for those containing O₂, the carrier was helium.

3.2 Gas Evolution Experiments

The experimental set-up was as follows. A 50 ml solution of the redox mediator was placed in a 1" diameter test tube. It was desirable for the mediator to be as concentrated as possible, so as to increase the probability of hole or electron injection. For the inorganic salts, this was typically in the 0.1-1.0 M range. The organics were usually kept in the millimolar range, however, due to either solubility limitations or the light attenuation effects for those which were intensely colored.

To each solution 200 mg of either TiO_2 or InP powder was added. Light from a 1000 Watt Xe arc lamp was passed through a water filter with 4 inch pathlength to remove most of the infrared and then focused with a quartz convex lens onto the test tube. The test vessel contained a stir bar so that the semiconductor powder suspension could be maintained throughout the experiment. The vessel had a side armature near the top, opening into the head space over the redox solution. This was connected to a gas measurement apparatus consisting of a hose leading into an inverted graduated cylinder. A septum cap on the test tube also enabled syringe sampling of any gas that percolated up into the head space for gas chromatographic analysis. A schematic of the experimental apparatus is shown in Figure 3.

Figure 3. Experimental Apparatus for Photolytic Gas Evolution Measurements

To measure O_2 -evolution, TiO_2 , sometimes catalyst modified with either Pt or Ir, would be placed into a solution containing the "Ox" or oxidized form of the redox couple of interest. For H_2 -evolution, InP , which was invariably platinized once control experiments showed that plain InP was poorly catalytic for the H_2 reaction, would be added to a solution contained the "Red" or reduced form of the redox couple.

3.3 Oxygen Evolution

For O_2 evolving experiments, the preferred solution was 1.0 M NaOH containing 0.2 M KIO_3 . To this solution was added 0.40 g of TiO_2 (Degussa or Fisher) that had been loaded with 1.0 wt% Pt or Ir. Other experiments were run using WO_3 as the semiconductor but for these 1.0 M H_2SO_4 was substituted for the NaOH. The WO_3 was either purchased from Fisher or prepared as colloids.

3.4 Preparation of WO₃ Colloids

The colloidal WO₃ was prepared using a procedure suggested by Augustynski.⁸ Dowex 50WX2 resin was prepared by stirring 25 g in distilled water overnight and then pouring the slurry into a column and draining off the excess water. The resin was then conditioned by passing 120 mL of 1 M H₂SO₄ through the column. The resin was next washed with distilled water until a neutral pH was obtained.

After preparing the column, 20 mL of 0.5 M Na₂WO₄ was slowly passed through the column, using water as the eluant. The product was collected once the pH of the liquid became acidic and was collected until it again became neutral.

Aliquots of the collected colloids were either used as is or were isolated from the solution by centrifuging if they were to be catalyst loaded.

3.5 Hydrogen Evolution

The H₂ evolving experiments also were run in 1.0 M NaOH but the redox mediator was KI and the semiconductor was InP (Strem or Cerac) loaded with Pt.

In experiments to study H₂ evolution in the presence of both I⁻ and IO₃⁻, the initial concentrations were 0.8 M and 0.2 M, respectively. The sample was illuminated for six hours and the gases analyzed by GC. The InP was isolated from the solution, washed with distilled water and placed back into the standard hydrogen evolving solution that was initially free of IO₃⁻ and rerun.

3.6 Catalyst Loading

Catalyst loading, in all cases, was accomplished using a borohydride reduction. The TiO₂ or InP was placed in a 1.0 M solution of NaOH and either IrCl₃ (Aesar) or H₂PtCl₆ (Strem) was added to load at 1.0 wt%. An excess of sodium borohydride was added to an addition funnel containing 1.0 M NaOH and this solution was slowly added to the semiconductor suspension, with stirring, under an inert atmosphere. After the reduction was complete, the catalyst-loaded semiconductor was isolated via vacuum filtration. For the catalyst loading of WO₃, it was necessary to substitute distilled water for the NaOH solutions.

4.0 RESULTS AND DISCUSSION

As a first step, based on the principles described above, we needed to identify photocatalysts for the two photoreaction modules that would perform the desired chemistry. Our initial candidate photocatalysts were TiO₂ in the O₂-evolving bed and InP in the H₂-evolving bed. A long series of photolysis experiments was commenced to determine whether H₂ or O₂ would indeed be evolved. In almost every case, gas of some sort was evolved. While the gas volume measurement apparatus gave reliable results for the most active systems, there were problems with the less active ones, where the gas evolution rate was only a few milliliters per hour or less. Irradiation with the Xe lamp caused heating of the test suspension from ambient to 60-80° C; this in turn

caused expansion of the gas over it. Typically we would measure 8 ml of volume expansion in our apparatus whether there was effervescence in the test suspension or not. This was in good agreement with ideal gas PV expansion calculations based on the temperature gain and initial dead volume determinations. One could still expect to circumvent this problem with prolonged irradiation times, but it was difficult to measure a steady gas evolution rate for any appreciable length of time.

Ultimately, gas chromatography was used to determine whether the gas evolved was H_2 , O_2 , or something else. Using injection standards, retention times for H_2 and O_2 were determined. In numerous cases with InP, the lone peak in the gas chromatogram was H_2 . In comparatively fewer cases as will be seen below, with TiO_2 , chromatograms were also obtained where the only peak was that of O_2 . While some adventitious O_2 would sometimes be observed in the InP chromatograms, there never was a stoichiometric 2:1 H_2 : O_2 relationship that would imply net water decomposition. In other cases, especially with the organic redox agents, photolysis would produce effervescence, but neither H_2 nor O_2 would be detected.

4.1 Identification of Compatible Redox Mediators

After selection of prototype photocatalysts, we concentrated our effort on identification of a redox equivalent transfer agent or mediator that was needed to provide the anodic half-cell reaction in the H_2 -evolving reactor and the cathodic half-cell back reaction in the O_2 -evolving reactor. The following redox couples were examined: Sn^{4+}/Sn^{2+} ; Anthraquinone-2,6-disulfonate; IO_3^-/I^- ; $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$; 1,4-Napthoquinone-2-sulfonate; Toluidine Blue; I_2/I^- ; Thionine/Leucothionine; BrO_3^-/Br^- ; Fe^{3+}/Fe^{2+} (SO_4^{2-}); 1,4-Benzoquinone/Hydroquinone; NO_3^-/NO_2^- ; VO_2^+/VO^{2+} ; Br_2/Br^- ; Cl_2/Cl^- ; and H_5IO_6 . Their standard redox potentials are listed in Table II below.

The series of redox reagents were irradiated with a Xe lamp in aqueous slurries of photocatalytic powders to probe the limits of energy storage that each semiconductor is capable of. For example, if the voltage generation requirement is shared equally between the two photoreactors, the redox mediator will have a standard redox potential of 0.6 V (acidic standard state). The further the mediator's redox potential departs from that value, the more uneven the energy storage load becomes. Realistically, about 1 volt of electrochemical potential should be generated in each module, so as to overcome unavoidable overpotential requirements.

In Table I below, evolution results are given for two-hour irradiation of TiO_2 and Pt-InP suspensions in the presence of various redox reagents. It was expected that those with the highest redox potentials would perform best for O_2 -evolution, while those with low redox potential would perform best for H_2 -evolution.

As it turned out, only a few clear cut cases for O_2 -evolution were found. One of these was H_5IO_6 , periodic acid, the reagent with the highest redox potential. O_2 evolution with H_5IO_6 does not clearly represent energy storage at all, since its redox potential is positive of water oxidation--the TiO_2 is acting as a photocatalyst, but not as an energy transducer. The only other examples of O_2 -evolution came from IO_3^- , VO_2^+ , and BrO_3^- .

Many representatives from the series of redox agents were tested as electron donors in the photocatalytic evolution of H_2 using InP. As can be seen in the Table I results, many of the redox reagents gave a positive result. When HCl solution itself gave a positive result, our suspicions were raised, since the valence band edge of InP was thought to be negative of the redox potential necessary for Cl_2 -evolution. After some prolonged photolysis testing, it was confirmed gravimetrically that the InP itself was being consumed and supplying electron equivalents to the H_2 .

Table I. O_2 and H_2 Evolution Results for Various Redox Mediators

<u>Mediator</u>	<u>E° (V vs NHE)</u>	<u>O_2 evolution from TiO_2</u>	<u>H_2 evolution from InP</u>
Sn^{4+}/Sn^{2+}	0.139	-	✓
Anthraquinone-2,6-disulfonate	0.228	-	-
$K_3 [Fe(CN)_6]/K_4 [Fe(CN)_6]$	0.46 (NaOH)		✓
1,4-Napthoquinone-2-sulfonate	0.47	-	-
Toluidine Blue	0.534	-	-
$KI/I_2, IO_3^-$	0.535	✓	✓
Thionine/leucothionine	0.563	-	-
$FeSO_4$	0.68	-	✓
1,4-benzoquinone	0.699	-	-
NO_3^-	0.84	-	-
$V_2O_5 (VO_2^+)/VOSO_4$	1	✓	-
$KBr/Br_2, BrO_3^-$	1.087	✓	✓
HCl	1.358	-	✓
H_5IO_6	1.7	✓	-

✓ = positive result; the desired gas was detected.

- = negative result; any gas evolution did not correspond to the substance of interest.

- = reaction not attempted.

Comparing the H_2 - and O_2 -evolution results, it is shown that respective Ox and Red species from the IO_3^-/I^- and $\text{BrO}_3^-/\text{Br}^-$ redox couples enabled both types of gas evolution. Therefore, one could conceive of constructing a dual bed system based on TiO_2 and Pt-InP with either of these couples as redox mediators.

4.2 Corrosion of InP

As it turned out, corrosion of InP was a problem. H_2 evolution from Pt-InP suspended particulates typically slowed considerably after a relatively short photolysis time. As shown in Figure 4 for Pt-InP in alkaline iodide solution, the total gas volume reaches a steady state in about an hour of illumination. This was interpreted as analogous to a "photostationary state", where a photochemical reaction generates products and depletes reactants until the reverse reaction rate equals the forward one.

Figure 4. Gas Volume versus Time for H_2 Evolution on Pt-InP

Inspection showed that the originally black powder had become gray, ostensibly due to oxide formation. As shown in Figure 5, the phosphorus peak in the material's X-ray photoelectron spectrum disappeared after being subjected to alkaline photolysis. It was first thought that photocorrosion was occurring according to

However, it was eventually discovered that InP was not compatible with the alkaline IO_3^- system found for TiO_2 . The InP was attacked, even in the dark, by IO_3^- ion:

Title: XPS PHOSPHORUS PEAK: In in InP (TOP), In in InP/IO3 (Lower spectra)
 Run:082901 Reg: 2 (P2p) Scan: 1 Base Cts: 4692 Max Cps: 8146
 Com:082902 Reg: 2 (P2p) Scan: 1 Base Cts: 3414 Scale: 1

Figure 5. X-ray Photoelectron spectrum of InP before and after photolysis in alkaline KI.

In the presence of iodide ion, the reduced form of the redox couple, photolytic H_2 evolution from Pt-InP initially proceeded quite vigorously, but as the photolysis continued, iodate ion began to build-up and the corrosion reaction shown above took hold. This underscores the need for materials compatibility, where both photocatalysts and the redox mediator are stable and functional under the same conditions.

4.3 Back Reactions

One aspect of concern was the propensity for back reaction. With O_2 and I^- being simultaneously produced in the photomodule, one can envision their recombination in a solution homogeneous

reaction. One can also speculate that TiO_2 itself may serve as a catalyst for back reaction. Consequently, we performed several experiments with the objective of measuring the extent of back reaction due the various mechanisms.

All solutions were 1.0 M KI in 1.0 M NaOH. Each solution was exposed to a stream of O_2 , with stirring. This fixed the O_2 concentration at its saturation level, as would be expected at the exit port of the O_2 -evolving photomodule. Two hour time trials were run under four sets of conditions, corresponding to Xe lamp irradiation or darkness, and with or without TiO_2 photocatalyst. Temperature was controlled in the two dark trials so as to compensate for any thermal effects that light absorption may generate. Once each trial was completed, a measured amount of solution was acidified with HCl and titrated with 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ and starch indicator. The endpoint corresponds to the amount of IO_3^- that was formed during each run. The solutions containing TiO_2 were first centrifuged to remove the suspended photocatalyst. Results are shown in the Table II below.

Table II. IO_3^- Concentration after 2-hr

Solution	Light	Dark
I^- , KOH, O_2 (45° C)	0.07 mM	0.13 mM
I^- , KOH, O_2 , TiO_2 (75° C)	0.65 mM	0.125 mM

First off, it was encouraging to note that in each case the extent of reaction was limited; only a fraction of a percent of the available iodide ion was consumed. This would indicate slow kinetics for the autoxidation of I^- to IO_3^- . Afterall, conversion of iodide to iodate is a 6-electron process:

Since both reactions in the dark proceeded essentially to the same extent, TiO_2 must not function as a heterogeneous catalyst in the dark. In the light, however, TiO_2 functions an effective photocatalyst, increasing the yield by nearly an order of magnitude over the irradiated solution. This is consistent with microscopic reversibility principles, in that the most effective mechanism for the back reaction is along the reverse path of the photocatalytic forward reaction. It is nevertheless an important result that the direction of reaction will be controlled at the surface of the photocatalyst instead of in the bulk of solution.

4.4 Use of Co-catalysts

We also compared the relative ability of platinum versus iridium in catalyzing the $\text{H}_2\text{O}/\text{IO}_3^-$ reaction. In control experiments where iodate ion was intentionally left out, xenon lamp-irradiated Pt- TiO_2 in alkaline solution produced no measurable O_2 , as expected. However, when Ir- TiO_2 was tested under the same conditions, both H_2 and O_2 were detected! This is shown in

Figure 6 below. Since we were near the detection limit of our gas chromatograph (at least for O_2 under an Ar carrier gas), we purchased new gas-tight syringes for collecting samples and making port injections. This eliminated some of the spurious air peaks seen earlier. Peak heights were compared to calibration curves for the respective gases and it was established that H_2 and O_2 had been evolved in a 2:1 ratio, corresponding to water-splitting stoichiometry. Blending of Pt- TiO_2 and Ir- TiO_2 powders gave even larger signals, suggesting a synergistic effect.

Figure 6. Detection of H_2 and O_2 from an Ir- TiO_2 //1.0 M KOH particle suspension under Ar.

We subsequently realized that comparison of the O_2 -evolution rates with and without redox mediator may provide a useful validation of the dual bed approach to photolytic water splitting over that of a single bed. Safety considerations aside, an increased rate of O_2 -evolution from a given oxidative photosystem by inclusion of a reversible mediator such as KIO_3 can be directly related to an improvement in solar energy conversion efficiency. Because going to a dual bed system instead of a single bed automatically cuts the quantum efficiency in half, one must derive at least a two-fold improvement in gas evolution rate with the redox mediator to break even.

In Figure 7 below, chromatographic peaks for gas evolution with and without KIO_3 are shown for the $\text{Pt-TiO}_2// \text{O}_2/\text{OH}^-$, IO_3^-/I^- system. It is seen that the extent of O_2 evolution is more than an order of magnitude greater in the presence of the mediator.

Figure 7. Comparison of O_2 evolution from Pt-TiO_2 with (r.h.s.) and without (l.h.s.) KIO_3 redox mediator.

4.5 Effect of CO_3^{2-} on O_2 Evolution

This work resulted from an IEA (International Energy Agency) interaction that began only last year. Our collaborators were Dr.'s H. Arakawa and K. Sayama of the National Institute of Materials and Chemical Research in Tsukuba, Japan. They had observed the stoichiometric, co-evolution of H_2 and O_2 from single pot, photocatalytic powder dispersions of TiO_2 and other photocatalysts in the presence of carbonate ion, CO_3^{2-} .⁹ The presence of carbonate ion had been found to be vital to the O_2 evolution process. Apparently the intermediate surface-adsorbed hydroxyl radicals generated from initial water oxidation are quite reactive, and will oxidize any available redox agent present, even background organic contaminants. The carbonate ion acts as a scavenger for hydroxyl radical, forming a peroxydicarbonate species that ultimately breaks down, releasing O_2 .¹⁰ Thus carbonate acts as a catalyst for O_2 evolution.

We decided to see whether the same effect could be observed for the O_2 -evolving half of our dual bed system. Accordingly, 250 mg dispersions of various photocatalysts were suspended in 50 ml solution and photolyzed. The relevant data are shown in Table III. At a 0.5 M CO_3^{2-} concentration, very little improvement was seen; in fact, for the most active Ir-TiO_2 system, a negative effect was apparent. Our interpretation is that the CO_3^{2-} ion adsorbs not only on the TiO_2 surface, but on the co-catalyst as well. For the dual bed approach to work, the redox mediator (IO_3^-) needs open access to the co-catalyst surface. By charge conservation principles,

the rate of IO_3^- reduction must match that of O_2 evolution. If the Ir surface is blocked by CO_3^{2-} ion, then any gains made on the TiO_2 surface are lost on the co-catalyst surface. Therefore, in the absence of any kind of favorable preferential adsorption, the use of carbonate ion in directing O_2 evolution in the dual bed system is inadvisable.

4.6 Evaluation of $\text{NiO}_x\text{-TiO}_2$ Photocatalyst

A black powder consisting of TiO_2 precipitated from $\text{Ti}(\text{i-PrO})_4$ and modified with 3 weight % Ni was given to us by Dr. Arakawa. Part of the agreement was to test the photocatalyst in Florida sunlight. While water-splitting may have occurred, it was at too low a production rate for us to reasonably detect it with our existing gas chromatographic apparatus.

Subsequent testing was done indoors in front of a Xe lamp. In conjunction with our IO_3^- redox mediator, it showed reasonable photoactivity, more than doubling the gas output in comparison to plain TiO_2 . On the other hand, Ir- TiO_2 still performs better by an order of magnitude. With an anticipated large scale loading of only 100 mg Ir/ m^2 , saving money on the cost of the co-catalyst does not justify enlarging the system to accommodate the lower photoactivity level.

Table III. Evaluation of $\text{NiO}_x\text{-TiO}_2$ as Alkaline O_2 -Evolution Photocatalyst:
Carbonate Effect

All solutions were 1.0 M NaOH

photocatalyst	light source	$[\text{CO}_3^{2-}]$	$[\text{IO}_3^-]$	O_2 evolved (ml)
$\text{NiO}_x\text{-TiO}_2$	sun	0	0	< 0.02
$\text{NiO}_x\text{-TiO}_2$	sun	0.5 M	0	< 0.02
$\text{NiO}_x\text{-TiO}_2$	Xe	0	0.2 M	0.98
$\text{NiO}_x\text{-TiO}_2$	Xe	0.5 M	0.2 M	0.93
TiO_2	Xe	0	0.2 M	0.40
Ir- TiO_2	Xe	0	0.2 M	11.7
Ir- TiO_2	Xe	0.5 M	0.2 M	3.93

4.7 Evaluation of Sol/Gel-Deposited WO_3 Photocatalyst

As a substitute for TiO_2 , it was decided to look at WO_3 . With a somewhat narrower band gap (2.7 eV), it promised to absorb more of the solar spectrum. The WO_3 work became part of another IEA collaboration. Dr.'s Jan Augustynski and Martinne Ulmann from the University of Geneva, Switzerland, had been working their own WO_3 preparations as part of a Swiss national collaboration on a tandem photoelectrochemical cell. A schematic of their dual, integrated photoelectrochemical cell arrangement is shown in Figure 8. Note that the WO_3 layer must be optically transparent in order for light to reach the dye-sensitized TiO_2 electrode. Their research therefore emphasized sol-gel methods for depositing transparent films of WO_3 . Their colloidal WO_3 had an effective band gap energy of 2.5 eV, something less than the literature value, so that it would absorb some 2.5 times as much sunlight as TiO_2 .¹¹

For our work, however, the colloids proved to be rather unstable, however. In the presence of a surfactant or other stabilizer, the colloidal state could be maintained, but only at the risk of blocking the surface photochemistry. In the absence of additives, the aqueous colloids could be maintained on their own for several days by continuously stirring in the dark, but the act of performing a photocatalytic evaluation on them accelerated their aggregation. The final material consisted of $1.0\ \mu\text{m}$ particles that were less photoactive than commercial grade WO_3 .

It was of interest to see whether the colloidal material synthesized in the laboratory would show better photoactivity than commercially obtained WO_3 powder. It was also of interest to see how it compared with our TiO_2 system.

Figure 8. Schematic of the "Grätzel Cell" or Tandem Photoelectrochemical Cell.
(courtesy of J. Augustynski, University of Geneva)

These results are shown below in Table IV. The data can be grouped into 3 categories, according to whether the photocatalyst has been modified with Pt, Ir, or not modified at all. Since the colloidal WO_3 was unstable above pH 3, we were obliged to test the other photocatalysts under the same acidic conditions. This presented a problem, in that our iodate electron acceptor in acid solution is susceptible to conproportionation with iodide to form the light-absorbing triiodide species, I_3^- :

Even so, the extent of purple color that developed was quite small, and so IO_3^- could be used in the acidic environment.

The colloidal WO_3 performed no better than, and in some cases, worse than, its commercial counterpart, even though it represented an approximate two order of magnitude increase in surface area. Data is missing for the colloidal WO_3 with Ir coating. We had difficulties with the borohydride reduction of IrCl_3 onto the colloidal material, because there was an incompatibility between their respective pH stability regions.

Table IV. O₂ Evolution from Photocatalyst Suspensions

1000 W Xe lamp radiation
 6 hr exposure
acid = 1.0 N H₂SO₄
base = 1.0 N NaOH
 0.2 M KIO₃
 250 mg photocatalyst
 F = Fisher brand
 c = colloidal

Photocatalyst	Solution	O ₂ evolved (mL)
WO ₃ (F)	a	0.05
WO ₃ (c)	a	0.06
TiO ₂	a	0.12
TiO ₂	b	0.58
Pt-WO ₃ (F)	a	0.44
Pt-WO ₃ (c)	a	0.14
Pt-TiO ₂	a	0.36
Pt-TiO ₂	b	1.3
Ir-WO ₃ (F)	a	1.72
Ir-WO ₃ (c)	a	-
Ir-TiO ₂	a	1.1
Ir-TiO ₂	b	2.5

It was found that the ion-exchange method WO₃ did not exhibit as high a photoactivity as commercial grades of the material, even though it was seen under the electron microscope to have a much higher surface area. One concern was that it was precipitating as a hydrous oxide, and that heating was necessary to release water and form the active material. Indeed, statements from our Swiss collaborators indicated that sol-gel films of the material annealed at 400° C performed better than those fired at 200° C. Accordingly, a sample of our precipitated ion-exchange WO₃ was subjected to thermogravimetric analysis. As can be seen in Figure 9 below, a single wave peaking at 212° C, corresponding to water loss, was obtained. Therefore, heating at least to 400° C became standard practice.

Figure 9. Thermogravimetric Curve for Ion Exchange-Precipitated WO₃

Because of difficulties maintaining the colloid in the suspended state, it was decided to look at the microparticles as cast dispersions. Once fixed on a solid support, the likelihood of particle agglomeration would be greatly reduced. On the other hand, there would also be an accompanying surface area loss that would make for lower rates of gas evolution. Nevertheless, it was felt that this approach would give us unambiguous results correlating photoactivity with particle size.

The Geneva group sent us fixed WO₃ dispersions on ITO/glass. A scanning electron micrograph of a typical dispersion is shown in Figure 10. We also prepared some WO₃ films on ITO in-house via sol-gel processing using the alkoxide method of film casting. First, tungsten oxytetrachloride is dissolved in an appropriate alcohol to make the alkoxide:

In our case, the isopropoxide was prepared. This material is applied to ITO substrate by successive dip coating and letting dry. Removal from the dry box immediately initiates oxide formation. The WO₃/ITO substrate would then be briefly heated to 400° C, cooled, and tested.

As shown in Table V below, the films, while nearly transparent, only displayed on order of 20% the photoactivity shown by the films supplied by Geneva. Their films are made from stabilized colloidal suspensions based on metastable tungstic acid solutions made via ion exchange. Scanning electron microscopy revealed that microcracks appearing on the newly hydrolyzed WO₃ film are largely annealed away under heat treatment.

Table V. O₂ Evolution from Sol-Gel Deposited Films of WO₃

1.0 N H₂SO₄
 0.2 M Fe₂(SO₄)₃ or KIO₃
 3.1 cm² film on ITO/glass substrate
 6 h Xe lamp illumination

Photocatalyst	mediator	O ₂ evolved (ml)
WO ₃	Fe ³⁺	negl.
WO ₃	IO ₃ ⁻	0.39
Pt-WO ₃	Fe ³⁺	0.03
Pt-WO ₃	IO ₃ ⁻	0.26
Ir-WO ₃	Fe ³⁺	0.03
Ir-WO ₃	IO ₃ ⁻	0.19

None of the acidic systems performed as well as the alkaline TiO₂ one, at least within the same category. Since the redox potential of IO₃⁻ shifts negatively with pH at the same slope as O₂ evolution, the same amount of energy is being stored in both acid and base solution. Furthermore, TiO₂ has a wider band gap than WO₃, so the latter would be expected to absorb more light. Iridium continues to do a better job of catalyzing O₂ evolution than Pt, in either acid or base. We are intending to do some X-ray photoelectron spectroscopy on the powders to confirm the oxidation state of the catalyst.

One aspect of WO₃ is that it is stable only in acidic media. Therefore, we needed to employ an acid-compatible redox mediator to evaluate it. Our collaborators had suggested Fe³⁺. So then we took the WO₃/ITO substrates, modified some of them with noble metal co-catalyst, and tested them for O₂ evolution. We also did runs with our IO₃⁻ mediator as well. The results are shown in Table I below. It is seen that the IO₃⁻ better facilitates the O₂ evolution process. Noble metal modification did not provide any advantage.

Figure 10. Electron Micrograph of Sol/Gel Deposited WO_3 on ITO

Because of our difficulties in maintaining the colloidal particle size of WO_3 obtained via ion exchange, our Swiss collaborators sent us their own preparations that had been immobilized via sol/gel techniques on ITO. Since their photocatalysts had been painted on a surface and lightly sintered before testing, the original particle size could be preserved. The porous dispersion consisted of 15-30 nm particulates.

We put together a special cell that could hold the WO_3 /ITO samples nearly perpendicular to the direction of irradiation while being surrounded by the redox mediator solution. Gas evolution into the head space was analyzed for O_2 via gas chromatography. Data for the photocatalytic behavior of these samples are shown in Table VI. As a comparison, a dispersion of Ir-TiO_2 was cast onto glass and tested in alkaline IO_3^- solution under the same conditions.

Because of the acid/base properties of WO_3 , the solutions were made 1.0 M in H_2SO_4 . It was seen that only modest concentrations of ferric ion are optimum; the 1.0×10^{-3} M solution actually generated more O_2 than the 0.1 M solution. This is due to an optical absorption effect: the 0.1 M solution was decidedly orange in color, and so absorbed much of the light that the WO_3 could have used. Co-catalysts did not improve the O_2 evolution rate. The iodate ion actually did rather well in the acidic solution, even though the risk of darkening the solution with triiodide at this pH was great. Rather than colorize the solution, there was some evidence that solid I_2 was precipitating onto the WO_3 surface. While from a practical device point of view this would be a prohibitive development, for a short batch photolysis experiment it did not significantly change the results.

Table VI. Evaluation of Sol/Gel-Deposited WO₃ on ITO as an O₂-Evolution Photocatalyst

Solution composition: [Fe³⁺] = 0.001 M, or [IO₃⁻] = 0.2 M; 1.0 M H₂SO₄

Photocatalyst	mediator	O ₂ -evolved (ml)
WO ₃	Fe ³⁺	0.04, <0.02 ^b
Pt-WO ₃	Fe ³⁺	0.03
Ir-WO ₃	Fe ³⁺	0.02
WO ₃	IO ₃ ⁻	0.4
WO ₃ (Fisher)	Fe ³⁺	<0.02
Ir-TiO ₂ (film) ^a	IO ₃ ⁻	2.3

^a solution was 1.0 M NaOH; ^b[Fe³⁺] = 0.1 M

The Ir-TiO₂ film was by far the most photoactive. Thus despite the inherent advantages of WO₃ in terms of solar absorption, it still lags TiO₂ in terms of overall photoactivity.

4.8 Organic Pigments as Photocatalytic Materials

Because of the problems encountered with inorganic semiconductors (too wide a band gap for TiO₂ and other O₂-evolving materials and corrosion of narrow band gap materials such as InP) we began to consider the use of organic pigments as photocatalytic materials. Their high extinction coefficients and good match with the solar spectrum was thought to compensate for comparatively low charge carrier mobilities. The number of organic compounds that could be tested was potentially huge, and so we began by employing theoretical methods for estimating whether a given compound could effectively absorb visible wavelength light and be able to photooxidize or reduce water.

The basic considerations are the same as would be employed in evaluating an inorganic material: it should have a band gap energy somewhere in the visible range, around 1.8-2.2 eV, and should have a valence band edge well positive of the O₂-evolution potential. However, tabulated data of this type for organics in the solid state are very scarce. Therefore, we approached the problem by calculating gas phase ionization potentials and HOMO/LUMO energy level differences.

We established a data base of about two dozen organic compounds for which IP and λ_{max} data were available and used it to evaluate the efficacy of various computer programs in making those determinations. The semi-empirical method AM1 within the SpartanTM molecular modeling program was evaluated on a Silicon Graphics workstation. For simple molecules, like benzene, pyridine, and benzoquinone, IP's were typically 4-11% higher than the literature values, a tolerable margin of error. However, for more complicated dye molecules, something like pinacyanol gave a theoretical IP 50% greater than the established value.

Another program, HMO-plusTM, developed by Allan Wisner at Wyeth-Ayerst, was evaluated. While it gave excellent results for the simple organics (within 1% of literature value), IP's for the known dyes were about 10% off. Moreover, the program would often give wildly erroneous

results when ring substituents that should only have had a secondary effect were included.

We subsequently consulted with Dr. Harold Freeman, Ciba-Geigy Professor of Dyestuff Chemistry at North Carolina State University. With his help we determined whether the HyperChemTM MO modeling program could do the job. It was specifically designed to make HOMO/LUMO determinations, and so we were confident that it or an equally sophisticated product would work.

After much consultation, study, and trial calculations, it was decided to purchase the CAChe (Computer-Aided Chemistry) molecular modeling software program from the Oxford Molecular Group. It contained a number of semi-empirical molecular orbital methods from which we hoped to predict ionization potential and bandgap separation data.

Ionization potentials for a series of 15 organic compounds whose gas phase ionization potentials were available from the literature were calculated using the ZINDO, AM1, and PM3 methods. These materials were: pentacene, violanthrene, perylene, naphthacene, coronene, pyrene, anthracene, phenanthrene, naphthalene, isoquinoline, quinoline, benzophenone, pyridine, phthalic anhydride, and benzoquinone.

An Extended Huckel method was also available, but was found to be a non-iterative method, in contrast to other EH programs, and so was quickly set aside. The series of organics included as many fused ring systems as possible, so as to reflect the type of molecular structures that we expected to encounter later on. As shown in Figure 11, IP values calculated by PM3 gave a linear plot with respect to experiment. It also gave the closest agreement with experiment, as denoted by the diagonal line connecting the opposite corners of the graph. PM3 was followed closely by AM1, with ZINDO significantly less accurate. The PM3 method was subsequently applied to a series of dye compounds whose features are likely to have the desired electronic structural characteristics.

Figure 11. Correlation between gas phase ionization potentials calculated by PM3 and literature values.

Having established a correlation between calculated and experimentally determined gas phase ionization potentials for a set of structurally related, fused ring organic compounds using the PM3 method, we were able to develop a correction factor to apply to dye compounds whose IP values were not known.

For the O₂-evolving photocatalyst, we needed to establish a target range of gas phase ionization potentials. The following calculation provided the middle of the range:

$$4.5 \text{ eV} + 1.23 + 0.5 - (0-0.84) + 1.3 = 7.5 \text{ eV},$$

where the values from left to right are used for the following parameters:

1. NHE on absolute scale
2. H₂O decomposition energy
3. built-in oxidation overpotential
4. pH correction factor; it can vary from 0 to 0.84, depending on whether the solution is acidic or basic. This must be included, because it is expected that the organic photocatalyst band edges will not track changes in pH as is the case for metal oxides.

5. gas vs surface IP correction factor; very little information on this is available, but based on the few papers which discuss the matter, 1.3 eV seems like a consensus value.

Allowing a spread of 0.7 eV in either direction to establish a reasonable number of compounds without compromise in performance, and compensate for discrepancies between theory and experiment, a target range of 6.8-8.2 eV will be defined.

The other physical attribute that we would like to be able to calculate is the energy separation between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), which approximates the forbidden energy gap that the pigment will possess in the solid state. Because of the greater mathematical complexity in determining excited state energy levels, estimates of energy gap were much less accurate than the IP values. However, it turned out that experimental λ_{max} data on dyestuffs are much more prevalent in the literature, and so our lack of predictive power does not pose an immediate barrier.

Many organic compounds representing the major classes of dyestuffs were evaluated for their suitability as O₂-evolving photocatalysts. Several trends soon emerged. Di- and triarylmethanes, phthalocyanines, polymethines, xanthenes, thioxanthenes, and acridines all tended to have insufficiently large ionization potentials. Other classes, such as anthraquinones, perylenes, quinacridones, and pyranthrones reliably gave ionization potentials that should be able to oxidize water. Consideration of water miscibility and light fastness helped narrow the field even further.

Ultimately, a set of nine pigments were identified: quinacridone, indanthrone, perylene tetracarboxylic acid anhydride, indanthrene bordeaux, pyrazolanthrone, violanthrone, acedianthrone, p-bis[dimethylamino]DPP, and dimethyl fluorubine. Their structures, calculated ionization potentials, and absorption maxima are listed in Appendix A. Their estimated valence and conduction band edges are shown in Figure 12, along with some of the more traditional inorganic semiconductors. Based on these early determinations, it would appear that we will be able to postulate compounds whose energy structure is optimized with respect to water-splitting and solar light absorption. Not all of them have significant commercial applications, and so were difficult to locate. With the aid of the ChemSources International vendor locator service on the Internet, we have been able to locate 8 of the original 10 compounds, plus many closely related derivatives.

Figure 12. Comparison of photocatalyst band edges to the water decomposition potentials.
 1) quinacridone; 2) indanthrone; 3) perylene tetracarboxylic acid anhydride;
 4) indanthrene bordeaux; 5) pyrazolanthrone; 6) violanthrone; 7) acedianthrone;
 8) p-bis[dimethylamino]DPP; and 9) dimethyl fluorubine.

Once a dye was acquired, the first step, of course, was to determine its aqueous solution stability. Since our intent was to use organic pigment particles as photocatalysts, insolubility of the compound is a necessary requirement. Solution stability also includes pH effects, particularly in alkali, since our iodate and bromate redox mediators require it. The next step was determine its stability against borohydride ion, the reducing agent most often used for our metal co-catalyst deposition. Reasonable lightfastness was also should looked at before performing a photolysis and looking for O_2 evolution.

Perylene tetracarboxylic dianhydride was the first dye to be examined. A small amount of O_2 may have been evolved. Its instability in base and decomposition with borohydride made it difficult to modify with noble metal catalysts. Indigo was studied next. It was found to be stable in alkaline borohydride solutions, so that it could be modified with iridium. After photolysis, a small but unambiguous signal indicating O_2 evolution was obtained.

4.8.1 Ionization potentials

It was considered necessary to experimentally confirm the ionization potentials calculated via the PM3 method. After many attempts to locate a research facility where a mass spectrograph is set

up to do these kinds of measurements, we came to realize that the technique has been overshadowed in recent years by photoemission methods. In particular, the method of ultraviolet photoelectron spectroscopy, or UPS, seems to be the preferred technique for obtaining ionization potential data. Locating a UPS instrument nevertheless proved to be a difficult task, as well. Finally, twin instruments, one set up to do gas phase UPS, and another set up to do solid phase UPS, were located at the Chemistry Department at the University of Arizona. Gas phase determinations will verify the theoretical calculations of ionization potential, while the solid phase measurements will give more of a practical figure of whether the immobilized solid pigments will be able to evolve O_2 .

In the laboratory, we have begun to map the electronic energy levels of several of the pigments via organic electrochemistry. An electrochemical cell designed to hold up to 25 milliliters of electrolyte was designed and put together. Platinum working and counter electrodes were constructed, and provision was made to accommodate a saturated calomel reference electrode.

A cyclic voltammogram for indigo in DMSO is shown in Figure 13. A reversible reduction wave is shown at an $E^0 = -1.01$ V vs SCE. This value can be related to the conduction band energy that the compound would have in the solid state. There was no oxidative activity within the anodic solvent limit for DMSO; even so, it is possible that indigo has an oxidation potential further out.

Figure 13. Cyclic voltammogram for indigo in DMSO

The easiest way of obtaining band gap information was via UV-visible absorption spectra of the various organic pigments. It proved difficult because of their limited solubility. Dissolution in concentrated H_2SO_4 was simple enough, but typically the original color of the pigment was lost; the acid ostensibly formed a charge transfer complex with the organic, substantially altering the electronic spectrum. Since the objective was to estimate the band gap energy that the organic

would have in the solid state, the value of the spectra obtained in concentrated acid media is of little value. Solubility issues also hampered the acquisition of redox electrochemical data. What appeared to be a solution would actually be a dispersion of pigment particles that did not yield well defined voltammetric waves.

Even so, electronic structure information could also be obtained via solid phase spectra. Most of the compounds were amenable to vacuum sublimation, and so solid films on glass could be prepared in this manner. It was intended to derive the effective energy gap of each material from the onset of absorption of its lowest energy transition. Some of the spectra were too broad and diffuse to identify a clear onset of absorption, so sometimes it was necessary to simply mark the peak maximum. A few were soluble in organic solvent, yielding clear absorption maxima.

In Table 7, effective band gap data are given for the 12 organic pigments that we acquired and tested. A general correlation was seen between the size of the band gap and the magnitude of the calculated ionization potential.

Table VII. Energy Gap and Ionization Potential Data for Organic Pigments

name	band gap energy (eV)	calculated IP (eV)
dimethoxy-violanthrone	2.08 ^e	6.93
indanthrene Gold Orange	2.4 ^p	7.96
Cromophtal Red 3B	2.2 ^s	7.27
isoviolanthrone	2.5, 2.0, 1.9 ^s	7.26
indanthrene Yellow GCN	3.2 ^s	8.56
indanthrene Black BBN	1.9 ^s	7.93
bis-(p-chlorophenyl) DPP	2.17 ^p , 1.98 ^e	7.02
indigo	1.84 ^p	7.42
pyranthrone	2.6 ^s	7.62
quinacridone	2.16 ^p , 1.98 ^e	6.67
indanthrone	1.89 ^p	6.24
perylene TCDA	2.20 ^p	8.45

^ssolution; ^ppeak; ^eedge

Meanwhile, voltammetric analysis of organic pigments sublimed onto indium-doped tin oxide (ITO) substrates was performed. Evidence of rectification was observed by alternatively taking voltammetric curves in the presence of potassium ferricyanide and methyl viologen. The ferricyanide ion, with a standard redox potential of +0.69 V vs NHE, represented the positive potential regime that favors photooxidation, while methyl viologen, with a redox potential of -0.42 V vs NHE, represented the negative potential regime that favors photoreduction. Some of the pigments are active for both photooxidation and photoreduction, implying a linear ohmic impedance that allows charge transfer with equal facility in both directions. Others appear to be rectifying, i.e., charge flows with greater facility in one direction than in the other.

As shown in figure 14, dimethoxyviolanthrone is essentially inert toward $K_3Fe(CN)_6$ in the positive potential regime, but allows the reversible electrolysis of methyl viologen in the negative regime. This is indicative of p-type rectification found for many semiconductors.

(a)

(b)

Figure 14. Voltammetry of a) $K_3Fe(CN)_6$; and b) methyl viologen on a dimethoxyviolanthrone thin film electrode.

4.9 "Tandemizing" the Dual Bed Configuration

Sunlight comes to us at an intensity of generally one kilowatt per square meter. The photovoltaic cell enables us to convert this radiant energy directly into electricity. Fundamental limitations of semiconductor physics place the power conversion efficiency of these devices in the 10-30% range.¹²⁻¹⁴ As a result, one must plan for a photovoltaic array of at least several square meters to deliver a kilowatt of electrical power.

In one approach to the future renewable hydrogen energy economy, one can envision a vast apparatus where photovoltaic power is used to power electrolyzers which decompose water to make hydrogen and oxygen. An alternative approach would be to build photoelectrochemical cells, where electrolyzer and photovoltaic cell are combined into a single device.^{15,16} This is accomplished by using the semiconductor material that produces the photovoltage as an electrode. Much effort has been expended trying to make the semiconductor material stable against the combined action of light and a corrosive electrolyte medium.

Despite the advances made in photoelectrode performance lifetime, one is still saddled with the basic problem of collecting enough light at a reasonable cost. In order to lower the cost of producing hydrogen in a photoelectrochemical manner, we have embarked on an effort to develop a photocatalytic system based on semiconductor compounds in particulate form.¹⁷ With this approach, much of the processing costs of forming and cutting wafers is avoided. The distribution of photocatalyst need only be a few g/m^2 , so that when the estimated module cost is broken down in its separate components, the semiconductor material itself becomes a minor factor.

Utilization of two photocatalytic beds automatically cuts the overall quantum efficiency in half. This may be considered a negative attribute, but perhaps more accurately it should be thought of as a trade-off between quantum efficiency and the need to make effective use of the solar spectrum. While net water decomposition to H_2 and O_2 has been observed in single component photocatalytic suspensions, the photocatalyst employed typically possessed a band gap energy of $> 3.0 \text{ eV}$.⁹ Less than 10% of the solar spectrum can be utilized by such materials.

The general strategy of fabricating devices consisting of two or more small band gap materials connected in series for effective absorption of sunlight while generating enough driving force for water splitting has been employed in a number of configurations. Principal among these is the "tandem" cell approach, where two dissimilar materials with different band gap energies are deposited onto one another. The material with the wider band gap is placed forwardmost to the direction of irradiation, so that light of longer wavelength passing through it can be absorbed by the narrower band gap material.

The dual bed photocatalytic system can be "tandemized" by essentially folding the second bed underneath the first one, as shown in Figure 15. If scattering losses in the uppermost module can be minimized, and complementary photocatalysts are employed, then one can achieve the tandem effect, that is, have high energy photons absorbed in the first semiconductor layer, and lower

Configuration Microview

Macroview

Dual Bed

Tandem Membrane

Perforated Tandem Membrane

Perforated Photo-conductive Tandem Membrane

L1-04-98

Figure 15. Future embodiments of the dual bed water-splitting system.

energy photons absorbed in the second layer. The circulating redox electrolyte would then flow from left to right across the top module and right to left across the lower one. The single unit would be tilted slightly so that evolved gases would percolate to a head space at the upper corner. Materials cost savings would also accrue, since the module area is basically cut in half, and the photocatalysts would be immobilized on either side of the same transparent membrane.

Another development in the evolution of the dual bed configuration has to do with the motion of the redox mediator working fluid. It is projected that an efficiency increase may be had by perforating the membrane or transparent support. In this embodiment, the redox mediator effuses through microporations in the photocatalyst support to reach the other immobilized photocatalyst dispersion. This feature eliminates the need to include a pump to move the redox solution across the surface of the photocatalyst; instead, a hopper supplying make-up water will suffice.

In the various tandem concepts, the photocatalysts are dispersed in layers on either side of a transparent membrane. One then has at least three laminates combining to form a single sheet. It has been demonstrated that the individual particles in each layer can communicate with each other, or in other words, an electron-hole pair generated well within a photocatalyst layer can migrate via particle-particle contact to the working fluid interface and perform redox chemistry. One can then speculate that if the photocatalyst laminates are thickened until they contact each other, there could be charge carrier flow across the membrane to the opposite interface. The optimum thickness of the photocatalyst layers at this point is uncertain, since it would be a trade-off between the penetration depth of the light each layer is expected to absorb, the diffusion lengths of the photogenerated charge carriers, and the mechanical strength of the photocatalyst bilayer.

If the two photocatalyst layers could electronically communicate with each other, then the need for a redox mediator would be obviated. The perforation feature would still have value; instead of having the mediator diffuse through the pores, the protons resulting from water oxidation (assuming acidic media) would be the mobile species. The pores could then be filled with a proton-conducting ionomer or other medium that would be selective toward the solvated species of interest. This would eliminate much of the parasitic gas intermingling that would occur through an open, perforated structure.

5.0 SOLAR PHOTOCHEMICAL PRODUCTION OF HBr FROM BROMINE AND STEAM FOR OFF-PEAK ELECTROLYTIC HYDROGEN PRODUCTION

Clovis A. Linkous, Nazim Z. Muradov, and Darlene Slattery

Solar Reactor Technologies, Inc. (SRT), of Miami, Florida, entered into a cooperative agreement with the U.S. Department of Energy to develop a renewables-based hydrogen production system employing solar energy and supplemental electrical power. The SRT system is represented schematically below in Figure 16. On the left of the figure is depicted a photochemical reactor driven by concentrated solar radiation. The reactor operates in conjunction with a reversible fuel cell, a single electrochemical device which can be run either in an electrolytic or galvanic mode. It is connected to the electric utility grid to alternately accept or input electrical power. Water and liquid bromine are converted in the solar reactor into gaseous oxygen, O₂, and hydrogen bromide, HBr, which can be stored for later use:

HBr is subsequently decomposed electrolytically in the fuel cell using low cost off-peak electricity into H₂ and Br₂ (l):

Hydrogen and Br₂ are stored for on-peak electrical power generation employing the fuel cell. The system operates in this mode as a load-leveling device. As off-peak power is available for twice the length of time on-peak is required during a typical day, H₂ can be produced for sale and Br₂ recycled to the photochemical reactor for continuing HBr production during the excess off-peak time. The system operates in this case in a H₂ production mode. This assumes, of course, that the cell current densities for HBr electrolysis and HBr production in the fuel cell mode are more or less the same.

FSEC's contribution to the SRT project was ultimately several-fold. Our initial objective was to assist in the development of the separation system for the effluent coming from the photoreactor. The O₂ is vented or collected for other uses; the HBr is separated out and sent to the electrolyzer; the Br₂ and water are to be returned to the photoreactor.

The O₂ is by far the most volatile of the components involved, and so could be separated out by air cooling the effluent, followed by passage through a water trap. This step must eventually be done anyway, as 80° C is likely the maximum temperature the HBr electrolyzer can accept. The major task will then be the removal of the HBr from Br₂(aq).

Figure 16. Schematic of SRT Concept for H₂ Production

It is known that the presence of HBr in aqueous solutions significantly affects the solubility of bromine in the H₂O/HBr binary system. Thus the higher the conversion of Br₂ in the high temperature photoreactor, the higher will be the concentration of Br₂ resulting condensate, as well as higher energy requirements for the separation of the products.

We have conducted a series of experiments on the solubility of Br₂ in aqueous solution with and without HBr. Using a Spectronic 601 spectrophotometer, we have determined the extinction coefficient of Br₂ in water as $\epsilon = 161 \text{ L mol}^{-1}$ at 400 nm. We also measured the solubility of Br₂ in distilled water at room temperature to be 3.0 g per 100 g water, or 0.19M. This compared well with the literature value of 3.58 g at 20° C. The solubility of Br₂ in 0.59 M HBr solution was found to be 7.5 g per 100 g of solution, that is, it increased 2.5 times than if it were in solution by itself.

At SRT's predicted conditions of photoreactor operation (3:1 molar ratio of steam to Br₂, with eventually 20% Br₂ conversion), a fairly good separation of the HBr from Br₂ would occur by simple cooling and condensing of the effluent stream. The molar proportions of the effluent under conditions described above would be 28 parts H₂O, 8 parts Br₂, 4 parts HBr, and 1 part O₂. Our estimation was that only 4% of the Br₂ would be found in aqueous solution; the excess would form a dark liquid phase beneath. In contrast, the HBr is much more water soluble: 221 g/100 cc H₂O for the binary system. It was uncertain how the bromine would influence that value, but even if all the HBr/H₂O effluent were condensed, [HBr] would still be less than one-third the above value.

Thus we began to consider a 2-stage separation, the primary one being simple cooling and collection of the heavy bromine liquid. The distribution of H₂O and HBr in this phase should be considered, however. The second stage would deal with the aqueous phase, that is predicted to be nominally 8 molal in HBr and 1 molal in Br₂, before allowing for polybromide formation.

The established equilibria for polybromide formation are:

Using the above equilibria, a hypothetical solubility curve for Br₂ and HBr was constructed, as shown in Figure 17. Saturating concentration was plotted for each against x_{HBr} , mole fraction HBr. Assumptions included the above equilibrium constants, plus literature values for solubility of the pure components: HBr-saturated solution, in the absence of Br₂ is 47.46 weight percent HBr, with a specific gravity of 1.79, resulting in an apparent molarity of 10.58 M; saturating concentration of Br₂ in the absence of HBr is 0.21 M.

The algorithm used to derive bromine solubility curve was:

```
col(1)=data(0,1,0.1)
```

```
HBr=col(1)*20
```

```
Br2=(1-col(1))*(0.21)
```

```
col(2)=HBr+Br3+Br5
```

```
Br3=16.85*Br2*HBr
```

```
Br5=1.45*Br2*Br3
```

```
col(3)=Br2+Br3+2*Br5
```

```
col(4)=col(2)+col(3)
```

Figure 17. Hypothetical solubility curve for Br_2 and HBr .

Additional assumptions here are that Br_3^- and Br_5^- ions can form without limit, at least to the extent that Br_2 and HBr are soluble, and that activity coefficients are near unity. At some point one would expect protonation of the polybromides to generate HBr_3 and HBr_5 . There is some reference to HBr_3 formation (), but it apparently cannot be isolated from solution.

Not surprisingly, the maximum total solubility of Br^- and Br_2 is at $x_{\text{HBr}} = 0.5$, or 1:1 Br_2/HBr . While HBr solubility was enhanced to as high as 16 M, Br_2 was raised to 12 M, or nearly 60 times its own saturation value. This effect would allow much more of the Br_2 to remain in the aqueous phase.

Our calculations predicted that the HBr would be mostly converted to Br_3^- , with about half of the Br_2 remaining in the aqueous phase. We tried to confirm the above considerations by experimentally measuring how much Br_2 came out of solution at nominal $x_{\text{HBr}} = 0.33$. The quantities used were as follows:

0.1456 mol HBr = 16.5 mL HBr = 11.79 g HBr
 0.2912 mol Br_2 = 15.0 mL Br_2 = 46.53 g Br_2
 1.0192 mol H_2O = 18.3 mL H_2O = 18.3 g H_2O

The Br₂ layer that was recovered was a total of 8.3 g/2.8 mL for a density of 2.96 g/mL. The literature value for the density is 3.102 g/mL. The aqueous phase had a density of 1.89 g/mL. Approximately 18% of the Br₂ was then recovered by simple gravity separation.

Confirmation that the HBr stayed in the aqueous phase was also done. A 1.0 mL aliquot of the aqueous phase was diluted to 100 mL and titrated potentiometrically with standardized 1.01 M NaOH. On trial 1, the endpoint was exceeded, but by estimating that 3.2 mL of the NaOH was used, the molarity of the HBr was calculated to be 3.23. On trial 2, the endpoint was approached more slowly and was found to occur when 3.05 mL of NaOH had been added. This gives an HBr concentration of 3.08 M. Based upon the amount of acid initially added to the solution, the HBr concentration was calculated to be 2.92 M.

The Br₂ concentration in the upper aqueous phase was nominally 5.05 M, based on the amount not accounted for in lower nonaqueous phase. This relatively large concentration indicated that the Br₂ was present as a mixture of tribromide and pentabromide species.

A conventional distillation of the condensed aqueous effluent was attempted. The first fraction began coming over at 55° C, just below the boiling point of pure Br₂. Collection was continued up to 100° C. By that time, the distillate was decidedly lighter in color, so a second fraction was begun. This fraction was continued up to 126° C, where the boiling point leveled out. The remaining solution was distilled to dryness at that temperature and collected as a third fraction. The first fraction was very dark brown, with a thin layer of yellow solution on top. This accounted for most of the Br₂. The second fraction consisted of a yellowish solution containing dilute HBr(aq). The third fraction consisted of concentrated HBr, i.e., the azeotropic mixture of HBr and water, since its boiling point and its density (1.485 g/ml) were in close agreement with literature values. Sixty percent of the HBr was accounted for in this fraction.

In summary, Br₂ can be largely separated from HBr(aq) via distillation; continued heating will drive off water mixed with HBr until the constant boiling mixture is obtained. The task of recycling and conditioning the components now becomes one of dealing with the middle aqueous fraction, where 40% of the HBr content could likely be reduced, but not eliminated, with a more sophisticated distillation apparatus. The use of organic solvents to extract Br₂ from aqueous polybromide solution is also a possibility.

5.1 HBr electrolysis issues

Another function of our interaction with SRT was to suggest performance characteristics of the electrolysis unit that would utilize off-peak utility power to generate H₂ and recycle the Br₂. We began by measuring the Nernst potential of various bromine solutions. The procedure was as follows:

1. Obtain a saturated calomel electrode (SCE) and replace the internal electrolyte with fresh solution.
2. Obtain a platinum flag electrode and clean by dipping in a 1:1 by volume solution of water:nitric acid and dry by heating to redness in a H₂ flame. Repeat cleaning step several times.

3. Mount SCE and Pt flag together in an assembly that can be conveniently immersed in test solutions. Since control of the atmosphere over the test solution is necessary, a 3-neck round bottom flask may prove useful as a test vessel. Insert the electrode of a pH meter, set in a voltage mode, into the test solution for measuring pH. Keep electrode ends wet when not in use.
4. Test the efficacy of this technique by measuring the voltage developed between the Pt flag and the SCE in the pH 4, 7, and 10 standard buffer solutions.
5. Once reasonable results in the standard solutions have been obtained, measure the potential developed between the Pt flag and the SCE for the following solutions: 1.0 M HBr, 1.0 M HBr and 0.001 M Br₂, 1.0 M HBr and 0.01 M Br₂, 1.0 M HBr and 0.1 M Br₂, 0.1 M Br₂, 0.1 M HBr and 0.1 M Br₂, 0.01 M HBr and 0.1 M Br₂, 0.001 M HBr and 0.1 M Br₂, concentrated HBr, 2-fold diluted concentrated HBr, 3-fold diluted concentrated HBr, and 4-fold diluted concentrated HBr.

Oxygen from dissolved air is electroactive and therefore was excluded from solution by purging with Ar or N₂ before measuring. On the other hand, especially for solutions containing excess Br₂, there was a risk of entraining the dissolved Br₂ and changing its concentration. This problem would be most evident for those solutions where the concentration of one of the components is comparable to O₂ and purge gas solubility levels, namely, at millimolar levels.

The best procedure might be to first go ahead and purge the solution with HBr in it, but once the Br₂ is put in, raise the bubbler tube out of solution and just blow into the atmosphere over it. This should be rigorous enough for gas purging for a few minutes.

Three purification scenarios could be envisioned: 1) after gravity separation, the aqueous phase is collected as is without distillation and sent to the electrolyzer (3.1M in HBr and 5.1 M in Br₂); 2) a partial distillation is performed, where only the Br₂ is carried over, and the remaining acid solution is fed to the electrolyzer (3.1M HBr); and 3) a complete distillation is performed, where the acid is concentrated to its azeotropic level (8.74 M).

A question arose over the trade-off between energy consumption for distillation versus electrolysis. In general, the higher the initial Br₂ content, the higher the electrolyzer voltage must be. Oppositely, the higher the initial HBr content, the lower the voltage.

To estimate how important this effect would be, we measured the open circuit voltage of a number of solutions, designed to represent a wide variety of Br_2 / HBr ratios. Results are shown in Table VIII below:

Table VIII. Nernst Potential Measurements on Br_2/HBr mixtures

All measurements made under Ar

	<u>Exp(V)</u>	<u>Theory(V)</u>	<u>Δ(V)</u>
0.1 M Br_2	0.093		
0.1 M Br_2 + 0.001 M HBr	0.928	1.00	-0.072
0.1 M Br_2 + 0.01 M HBr	0.900	0.946	-0.046
0.1 M Br_2 + 0.1 M HBr	0.862	0.887	-0.025
1.0 M Br_2 + 0.1 M HBr_2	0.775	.0755	-0.053
1.0 M Br_2 + 0.01 M HBr_2	0.752	0.798	-0.046
1.0 M Br_2 + 0.01 M HBr_2	0.722	.0769	-0.047
1.0 M HBr	0.661		
2.2 M HBr	0.647		
2.9 M HBr	0.625		
4.4M HBr	0.579		
Concentrated HBr	0.492		

An anode having to perform electrolysis on the Br_2 / HBr solution would have an open circuit potential of nearly 0.9V. If the Br_2 were distilled out, the voltage would drop to about 0.62 V. If the HBr solution is further distilled to its concentrated form, voltage would fall still further to 0.492 V.

These results can only approximate the true situation, since actual power consumption will depend on the current-voltage characteristic of the cell. Furthermore, the cathode potential is also likely to change somewhat as varying proton activities are presented. A subsequent task would be to put together an operating cell and measure the power consumption per unit H_2 produced.

Another contribution to the SRT project was providing assistance to Energetics, Inc., in their cost analysis determination for the SRT method of H_2 production. Their findings were that the typical 10-20% conversion rate per pass of Br_2 to HBr was unattractive, economically. The program emphasis then shifted toward other halogens, specifically, Cl_2 . We had several discussions with Energetics about HCl electrolysis. Historically, HCl electrolysis has made more of a commercial impact than that of HBr , because at one point there was a need for HCl electrolysis in the organic chemicals industry. In comparison to Br_2 , a steam/chlorine cycle promises a greater conversion per pass, based on equilibrium thermodynamics, but is a poorer absorber of solar radiation, and so will be more difficult to heat via direct light absorption and to generate any photochemical gain. The applied electrolysis voltage will be greater than that for Br_2 , requiring on order of 25% more energy. We provided a stack of papers on HCl electrolysis to Energetics to assist in their economic evaluation of a steam/ Cl_2 cycle.

5.2 Gas Phase Photocatalytic Water-Splitting

With a typical 10-20% conversion rate found to be unattractive, we shifted our effort into improving the $\text{Br}_2/\text{H}_2\text{O}$ conversion process.

We began a series of experiments to ascertain whether solid photocatalysts can be employed to augment the production of HBr from $\text{Br}_2/\text{H}_2\text{O}$ in the gas phase. Building on our work on the dual photocatalyst bed approach to decomposition of liquid H_2O , we considered whether TiO_2 , our O_2 -evolving photocatalyst, could be applied to the SRT process. Glass beads of 5 mm diameter were coated with TiO_2 Degussa P-25 powder and fired in an oven at 400°C for 2 hours. The coated beads were then poured into a vertical column. While heating with a heat gun and irradiating with a Xe arc lamp, a mixture of $\text{Br}_2/\text{H}_2\text{O}$ vapor was passed over the supported photocatalyst. The temperature inside the reactor was approximately $250\text{--}275^\circ\text{C}$. The effluent was condensed and collected as an aqueous solution. The solution was first distilled enough to remove the unreacted Br_2 , and then titrated to determine the HBr content. The results are shown in Table IX.

Even before distillation we knew that at least some HBr had been made, since the pH in the collection flask had dropped considerably lower than in the control experiments. The controls were done to isolate the effects of temperature and surface catalysis on the part of the TiO_2 .

Table IX. Photocatalytic conversion of $\text{H}_2\text{O}/\text{Br}_2$ vapors.

	<u>TiO_2, light</u>	<u>TiO_2, dark</u>	<u>light only</u>	<u>dark only</u>
final pH:	0.83	2.23	1.83	2.1
[HBr] :	17.1 mM	15.5	7.77	5.37
% Br_2 conversion:	9.3%	8.1	4.0	2.7

These results indicated both a dark and photocatalytic effect on the part of the TiO_2 .

The amount of HBr that would be formed in a gas phase reaction in the dark at that temperature would be infinitesimally small. To consider the possibility of forward reaction in the collection vessel, a conversion estimate was made at room temperature, under condensed phase conditions, for the reaction

With $K_{\text{eq}} = 7.2 \times 10^{-9}$, and an effective initial Br_2 concentration of 0.09 M, only 0.028% of the Br_2 would have converted on its own. Thus it would appear we achieved some degree of solar gain, although our control experiments suggest additional means of HBr production were also present.

Other discussions with SRT on how best to achieve the required conversion rate have dealt with the use of methane as a reductant in the photosystem. Production of COBr_2 drives the reaction

to completion, but then one must deal with the bromoketone that is basically the bromine analogue of phosgene.

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Appendix A. Structures of Photocatalytic Organic Pigments

Quinacridone Red	Red	6.67	380
Isoviolanthrone	Bluish green	7.26	250
Indanthrone	Blue	6.24	>200
Indigo	Blue	7.42	240

Perylene tetracarboxylic dianhydride

Red

8.45

350

bis(chlorophenyl) DPP

Violet

7.02

300

Pyranthrone

Orange

7.62

230

Indanthrene
Yellow GCN

Yellow

8.56

Indanthrene Black BBN

Black

7.93

Dimethoxy Violanthrone
(Vat Green

Green

6.93

<300

Indanthrene Gold Orange

Orange

7.96

Task 2 Report

Investigation of Sulfonated High Temperature Polymers as Proton Exchange Membrane Electrolytes

Final Report

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Submitted to:
U.S. Department of Energy
Mr. Douglas Hooker
1617 Cole Boulevard
Golden, CO 80401

Submitted by:
Robert W. Kopitzke
Clovis A. Linkous

Florida Solar Energy
1617 Clearlake Road
Cocoa, FL 32922-5703

INVESTIGATION OF SULFONATED HIGH TEMPERATURE POLYMERS AS PROTON EXCHANGE MEMBRANE ELECTROLYTES

Prepared by:

Robert W. Kopitzke
Clovis A. Linkous
Florida Solar Energy Center
1679 Clearlake Road
Cocoa, FL 32922-5703

June 1999

1.0 SUMMARY

The sulfonic acid derivatives of five aromatic high temperature polymers were synthesized and characterized as proton exchange membrane electrolytes. Three of the polymers, polyether(ether)ketone (PEEK), polyethersulfone (PES) and polybenzimidazole (PBI) were made by derivatization of the polymer using established methods. A fourth polymer, polyphenylquinoxaline (PPQ), was sulfonated as the already cast film using a novel method termed the soak and bake procedure. The fifth sulfonated polymer, a polyimide copolymer (PI), was prepared using a sulfonated diamine monomer, but it had very poor hydrolytic stability.

Characterization of the sulfonated films included water uptake, ionic conductivity and coulombic efficiency. The water uptake of most of the polymers ranged from roughly five to ten water molecules per sulfonic acid group, but the water uptake of the sulfonated PEEK films ranged from 22 to almost 50. The proton conductivity of these materials ranged from one to several orders of magnitude lower than Nafion[®]. This may be due to the lower acidity of the aromatic sulfonic acid relative to Nafion's[®] perfluorosulfonic acid. Coulombic efficiency measurements were near 100% for all of the polymers tested.

The thermal stability of these materials were evaluated under inert and saturated vapor conditions. Under inert conditions, sulfonation lowered the thermal stability of the aromatic polymers by as much as 150°C, but under saturated steam by only 10°C to 40°C. All of the polymers tested were not stable above 200°C in saturated vapor conditions. In one atmosphere of superheated steam, the polymers decomposed thermally. In saturated vapor, simple thermal decomposition products were not detected, but evidence of hydrolytic degradation and desulfonation was found.

2.0 INTRODUCTION

2.1 Hydrogen Economy

One of the most important challenges that our world will face in the twenty-first century will be continuing to meet the ever increasing energy needs of its citizens. Along with the need to find a renewable long term energy source is the need to find a more environmentally friendly one. An often mentioned solution to these problems is the hydrogen economy.¹ In this economy, hydrogen is produced by a renewable energy source such as solar or geothermal, then used as fuel for transportation and stationary applications. Most hydrogen is made by the steam reforming of natural gas,² but this does not represent a renewable source. Other methods, such as the thermal cracking of hydrocarbons or the reaction of steam with carbon at high temperature suffer from the same problem.

The best source of renewable hydrogen is from the splitting of water by electrolysis. This process produces pure hydrogen, which can be used as a fuel, and oxygen, which is released into the environment. When hydrogen is used to produce energy by combining with oxygen in a fuel cell, the only byproduct is water. This represents a completely renewable system (Figure 1).

Hydrogen Economy

Figure 1. Schematic of a fully renewable hydrogen economy.

Two of the key technologies in this system, the splitting of water by electrolysis and the utilization of hydrogen in a fuel cell, use an electrochemical cell. An electrolysis cell is one that consumes energy and a fuel, or galvanic, cell is one that produces energy. Although there are a number of differences between the two technologies, the major components of the cell are the same. The cells contain two electrodes where the electrochemical reactions occur and an electrolyte which allows for the movement of an ionic species. These cells are usually referred to by the type of electrolyte material they use.

The most developed electrolysis technology is a cell employing a concentrated alkaline solution as the electrolyte, a nickel plated iron anode where the oxygen is evolved, an iron cathode where the hydrogen is evolved and an asbestos diaphragm to separate the two electrodes.³ This cell is typically run at 80°C, although it can be run at higher temperatures. Other electrochemical cells are based on solid polymer electrolytes (SPE's) which can function both as the electrolyte and as the separator for the cell. Two examples of SPE's are ceramic based oxide conductors which operate at high temperature (e.g. 1000°C) and polymer based proton conductors which run at temperatures up to 150°C. These latter proton conductors, also known as proton exchange membranes (PEM's), are attractive alternatives to the alkaline system for several reasons. First, the polymer membrane allows for cells to be easily stacked in series using the polymer to seal the

system. This helps to keep the weight of the system down. Second, no corrosive liquid is free-flowing in the cell and thus corrosion problems are reduced. Third, these cells have a demonstrated long life.⁴ These advantages make PEM based fuel cells particularly attractive for transportation applications. These polymeric, proton exchange membranes are the focus of this work.

2.2 Proton Exchange Membranes

A PEM based electrochemical cell consists of an electrolyte, two electrodes, a machined cell body and plumbing. The cell body and the plumbing are more engineering concerns and will not be discussed in any detail. The electrodes used are carbon based, gas diffusion electrodes which are usually coated with a platinum catalyst. The electrolyte must have a source of mobile protons to be conductive. This acidic functionality is almost always a sulfonic acid.

In an electrolysis cell, oxygen from water is oxidized at the anode to molecular oxygen, and the free hydrogen ions are transported to the cathode where they are reduced to molecular hydrogen. In a fuel cell, hydrogen at the anode is oxidized to protons which are conducted through the electrolyte to the cathode. At the cathode, molecular oxygen is reduced and combined with the transported protons to form water (Figure 2).

Figure 2. Schematics of proton exchange membrane (PEM) based electrochemical cells.

The first commercially produced PEM was polystyrene sulfonic acid. Then in the 1960's, DuPont developed an ionomer consisting of a polytetrafluoroethylene backbone with perfluorsulfonic acid side chains. This material, Nafion[®], is superior to polystyrene sulfonic acid in terms of conductivity and long term stability.⁴ Nafion[®] membranes, which are used commercially in the chlor-alkali business, have a maximum operating temperature of approximately 125°C.⁵ Later, Dow Chemical introduced an ionomer, DOW 600, similar in structure to Nafion[®], but with a shorter side chain. This material had better conductivity than Nafion[®], but its cost was more than double that of Nafion's[®].⁶

Figure 3. Structures of some early PEM materials.

The last twenty years have seen numerous groups work to develop alternatives to these expensive perfluorinated sulfonic acids. A number of papers have focused on doping polyethylene oxides (PEO). For example, a PEO + NH₄CIO₄ system gave a maximum conductivity of 5 x 10⁻⁵ S/cm.⁷ A similar system using PEO and NH₄I system gave a conductivity of the same magnitude.⁸ As compared to Nafion[®], which possesses a conductivity of roughly 10⁻² S/m these system are far too resistive to be useful for hydrogen production or power generation. Much better results were obtained by doping an ethylene oxide-propylene oxide copolymer with an alkali metal salt. This system had a conductivity ranging from 10⁻⁵ at room temperature to greater than 10⁻³ at 100°C.⁹

A number of materials have been developed that mimic the DuPont and DOW membranes in that fluorinated backbones are a key component. One of the leaders in fuel cell technology, Ballard Power Systems, has developed their own membrane for use in fuel cells. This material is a derivative of polystyrene sulfonic acid in which the vinyl derived backbone is perfluorinated. Although no conductivity data has been reported for this material, known as BAM3G, its fuel cell performance data is excellent.¹⁰ A second example, very similar to Nafion[®] and the Dow membrane is Aciplex-S[®] which is made by Asahi Chemical.¹¹ This perfluorosulfonic acid also has excellent fuel cell performance characteristics. A final example is a perfluorosulfonamide membrane, developed by researchers at Clemson University, which possesses the best thermal stability of any of the perfluorinated membranes, nearly 200°C.¹²

All of the above examples require water to be effective proton conductors because the charge carrier is the hydronium ion, H_3O^+ . The mechanisms proposed for the proton conductivity in these membranes are the Grotthuss mechanism, which involves the transfer of protons between water molecules and the reorientation of these molecules, and the vehicular mechanism, which is the translational motion of the hydronium ions.¹³ A second category of PEM's are those that work in the absence of water. One type of these water free membranes uses a polyethylene oxide backbone complexed with sulfamide salts. For example, this system doped with guanidine as a proton-vacancy inducer yielded room temperature conductivities on the order of 10^{-5} S/cm.¹⁴ A second type of water free PEM's is the acid/polymer blends. These consist of a polymer, such as polyvinyl alcohol, with a mineral acid such as sulfuric or phosphoric acid. One of the better results from this class of PEM's comes from a polyacrylamide doped with sulfuric acid, which had a conductivity of 1.4×10^{-2} S/cm at 100°C .¹⁵

The performance of these PEM based electrolytic or fuel cells varies with the membrane used. The cells based on the perfluorinated membranes do have acceptable performance, but the cost of the cells is very high. The cost of producing hydrogen by water electrolysis is also very high because of the energy requirement. One potential solution to these cost problems is to operate the cells at higher temperature. Higher temperature would not only be beneficial from a cost standpoint but also from a performance one. A brief description of the advantages that higher temperature offers to electrochemical cells follows.

The performance of an electrochemical cell is determined by its current at a given voltage. In the case of an electrolytic cell the higher the current (or current density) at a given voltage, the better the performance. For a galvanic cell, where the power output (power = current x voltage) is the key parameter, performance is increased by maximizing the voltage at which a given current density can be obtained. The theoretical open circuit voltage of these cells is 1.23 volts at room temperature. Deviations from this theoretical value are caused by several factors including the resistance of the cell, the rate of the reaction at the electrode surface and the change in concentration of the reactant in the electrolyte around the electrode surface. All of these factors are termed overpotentials. The resistance of the cell is termed ohmic overpotential, the loss due to electrode kinetics is termed activation overpotential and the effect of changes in concentration of the reactant is concentration overpotential.⁴ Each of these factors can be reduced by operating the cell at a higher temperature. The cell resistance will be lower at higher temperature due to the more rapid transport of protons through the membrane. The kinetics of the electrode reaction will also be improved as higher temperature helps to overcome the activation barrier associated with this step. The rate of diffusion of the reactant to the electrode will also increase with temperature. In addition, higher temperature offers the possibility of using non noble metal catalysts which could lead to cost savings. Therefore, higher temperature, from a kinetic standpoint, will improve the performance of electrochemical cells and may also reduce their cost.

In addition to the kinetic advantages of higher temperature, there is also a thermodynamic one for electrolytic cells. The theoretical open circuit voltage required to split water decreases with

increasing temperature. At room temperature this voltage is 1.23 volts, while at 1000°C it is approximately 0.9 V.⁴ Thus the electrical energy input required to produce hydrogen will be reduced at higher temperature. This represents an additional cost savings. Since the temperature at which these cells can be run is limited by the thermal stability of the electrolyte membranes, the development of highly thermally stable PEM's is an important endeavor.

2.3 High Temperature Polymers

In order for a proton exchange membrane to exhibit good thermal stability, it is necessary that the polymer from which it is derived also have good temperature stability. High temperature or engineering polymers, are a family of materials that are specifically tailored for use at higher temperatures.¹⁶

These polymers are almost always aromatic polymers linked together either in a single chain or in a ladder or step-ladder arrangement. Totally aromatic engineering polymers are usually very difficult to process, so more flexible linking groups are often put between the aromatic rings. The improved processability the linking groups afford is offset by reduced thermal stability. For example, in a nitrogen atmosphere, polyphenylene has a decomposition temperature of 675°C while polyphenylene sulfide's is 480°C.¹⁷ Linking groups that impart good flexibility while still maintaining good thermal properties include ketones, sulfones, sulfides, oxides and perfluoroalkyl groups. These linkers give rise to many of the different engineering polymer families such as polyketones, polyarylethers and polysulfones. Aromatic ladder polymers or step-ladder polymers usually contain one or more heteroaromatic structures; examples include polybenzimidazoles, polybenzoxazoles and polyimides.

Some fully conjugated engineering polymers display electrical conductivity, but unless they are modified they will not conduct protons. However a variety of high temperature polymers have been made that contain ionic groups. For example, a number of ionically conducting polyimides have been reported in the literature. The best of these, a quaternary copolymer consisting of a polyimide-polysiloxane doped with LiCF_2SO_3 had a conductivity of 10^{-7} S/cm at 250°C.¹⁸ A second high temperature polymer, a poly(benzylsulfonic acid)siloxane with a thermal stability of 300°C, displayed conductivities ranging from 2×10^{-3} to 10^{-2} S/cm at room temperature.¹⁹ A final example, a sulfonic acid containing polyethersulfone with an ion exchange capacity of 3 meq/g, had slightly lower resistance than that measured for Nafion®.²⁰

In addition to these, ion containing polymers have been reported for polyetherketones, polyethersulfones and polybenzimidazoles, the last of which is sold commercially. However, no study in the literature has focused on the thermal stability of ionically conductive engineering polymers under electrolysis type conditions, i.e. high temperature, hydrolytic conditions. Furthermore, although there is extensive data on the temperature limits of non-ion containing engineering polymers, most of this is done under either an inert atmosphere or in air. Very little

information exists on the thermal stability of these polymers under severe hydrolytic conditions. One study has attempted to investigate this by examining the weight loss of approximately 40 different engineering polymers upon exposure to high temperature steam at one-half atmosphere of steam pressure under both oxidizing (O₂) and reducing (H₂) conditions.²¹ These polymers were subjected to these conditions for 24 hours at 200°C, 300°C and 400°C. From this, several polymers were identified, representing different classes of engineering polymers that would be suitable for development as high temperature proton conductors in a water electrolysis cell. The polymers chosen were a polyetheretherketone, a polyethersulfone, a polybenzimidazole, a polyphenylquinoxaline and a partially fluorinated polyimide (Figure 4). The goal of this research is to make the sulfonic acid bearing derivatives of each of these polymers and to investigate these as electrolyte materials. Before the specifics of the research are discussed, a brief review of research on ion containing derivatives of the five candidate polymers will be given.

Polyetheretherketone

Polyethersulfone

Polybenzimidazole

Polyphenylquinoxaline

Partially fluorinated polyimide

Figure 4. Structures of the five candidate polymers.

2.4 Review of the Candidate Polymers

Three of the five candidate polymers have been previously derivatized as sulfonic acids. Of these, the polyether(ether)ketone has been studied most. Sulfonated aromatic polyetherketones were first prepared back in the early 1980's.²² This polymer can be sulfonated by dissolving it as a powder in concentrated sulfuric acid, followed by precipitation into water to give the desired product.²³ Several other studies have reported variations of this procedure with the focus being on controlling the degree of sulfonation.²⁴ This polymer has been extensively characterized as well. Studies on molecular weight determination,²⁵ water uptake²³ and glass transition temperature versus degree of sulfonation / cation type (H^+ , Na^+ , Zn^{2+})²⁴ have been made. The effect of sulfonation level on the crystallinity of the polymer and on the microstructure of the polymer have been investigated as well.²³ Finally, thermogravimetric analysis of these polymers under nitrogen has been done with different cations and at several levels of sulfonation.²⁴

Sulfonated polyethersulfones have been made by polymerization of sulfonated monomers²⁶ and by derivatization of the polymer with chlorosulfonic acid,²⁷ sulfur trioxide²⁰ and sulfur trioxide complexed with triethylphosphate (SO_3 -TEP).²⁸ Thermal characterization of these polymers has included measurement of the glass transition temperature as well as thermomechanical and thermogravimetric analysis.²⁶ One paper has studied the membrane characteristics of this polymer including water uptake, resistance, permselectivity and current-voltage behavior at room temperature.²⁰

Sulfonated polybenzimidazoles (S-PBI) have been prepared by conventional polymerization of a tetraamine with sulfonated terephthalic acid.²⁹ In addition, S-PBI can be made by first soaking PBI in dilute sulfuric acid to form the ammonium hydrogensulfate salt followed by heating at $400^\circ C$ to $500^\circ C$ for several minutes to form the covalently bonded sulfonic acid.³⁰ The latter "soak and bake" process is used by Hoechst Celanese to produce sulfonated PBI fiber commercially. Because the sulfonated fiber is a commercial product, its mechanical and thermal properties have been extensively studied. Thermal gravimetric analysis coupled with mass spectrometry showed decomposition producing SO_2 beginning at around $320^\circ C$ and peaking at approximately $475^\circ C$.²⁹ Conductivity measurements have also been made on S-PBI films.³¹

No report of sulfonated polyphenylquinoxaline is present in the literature. One reference does report on the ultraviolet spectrum of the ammonium hydrogensulfate salt of this polymer.²⁷

Although the partially fluorinated polyimide has not been sulfonated, several reports of sulfonated polyimides are found in the literature. As mentioned earlier, several papers describing the synthesis of polyimide copolymers incorporating diaminobenzenesulfonic acid are in the literature.¹⁸ The ionic conductivity versus temperature behavior of these polymers were studied

as was the thermal stability. A polyimide based on a sulfonated dianhydride has also been synthesized, but not fully characterized.³³

The above review illustrates that while the idea of making sulfonated ionomers from high temperature polymers is not new, no attempt has been made to thoroughly characterize their use as electrolytes in electrochemical cells. There is no coulombic efficiency data or thermal stability data under saturated vapor conditions. Most of the sulfonic acids that have been made are studied in the Na-salt form in an attempt to increase the glass transition temperature and these studies seldom examine proton conductivity or steam resistance. Several of the studies included some conductivity data and several even reported limited current - voltage behavior, but no attempt has been made to examine the thermal stability of these materials under conditions found in electrochemical cells or to test the limits of that stability with a variety of structures.

3.0 EXPERIMENTAL

3.1 General

Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 IR spectrometer. NMR spectra were recorded on a Bruker AMX 360 at 360 MHz for ¹H and 90 MHz for ¹³C spectra. Chemical shifts are reported in ppm referenced to residual solvent nuclei. Electron impact mass spectra were obtained on a Hewlett Packard G 1800 A GDC system GC/MS. Thermogravimetric analyses conducted in air and helium were done on a TA Instruments Hi Res[®] TGA 2950 thermogravimetric analyzer using the "Hi-Res" method and heating to 700°C. Differential scanning calorimetry was done on a Perkin-Elmer DSC 7 at 20°C/min. Tube furnace experiments were done in a Thermolyne 21100 model tube furnace and saturated vapor experiments in a PARR reactor. Gas chromatography was done using an SRI 8610A with an Alltech Hayesep[®] DB column (30' x 1/8') with helium as carrier gas. Elemental analysis was done by Galbraith Laboratories, Inc. Nafion[®] 117 films were obtained from Solution Technologies Inc.

For synthetic work conducted under dry conditions, the glassware and appropriate chemicals (i.e. solid, thermally stable reagents) were dried at 110°C - 115°C overnight and cooled in a dessicator or assembled hot and allowed to cool under a stream of dry argon. Commercially available, "ultra-pure" argon (>99.999%) was used in all procedures utilizing inert gas. Unless specified, all reagents were used as received from commercial vendors.

3.2 Sulfonation of Polyether(ether)ketone

The level of sulfonation of PEEK was controlled by varying either the reaction time or the reaction temperature using a procedure found in the literature.²³ The following description represents a typical experiment.

Concentrated sulfuric acid (100 ml) was placed in a dry 250 ml 3-neck flask equipped with a mechanical stirrer, an addition port and an inert gas supply. While stirring, dry PEEK powder (10 g) was added in small portions with a spatula. After all the powder was added, the inert gas purge was replaced with a drying tube and the flask was sealed. As the tan powder dissolved, the solution turned blood red. Dissolution time varied with the temperature of the reaction but was typically several hours. After the desired reaction time, the reaction was quenched by slowly pouring the polymer solution into approximately 700 ml of water. The polymer precipitated instantly, forming white, spaghetti-like strands. The precipitated polymer was washed extensively with water to remove all residual acid, dried under vacuum at 100°C overnight and titrated to determine the level of sulfonation.

3.3 Sulfonation of Polyethersulfone

Sulfonation of PES was done according to a literature procedure,²⁰ and an example experiment is described below. Dry PES (typically 5 g of PES film) was dissolved in 50 ml of dry (molecular sieves) CH₂Cl₂ in a dry 3-neck flask equipped with an inert gas purge. Stirring was accomplished with a magnetic stir bar. The polymer readily dissolved to form a pale yellow solution. Stirring overnight under argon caused the polymer to precipitate from solution forming a fine white suspension. This suspension was cooled in an ice/water bath and an addition funnel was added to the system. The desired amount of a 10% solution of SO₃ in CH₂Cl₂ was added dropwise through the addition funnel. During the addition it was necessary to add more solvent (25 to 50 ml) to maintain stirring. The reaction was allowed to stir for two hours in the ice bath, and then warmed to room temperature. The reaction slurry was filtered through a coarse sintered glass funnel and washed with water until neutral. After drying, the sulfonated polymer was titrated to determine percent sulfonation.

3.4 Sulfonation of Polyphenylquinoxaline

The unsulfonated polymer (calculated M_n 28,544; η_{inh} = 1.06 dl/g) was received as a 15% solids solution in m-cresol from P. Hergenrother of NASA Langley. This was solvent cast and dried in a vac-oven at 160°C for several days to give a thin film (approx. 1.5 mil.). The dried film was weighed, soaked in 50% H₂SO₄ for two hours, blotted dry with a paper towel to remove surface moisture and briefly heated for 90 seconds in a muffle furnace at 300°C. The sulfonated film was leached in distilled H₂O to remove excess acid, oven dried at 105°C and weighed, and in some cases titrated, to determine the level of sulfonation.

3.5 Sulfonation of Polybenzimidazole

The sulfonation of PBI was done on thin films according to a procedure found in the patent literature.³⁰ A piece of dry, preweighed PBI film was placed in enough 10% H₂SO₄ to cover it completely. After two hours the film was removed and dabbed dry with a paper towel to remove surface moisture and placed in a furnace at 500°C for 90 seconds. Following this heat treatment,

the film was soaked in DI water repeatedly to remove all of the unreacted acid. Following drying, the sulfonation level was determined by weight uptake and by titration.

3.6 Synthesis of a Sulfonated Polyimide

Commercially available 90% 2,5-diaminobenzene sulfonic acid (S-DAB) was recrystallized three times from distilled water. It was converted to its lithium salt (S-DAB-Li) by reacting with one equivalent of LiOH. After evaporating the water, the product was dried at room temperature under vacuum in the presence of P₂O₅. The unsulfonated diamine, 4,4'-oxydianiline (ODA) was recrystallized from MeOH and dried under vacuum before use. Pyromellitic dianhydride (PMDA) was sublimed and stored at 105°C prior to use. The solvent, N-methylpyrrolidone (NMP) was purified by vacuum distillation from P₂O₅ and stored over molecular sieves until use.

The ratio of S-DAB-Li to ODA was varied to give different equivalent weights. The synthesis described below is for a ODA:S-DAB-Li ratio of 4:1. To a dry 100 ml 3-neck flask equipped with a mechanical stirrer and an argon purge was added 174 mg (0.92 mmol.) of S-DAB-Li and 740 mg (3.70 mmol) of ODA. These were dissolved in 14 ml of NMP at 40°C. To this stirred solution 1027 mg of PMDA (4.71mmol or 1.02 equiv.) was added in one portion. This was rinsed in with 5 ml of solvent to give a 10% solids content. The solution began to thicken and darken almost immediately. The reaction was allowed to continue at 45°C overnight. A sample of the polyamic-acid solution was taken for viscosity testing ($\eta_{inh} = 1.15$ at 20°C). The polymer was solvent cast onto a glass plate and cured by ramping to 80°C at 2°C/min, holding for one hour, then ramping to 300°C at 5°C/min and holding for one hour. The cured film could be removed from the glass plate by briefly soaking the film in water.

The inherent viscosity of the polyamic acids were determined at 20°C using a Cannon-Fenske size 100 kinematic viscometer at 0.5 g/dL.

3.7 Synthesis of 2,4,5-trimethylbenzaldehyde

Five grams (0.037 mol.) of durene (1,2,4,5-tetramethylbenzene) was dissolved in 50 ml of 50% acetic acid and heated to 50°C. A solution of 182g (4equiv.) of ceric ammonium nitrate (CAN) dissolved in 125 ml of 50% acetic acid was added slowly via an addition funnel to maintain a temperature of 50-55°C (approx. 2 h.). The reaction was allowed to cool to room temperature then quenched by adding to an equal volume of distilled water. This was extracted 3 times with an equal volume of diethylether, the ether was washed with 1M NaOH to remove any residual acetic acid, dried with MgSO₄, filtered and the solvent removed with a rotary-evaporator. The crude product could be purified by column chromatography on normal phase silica eluting with 30% CH₂Cl₂ in hexanes to give the pure product. Yields varied, but typically were around 50%.

3.8 Sulfonation of 4'',4'''-(hexafluoroisopropylidene)-bis(4-phenoxyaniline)

The diamine (4-BTDA) was dissolved in concentrated H₂SO₄ (10 ml/g) to give an olive green solution. This was allowed to react overnight at room temperature, then quenched by adding dropwise into 50 ml of 0°C distilled water, precipitating the product as a pale pink solid. The solid was washed with cold water to remove any unreacted acid and dried in an oven at 110°C.

3.9 Titrations

The sulfonic acid content of the derivatized polymers was determined by acid-base titration. In cases where the polymer was soluble in water or in a solvent miscible with water, the acid content was determined by potentiometric titration done on a solution of the polymer. In other cases the acid was exchanged by soaking the polymer for two hours in a 3M NaCl solution, followed by titration of this solution. Longer soaking times (overnight) did not significantly change the results. The percent sulfonation (100% means one acid per monomer unit) was calculated using the following formula:

$$\% \text{ sulfonation} = \frac{\text{moles acid} \times \text{monomer weight}}{\text{sample weight} - (80 \times \text{moles acid})}$$

where moles acid is the moles of titrated acid and sample weight is the weight of the titrated polymer in grams. Monomer weight is the weight of a single repeat unit of the polymer and 80 is the weight of a sulfonic acid group, again both in grams. Solving this equation and multiplying by 100 gives the percent sulfonation.

The acid content of the polymer is more conveniently expressed as the equivalent weight (EW), which is the average weight of a polymer segment that contains one sulfonic acid group. This is determined by dividing the monomer weight of a given polymer by the percent sulfonation (as a decimal) and adding 80 to account for the weight of the sulfonic acid. For example, the equivalent weight of 35% S-PEEK would be calculated as follows:

$$\text{EW} = (288/0.35) + 80 = 903 \text{ grams per equivalent}$$

where 288 is the monomer weight of PEEK.

3.10 Film Casting

Solvent cast polymer films were made by several methods. Initially, polymer solutions were cast by evaporating a solution in a beaker. Later, a spreader was used to cast the films onto glass plates. The films were dried by heating on a hot plate to remove the majority of the solvent then heated under vacuum for several days. Films cast from high boiling solvents such as DMF, NMP

and m-cresol were heated to 150°C for this last step. Some of the polymer films tended to curl during the drying process, and this made their use difficult in the cells. These films were dried under vacuum in a 2" x 2" steel press that allowed the film to be clamped around its edge.

3.11 Water Uptake

Dry, solvent cast polymer films were weighed, soaked in water overnight, dabbed dry with a paper towel and reweighed. The weight uptake was calculated as the percentage of the initial film weight.

3.12 Conductivity/Thermoconductimetric Analysis

The conductivity of the polymers was determined using a Teflon based cell containing two platinum foil contacts connected to an a.c. bridge at 1000 Hz.³⁴ The membranes were swelled in boiling water and their dimensions measured prior to being mounted in the cell. Samples that were soluble in boiling water were swelled in hot water at the maximum temperature that would still give a usable film. The cell was submerged in deionized water and its resistance was measured. The change in conductivity with temperature was determined by submerging the cell in water inside of a PARR reactor equipped with electrical feedthroughs. The temperature was ramped at 0.5°C/min until the resistance of the cell increased dramatically, indicating failure of the film. The resistance was measured every 10°C throughout the experiment, more frequently when the resistance neared its minimum.

3.13 Water Electrolysis/Coulombic Efficiency

Electrolysis curves were obtained by mounting 1.0 in² membranes in a graphite test cell obtained from Electrochem Inc.. The exit port on the cathode compartment was fed into an inverted buret to measure the rate of H₂ gas evolution. For the S-PEEK samples, the films used were cast onto glass onto which had been spread 4 mg/cm² of iridium black powder. The iridium-coated side was contacted with carbon cloth and used as the anode, while the cathode consisted of a piece of PSI carbon cloth onto which Pt had been electro-deposited. For samples of the other polymers, both electrodes were platinum coated (4 mg/cm²) carbon, gas diffusion electrodes supplied by Energy Partners Inc., and no iridium was used in the cell. The membrane/electrode assembly was centered between the graphite blocks and the entire cell was bolted together. Feed water was contained in a vertical column connected to the inlet port of the anode.

Once completely assembled (Figure 5), 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 a heating tape attached to the test cell maintained constant operating temperature. Coulombic efficiency was determined by collecting the evolved hydrogen in the inverted buret for a set time at a constant current output.

Figure 5. Schematic of the cell used for water electrolysis of the S-PEEK membranes.

3.14 Thermogravimetric Analysis in Saturated Vapor

Samples (about 100 mg) were dried, weighed, placed in glass beakers and placed at the bottom of a PARR reactor. Enough water was added to the reactor to ensure saturated vapor conditions at the desired temperature. The reactor was sealed, pressure tested and flushed for ten minutes with argon to provide an inert atmosphere for the tests. The reactor was heated to the desired temperature and held there for 24 hours. A pressure gauge was used to monitor the internal pressure throughout the experiment. Saturated conditions were verified by comparing this pressure to steam tables.³⁵ After 24 hours the reactor was allowed to cool and the samples were removed, dried overnight and weighed.

3.15 Superheated Steam Decomposition Analysis

Dried samples (typically 0.5 g) were weighed into a tared ceramic combustion boat. This boat was placed in a borosilicate glass tube equipped with one male and one female joint which was placed inside of a tube furnace. The tube was connected with a glass adapter to a flask containing water and to a series of cold traps via a second adapter. The entire system was flushed with argon. The experiment was run by heating the tube furnace to the desired temperature and holding for six hours. One atmosphere of steam was supplied by heating the water to 100°C and passing argon at 25 ml/min through the system. Heating tape was used on the adapter leading to the tube to ensure that the one atmosphere was maintained into the tube. Two cold traps were used to condense the steam and any decomposition products; the first was an ice/water trap and

the second a dry ice/acetone trap. Following the six hour run, the system was cooled under argon and the sample was removed, dried overnight and reweighed.

The inside of the tube and the adapter leading to the first trap were washed with dichloromethane to remove any condensed material. The ice/water trap condensate was diluted to 50 ml and its pH measured. Acid containing samples were treated with BaCl_2 to precipitate the acid as its barium salt. This salt was collected by centrifugation. The pellet was washed twice with deionized water, dried and analyzed by infra-red spectrometry. The condensate was extracted with 3 x 50 ml dichloromethane and the organic fraction was dried with MgSO_4 , filtered and concentrated. These extracted organics were analyzed by GC/MS.

3.16 Saturated Vapor Decomposition Analysis

These experiments were run at 225°C as described in the saturated vapor TGA section of this chapter. IR analysis of the dried polymer residues was done using KBr pellets for crushable samples and H-ATR for films. Decomposition products were collected by decanting the water, washing the inside of the PARR reactor with water, methanol and dichloromethane, combining these washings with the decanted water and concentrating this to dryness. Analysis was done by IR and NMR.

4.0 SYNTHESIS

This section will present the details related to the synthesis of the sulfonic acid polymers. This will include both a discussion of the methods used for the synthesis and a presentation and discussion of the evidence used to determine the presence and location of the sulfonic acid groups. Comparisons between this work and comparable literature will also be made. A summary of the key results from all of the synthetic work will be given at the end of this section.

4.1 Sulfonation of Polyether(ether)ketone

Polyether(ether)ketone was readily sulfonated by dissolution in concentrated sulfuric acid as reported in the literature.²³ Since the goal of this synthetic effort was to produce sulfonated polymers possessing a range of sulfonation levels for evaluation as electrolyte materials, no systematic study of reaction parameters was attempted. However, a large number of experiments were performed, so some comparison to previously published work is possible.

The four key parameters that affect the extent of the reaction are time, temperature, concentration and water content. Sulfonation levels ranging from 20 percent to in excess of 150 percent were obtained by varying these conditions. In previous reports no sulfonation levels above 100% were reported.^{23,24} The reason for this is that after the first sulfonic acid is added to a monomer unit within the polymer, which occurs at one of the four equivalent sites on the electron rich diether-bearing ring (Figure 6),²⁴ all of the aromatic rings in that monomer unit contain functional groups that are strongly deactivating to electrophilic aromatic substitution. One reaction in this study,

run at 50°C for six days produced a polymer with a sulfonation level of 150%. This polymer dissolved in water with mild heating. Two other reactions were run at 90-95°C for one day and one week. These polymers would not precipitate when the reaction was quenched into water, indicating a very high level of sulfonation. No reactions run at or near room temperature exceeded the one sulfonic acid per monomer threshold.

Figure 6. Structure of sulfonated polyether(ether)ketone

All of the experiments are summarized in Table I. The most obvious feature gleaned from this data is the lack of reproducibility of the sulfonation level versus the conditions. The two variables that are not given are concentration and water content. Most of the reactions were run with a solids content of 10% (10g PEEK in 100 ml H₂SO₄), however entry 1 was run at 20% solids and entries 4,5,7,13 and 14 were run at 7.5%. The literature states that control of the last variable, water content, is crucial for obtaining reproducible results. All of the reactions were run with 95.8% H₂SO₄ (based on the suppliers label), but the adventitious water from the air may account for the differences seen. Better control of both moisture and temperature are required to give the reproducible results reported in the literature.

Table I. Summary of PEEK sulfonation reactions.

Entry	Reaction Time (hours)	Reaction Temperature	Percent Sulfonation
1	186	room temp.	20
2	138	29°C	23
3	110	room temp.	30
4	136	35°C	32
5	136	40°C	32
6	210	room temp.	32
7	136	30°C	35
8	170	room temp.	45
9	138	room temp.	47
10	138	32°C	65
11	138	43°C	68
12	138	33°C	75
13	136	45°C	99
14	136	50°C	150
15	16	95°C	unknown
16	138	92°C	unknown

All of the sulfonated samples reported above were soluble in dimethylformamide (DMF). This is in contrast to literature reports that samples below 30% sulfonation are insoluble in all common solvents and samples above 30% in hot DMF and other polar aprotic solvents.²³ Our samples also showed a greater tendency to dissolve in water than was reported previously. Samples with sulfonation levels above 40% could be completely dissolved in boiling water while the literature reports that 100% sulfonation was necessary for water solubility. The most obvious reason for the differences in solubility would be that some cross-linking occurred in the samples reported in the literature. Elemental analysis data in the literature comparing sulfur to sodium content refutes this however.²³

A second possibility is that the molecular weights of the samples are different. Commercially, PEEK is made in two grades: 450P ($M_w = 37,000$) and 150P ($M_w = 24,000$). The solubility data reported in the literature was for S-PEEK made from the higher molecular weight material. Unfortunately, the molecular weight of our material was not known. To determine the molecular weight of our PEEK powder, samples of P150 and P450 grade PEEK beads were obtained from the supplier and their melting points were determined by DSC. The values obtained for P150 and P450 of 344°C and 340°C respectively were in good agreement with the values obtained from the manufacturer. The melting point measured for the unknown PEEK was 336°C, which suggests a different molecular weight than either of the known samples. An attempt to compare the viscosity of the samples in H_2SO_4 was made by measuring the time required to drain two ml of a solution from a volumetric pipet. All concentrations and dissolution procedures were kept constant. The samples required 192, 192 and 232 seconds to drain for the unknown, P150 and P450

respectively. This gives support to our S-PEEK sample being of lower molecular weight than those reported in the literature, which may explain the differences seen in solubility.

The S-PEEK films used in the electrochemical and thermal studies discussed later were prepared by casting films from solutions of the polymer in DMF. Removal of the DMF required heating the polymer under vacuum for several days at 150°C. A concern arose that under these conditions the acidic sulfonic acid might decompose the solvent to form the dimethylammonium sulfonate salt (Figure 7) as this is reported to occur with Nafion[®].³⁶

Figure 7. Potential reaction of a sulfonic acid with DMF.

The ¹³C NMR chemical shift of the N-methyl protons in dimethylamine and in its ammonium salt are found at 38.2 and 36.2 ppm respectively.³⁷ These assignments were confirmed by running samples of dimethylamine (37 ppm) and the dimethylammonium salt of benzene sulfonic acid (34 ppm). These signals were not present in our S-PEEK spectra. The much greater acidity of Nafion's[®] perfluorosulfonic acid group probably accounts for this reported reactivity.

4.2 Sulfonation of Polyethersulfone

Initial attempts to sulfonate PES were done by dissolving the polymer in sulfuric acid under the conditions used to sulfonate PEEK. The resulting polymer would not form films when cast from DMF, but would instead break up into small pieces. This sulfonation method was abandoned because it was suspected that decomposition of the polymer was occurring.

PES was successfully sulfonated by adding SO₃ dissolved in dichloromethane to a slurry of PES in this solvent at 0°C.²⁰ The degree of sulfonation was controlled by varying the equivalents of SO₃. In this way polymers sulfonated at 10, 18, 28, 41, 49, 53 and 72% were prepared. Like the S-PEEK samples, these readily dissolved in polar aprotic solvents, and clear, flexible films were cast from solutions dissolved in DMF.

The site of sulfonation is known from earlier work,²⁰ and is reported to be ortho to the ether linkages (Figure 8), which is expected based on the relative electronic contributions of the ether and the sulfone groups.

Figure 8. Structure of sulfonated polyethersulfone

4.3 Sulfonation of Polyphenylquinoxaline

Experiments were conducted on two different forms of PPQ, one containing an ether linkage (PPQ) and one without (PPQ-1) (Figure 9). Attempts to sulfonate PPQ-1 by dissolving it in concentrated H_2SO_4 were not successful. The polymer readily dissolved to give a deep purple-red solution, but quenching the reaction into water resulted in the precipitation of unreacted polymer. Using heat to drive this reaction also did not result in sulfonation. It is more likely that this method would be effective on the ether containing PPQ because of its electron donating ability, but these experiments were not tried.

PPQ was successfully sulfonated by a procedure which we have called the “soak and bake” method, which is based on a procedure reported in the patent literature for sulfonating PBI (see next section),³⁰ and on methods for sulfonating aromatic amines found in older literature.³⁸ Soaking the amine in acid results in the formation of the ammonium hydrogensulfate salt and heating (baking) converts this salt to the covalently bound sulfonic acid.

Figure 9. Structures of PPQ and PPQ-1

Initial experiments with PPQ-1 were done by soaking the polymer in 10% H_2SO_4 , which was the concentration that had been used in the PBI patent. At this concentration the polymer did not uptake any acid. Soaking pieces of PPQ film overnight in 20% and 30% H_2SO_4 gave weight uptakes of 0.87% and 2.0% respectively. However, soaking the film in a 35% solution of the acid gave uptakes in excess of 100%. Heating these films at 300°C resulted in films with modest water uptake, evidence that some sulfonation was occurring. Because of material availability, the experiments shifted from PPQ-1 to PPQ.

PPQ was soaked in 50% H_2SO_4 which was the concentration necessary to form the ammonium - hydrogensulfate salt. The membrane was soaked for two hours in order to fully sulfate the membrane; soaking overnight did not have any effect on the final sulfonation level. A bake temperature of 300° C was the minimum required to convert the hydrogensulfate salt to the covalently bonded sulfonic acid. Below this temperature, the post-bake leaching process required many days and resulted in very low levels of sulfonation (based on weight increase). The 90 second bake time was not optimized, but was used because it consistently produced flexible, sulfonated films.

Infrared spectra of dried films of S-PPQ showed new absorption maxima at 1194 cm^{-1} and 1033 cm^{-1} , which are indicative of the sulfonate anion (Figure 10). This indicates that the dried film exists as a zwitterion. The literature reports that protonation of the amino groups of the quinoxaline ring system of unsulfonated PPQ causes a shift from yellow to red,³² and this is

supported by our own observations that PPQ films undergo this color change as acid is taken up to form the ammonium salt. Further support is given by the reversible color change from orange to red as the sulfonated film is alternately dried and rehydrated.

Figure 10. Comparison of the IR spectra of PPQ and 72% S-PPQ

Sulfonation levels ranged from less than one sulfonic acid per monomer to as high as four using the same sulfonation procedure. The reason for this large variation is not clear but may be related to the crude precision of the heating step. Routinely, the sulfonation levels were determined by the weight change between starting material and product. Elemental analysis and acid-base titration were used as a check of the reliability of this method. An S-PPQ sample with 138% sulfonation based on gravimetry, gave levels of 100% for titrimetry and 120% elemental analysis based on C-N-S ratios. The difference between the gravimetric and the elemental analysis data can probably be accounted for by some bound water in the membrane; this is supported by weight loss attributable to water in the TGA experiments. The difference between the titrimetric data and the other methods indicates that some crosslinking may have occurred.

The sulfonation of PBI by the soak and bake method is thought to occur on the fused benzene ring³¹. However, this fused ring of PBI is more reactive towards electrophilic attack than is the equivalent fused ring on PPQ because of the greater electron density of the imidazole ring versus that of pyrazine. Sulfonation of PPQ would be expected to initially occur on the oxygen bearing ring ortho to the electron donating ether linkage. Attempts to investigate this by NMR spectroscopy were unsuccessful due to poor solubility of the sulfonated polymer.

S-PPQ exhibited solubility properties that were substantially different from that of its unsulfonated analogue. While PPQ is soluble in *m*-cresol and chloroform, all of the S-PPQ samples showed some solubility in common polar, aprotic solvents such as DMSO and DMF. Some of these samples were fully soluble, but in other cases part of the polymer dissolved easily, while the remainder would not dissolve even after prolonged refluxing. This suggests that either crosslinking is occurring or that some of the polymer is not being sulfonated. The sulfone

functionality, which would be present in cross-linked samples, was not evident in any of the IR spectrum, so a lack of homogeneous sulfonation in some of the samples is the likely reason for the differences seen in solubility.

4.4 Sulfonation of Polybenzimidazole

Initial attempts to sulfonate PBI were done by dissolving the polymer in concentrated H_2SO_4 . As was the case for PPQ, quenching of the reaction into water precipitated the unreacted polymer. An attempt was also made to sulfonate PBI by passing heated SO_3 vapor through a bed of the polymer in powder form. This too was not successful.

Many attempts were made to sulfonate PBI by the soak and bake method reported in the patent literature.³⁰ Soaking the film for two hours in 10% H_2SO_4 followed by heating the polymer at 500°C for 1-2 min and soaking the films in deionized water to remove all unreacted acid, resulted in films with a sulfonation percentages ranging from 50-110% based on weight uptake alone. Other attempts using this soak and bake method were made by varying the conditions of the above sequence. Soaking time, acid concentration and heating time were all varied in this sequence, with very little affect on the final weight change. The reaction sequence for this soak and bake method consists of formation of the ammonium hydrogensulfate salt during the soaking period and conversion of this salt to the covalently bonded sulfonic acid during the heating. As stated, the site of sulfonation is thought to be on the fused benzene ring of the benzimidazole moiety (Figure 11).³¹

Figure 11. Two step process for the sulfonation of PBI.

All attempts to titrate these films by NaCl exchange revealed no acid within the films. These films were found to be insoluble in polar, aprotic solvents such as DMF, NMP and DMSO and their water uptake and conductivity were actually lower than those of untreated PBI films (see chapter four). This suggests that extensive cross-linking is occurring during the baking process. These

results are corroborated by researchers at Hoechst Celanese Corporation, the holders of the soak and bake patent.³⁹ Attempts to sulfonate PBI by baking the film at lower temperatures resulted in lower weight uptake, but no improvement in the polymer's properties.

The original patent procedure was reported to be done in the absence of oxygen, so it was reasoned that perhaps oxidative cross-linking was occurring. Several attempts were made to perform the baking process in the muffle furnace with the exclusion of oxygen, but the reliability of this method

Figure 12. Comparison of H-ATR infrared spectra of tube furnace reacted S-PBI samples with unreacted PBI.

was judged to be quite low. Instead, the bake process was done inside of a long glass tube, thoroughly flushed with argon and heated with a tube furnace. This identical process was repeated in an air atmosphere and infrared spectra of the films collected by horizontal attenuated total reflectance (H-ATR) were compared to a spectrum of the starting material (Figure 12). The sample baked in air was identical to the sample baked in argon, which indicates that oxygen does not play a role in the mechanism of cross-linking. The one unambiguous difference between the two reacted samples and PBI is the former two have an absorbance at roughly 1040 cm^{-1} which is absent in PBI. The absorbance in the region from $1200\text{--}1150\text{ cm}^{-1}$ is also more intense relative to the rest of the spectrum in the two "sulfonated" samples. These two regions are typical of sulfonate (R-SO_3^-) ions, but this assignment does not help explain the nature of the cross-linking group.

4.5 Comparison of PBI and PPQ Sulfonation

There are two key differences in the soak and bake procedures used for PBI and PPQ. First, much lower acid concentration is required to form the ammonium hydrogensulfate salt of PBI than is required for PPQ. The procedure in the patent literature reported using as low as 2% H_2SO_4 to react with PBI while PPQ-1 and PPQ required 35% and 50% respectively. Second, the temperatures required to convert the salts to the covalently bound sulfonic acids are much different. For PBI a temperature of 450-500°C was necessary, but for PPQ and PPQ-1 300°C was sufficient.

A reasonable explanation for the difference seen between the acid concentration required for uptake is the difference in basicity of the polymers. The pK_a 's of protonated quinoxaline and benzimidazole in aqueous solutions are 0.56 and 5.53 respectively.⁴⁰ This means that PPQ is much less basic than PBI and thus a higher concentration of acid is required for its protonation.

The difference seen between PPQ-1 and PPQ is not so straightforward. The only structural difference between these two is the presence of an ether linkage on PPQ. This electron donating group is enough removed from the site of protonation that it would be expected to have very little influence electronically on the basicity of the polymer. If increased electron density had any effect, it would make the nitrogen more basic and decrease the concentration of acid required, just the opposite of what is observed. The other influence the ether linkage might have would be to make the polymer more flexible and hence more permeable to water uptake. Again, this is opposite of what is observed. Since the chemical nature of the polymers do not explain the differences observed, the differences must come from other factors such as processing or molecular weight. Both polymers were supplied as solutions in m-cresol and cast in our laboratory. The molecular weight of the PPQ is known (see experimental) but that of PPQ-1 is not.

The relative basicities of PPQ and PBI also can be used to rationalize the different baking temperatures required for reaction of their respective hydrogensulfate salts. Since PBI is much more basic than PPQ, its sulfate salt is more tightly held. Therefore, the higher temperature is required to promote the reaction of this more stable salt.

4.6 Synthesis of a Sulfonated Polyimide

All attempts to sulfonate the partially fluorinated polyimide failed. The polymer was supplied as a viscous polyamic-acid solution in NMP. This solution was cast and cured to the fully imidized polymer by heating for 4 hours at 80°C, ramping at 3°C/min to 240°C and holding for 2 hours. A post-cure was also done by ramping at 3°C/min to 357°C and holding this for two hours.⁴¹ Attempts were made to sulfonate this polymer using concentrated H_2SO_4 and 30% oleum as solvents, but this only slightly discolored the solution, leaving the bulk of the material untouched.

The soak and bake method was not successful because the polymer film would not take up any acid.

Attempts were made to sulfonate one of the two monomer components and then polymerize them. Polyimides are usually made by reacting a diamine bearing monomer with a dianhydride bearing monomer. For the partially fluorinated polyimide, these two components are pyromellitic dianhydride (PMDA) and 4'',4'''-(hexafluoroisopropylidene)-bis(4-phenoxyaniline) (4-BTDA) (Figure 13). The diamine readily dissolved in concentrated H_2SO_4 to give a pale green solution, and its sulfonic acid

Figure 13. Structures of diamine (4-BTDA) and dianhydride (PMDA) monomers.

derivative precipitated when the acidic solution was quenched into an excess of cold water. Sulfonation could occur ortho or meta to the amine group. The most reactive site is ortho to the amine, but if this amine is protonated first, then the meta position is more reactive. NMR evidence suggests that the product is a mixture of these two isomers. Attempts to polymerize this with PMDA were unsuccessful. A discussion of the polymerization reaction will come later.

Attempts to sulfonate the dianhydride were also unsuccessful. PMDA, or its hydrolyzed equivalent, 1,2,4,5 benzene tetracarboxylic acid, contains 4 electron withdrawing groups that deactivate the ring to electrophilic aromatic substitution. A sulfonation of a dianhydride is reported in the literature using oleum (percentage not given) at 210°C ,³³ but PMDA did not react in refluxing 30% oleum. An attempt was made to synthesize sulfonated PMDA starting with 1,2,4,5-tetramethylbenzene (durene). The direct sulfonation of durene causes rearrangement of the aromatic methyl groups,⁴² so it was first oxidized with ceric ammonium nitrate to the mono-aldehyde derivative (Figure 14). Attempts to sulfonate this system with concentrated H_2SO_4 , 30% oleum and SO_3 were not successful, probably due to steric hinderance to the reaction, so this route was abandoned.

Figure 14. Attempted synthesis of sulfonated PMDA.

Successful polymerization of a sulfonated diamine with PMDA was done using the lithium salt of the commercially available 2,5-diaminobenzene sulfonic acid (S-DAB). In order to achieve a sufficient degree of polymerization to allow the casting of films, it was necessary to incorporate a second diamine, oxydianiline (ODA), as a comonomer. Flexible films could be cast by reacting the two diamines with a slight molar excess of the dianhydride in ratio's of 4:1, 3:1 and 2:1 ODA:S-DAB (Figure 15). The inherent viscosities of the polyamic-acid solutions of these three random polyimide copolymers in NMP were 1.15, 1.61 and 2.28 for the 4:1, 3:1 and 2:1 copolymers respectively. The increasing viscosity with increasing S-DAB content is probably not an indication of increasing molecular weight but a reflection of the increasing ion content of the polymer solutions.⁴³ A number of unsuccessful polymerization reactions were done prior to finding the conditions necessary for high molecular weight polymer, and a discussion of these is instructive.

Figure 15. Synthesis of sulfonated polyimides.

The first attempts to polymerize S-DAB with PMDA were done with no unsulfonated diamine comonomer. S-DAB, used in its acid form, did not form high molecular weight polymer with PMDA. An analysis of the ¹H NMR of S-DAB (Figure 16) reveals a broad signal centered

Figure 16. ^1H NMR of 2,5-diaminobenzene sulfonic acid (S-DAB).

Figure 17. ^1H NMR of the lithium salt of 2,5-diaminobenzene sulfonic acid (S-DAB-Li).

around 8.4 ppm which is characteristic of aromatic ammonium cations. Any free primary amine, typically found from 2.5-5.0 ppm is obscured by the large water signal from 3-4 ppm. The presence of the ammonium protons indicates that S-DAB is a zwitterion. Thus, one of the amine groups in S-DAB is not available for polymerization. The polymerization of S-DAB with PMDA (with ODA as a comonomer) has been reported in the literature, but in the presence of lithium salts.¹⁸ These lithium salts doubtless are exchanging with the acidic protons in solution. Reacting S-DAB with one equivalent of LiOH, drying and obtaining a ¹H NMR spectrum reveals the appearance of an aromatic primary amine signal at 4.5 ppm and no broad ammonium signal (Figure 17).

Attempts to polymerize the lithium salt of S-DAB (S-DAB-Li) did not result in high molecular weight polymer based on the inability to cast flexible films from the polymer solutions. That the desired reaction was occurring is indicated by IR spectrum of the reaction product which shows two absorptions diagnostic for imides in 5-membered rings at 1780 and 1724 cm⁻¹.⁴⁴ One requirement for high molecular weight polymers is to have sufficiently reactive monomers. For polyimides, electron donating groups increase the reactivity of the diamine and electron withdrawing groups decrease it. Thus, S-DAB-Li is a quite unreactive monomer, which makes formation of high molecular weight polymer very difficult.

Next, attempts were made to copolymerize S-DAB-Li with its unsulfonated analogue, 1,4-diaminobenzene (DAB), in hopes that this more reactive monomer would allow formation of high molecular weight material. Again, an infrared spectrum of the cured film showed imide formation, but no flexible films could be cast from these polymer solutions. In addition, attempts to produce high molecular weight polymer from DAB and PMDA only were not successful. The difficulty of obtaining flexible polyimide films from both meta and para-diaminobenzene has been reported previously.⁴⁵

In contrast, polymerizing PMDA with oxydianiline quickly led to a viscous solution ($\eta_{inh} = 1.22$) from which flexible films could be cast. The success of this formulation, which is sold commercially as Kapton, is due to two factors. The oxygen linkage on the diamine monomer increases the reactivity of this monomer, and the flexible nature of this linkage also lends flexibility to the cast films. Thus, flexible polyimide films containing S-DAB could be prepared using ODA as a diamine comonomer. Infrared spectra of these cast films show an absorbance characteristic of a sulfonate ion at 1030 cm⁻¹ which is not present in films cast from ODA/PMDA based polymers (Figure 18). The ratio of this absorbance to that of its nearest neighbor at 1015 cm⁻¹ increases on going from the 4:1 ODA:S-DAB to the 3:1 polymer and again on going to the 2:1 ODA:S-DAB polymer. It could be suggested that the S-DAB is not polymerizing and that the increasing amount of sulfonate ion is simply an increasing amount of unreacted monomer incorporated into the polymerized film. However, if the S-DAB was simply a non-reacting component in the reaction mixture, then a large excess of dianhydride would be present relative to ODA and high molecular weight polymer would not form.^{46,47}

Figure 18. Infrared spectrum of ODA:S-DAB:PMDA based polyimide with ODA:S-DAB ratio of 4:1.

In order to examine the properties of the sulfonated polyimides, it was necessary to exchange the salt to its free acid form. To do this the films were soaked in 1M HCl overnight then washed with DI water to remove excess acid. This process resulted in the embrittlement of the films. It was also found that soaking these films in water or exposing them to the atmosphere for several weeks caused embrittlement. In contrast, samples that remained in an oven at 105°C for months showed no brittleness. Polymer samples synthesized from ODA and PMDA did not turn brittle after three weeks in 1M HCl. Similarly, a polymer sample made from ODA:DAB:PMDA with a ODA:DAB ratio of 2:1 ($\eta_{inh} = 1.75$) did not become brittle after soaking in water or 1M HCl. It seems obvious that the sulfonated polymer is undergoing hydrolytic decomposition causing lowered molecular weight and embrittlement. What is not obvious is why the sulfonated material is so much more susceptible to this hydrolytic decomposition than its unsulfonated analogue. Comparison of infrared spectra of the polymers before and after embrittlement offered no clue as to the nature of the hydrolysis.

The presence of the sulfonic acid or its salt may affect the susceptibility of the polymer to hydrolysis in several ways. First, the presence of this hydrophilic group increases the water uptake of the polymer (see next chapter) and this water is associated with this hydrophilic group. Because the sulfonic acid is in close proximity to the imide ring this may afford a better opportunity for the imide hydrolysis reaction to occur. However, imides are not known to undergo hydrolysis in neutral water at room temperature.⁴⁸ A second rationale is that the

sulfonic acid, which renders the diamine less reactive because of its electron withdrawing nature, increases the ease of hydrolysis by making the nitrogen a better leaving group. It is possible to draw a resonance structure to delocalize the nitrogen lone pair through an ortho sulfonic acid which would make the amine a better leaving group and therefore more susceptible to hydrolysis (Figure 19). However, the strongly electron-withdrawing nitro group actually inhibited the hydrolysis of an ortho substituted benzamide through steric hinderance of the amide group.⁴⁹

Figure 19. Resonance structures of an ortho-sulfonic acid imide.

The favored rationale for the hydrolytic degradation of these materials is that the sulfonic acid salt inhibits the thermal imidization reaction, leaving some uncyclized polyamic acid which is known to be susceptible to hydrolytic depolymerization.⁴⁷ This inhibition is due to steric hinderance caused by the large functional group in the ortho position. This is the same factor that reduced the rate of hydrolysis of the o-nitrobenzamide discussed previously. This hypothesis is neither supported nor refuted by infrared data. In Figure 18 the broad imide absorbance at 1713 cm^{-1} obscures any residual acid or amide signal that would be found from 1700 cm^{-1} to 1650 cm^{-1} . Hydrolytic and curing studies with the analogous monomers as models would be a good way to investigate these possibilities.

4.7 Summary

Five different families of high temperature polymers were sulfonated by a variety of methods. The sulfonation of polyether(ether)ketone and polyethersulfone was accomplished by literature methods and produced materials with a broad range of acid contents. Polyphenylquinoxaline films were sulfonated by a novel solid phase synthetic procedure which has been called the "soak and bake" method.⁵⁰ This represents the first report of this sulfonic acid containing polymer. Attempts to sulfonate polybenzimidazole by the soak and bake method resulted in insoluble, cross-linked films. Higher baking temperatures were required for PBI than for PPQ. This is probably due to the greater stability of the ammonium hydrogensulfate salt of PBI which in turn is due to the greater basicity of the imidazole nitrogen. Sulfonic acid salt bearing polyimides were synthesized by polymerization of appropriate monomers. These materials displayed unusually poor hydrolytic stability. The best explanation for this is that the sulfonic acid salt sterically hinders the cyclization reaction leaving residual polyamic-acid which is susceptible to hydrolysis.

5.0 ELECTROCHEMISTRY

The experimental results discussed in this section all relate to the performance of a proton exchange membrane in an electrochemical cell. The purpose of these experiments is twofold. First, to measure the parameters that affect the electrolyte performance and second to gain an understanding of the structure property relationships in order to guide further research. The two most important parameters, water uptake and conductivity are directly related because water is the charge carrier in these materials. Water uptake will first be discussed apart from its influence on conductivity and then along with other properties as they relate to the ionic conductivity of the membrane. The influence of temperature on conductivity in a saturated environment will also be discussed. Current - voltage behavior and coulombic efficiency in electrolytic cells will also be discussed in this chapter. Unless stated otherwise, the data presented in this chapter represents individual experiments, not average values.

5.1 Water Uptake

The water uptake data for the five polymers is presented in Table II. The sulfonic acid content of the polymers is given in terms of equivalent weight, the number of atomic mass units per acid group, with lower equivalent weight meaning a higher acid content. The water uptake is given both as the percent weight increase relative to the initial weight and as the number of water molecules per acid group (n). These representations allow more meaningful comparisons to be made. Water uptake results in the following discussion will be made in these terms.

The general trend observed for each of the different polymers is increasing water uptake, by weight, with increasing acid content. This is most clearly seen for the S-PEEK, S-PES and S-DAB:ODA samples. The S-PPQ and S-PBI samples show some variability which is probably due to poorly controlled cross-linking in these samples.

Water uptake results have been reported for Nafion[®], S-PES and S-PEEK in the literature. Nafion[®] 's' water uptake ($n=11.5$) agrees very well with the value ($n=12$) reported in the literature for samples dried in an oven at 105°C.⁵¹ Greater water uptake ($n=21$) is reported for Nafion[®] films that undergo no thermal treatment. For the S-PES samples, the variation in water uptake with changing equivalent weight was less than reported previously. Previously, uptake values of $n=4.8$ and $n=11.8$ were reported for S-PES samples with equivalent weights of 783 and 381 respectively.²⁰ This is a much broader range of values than is reported in Table 2. In contrast, the lower equivalent weight samples in our study were soluble in boiling water, while the samples reported in the previous study were not.

The only water uptake data reported for S-PEEK is for its sodium salt analogue. Submerged samples equilibrated at room temperature had uptakes ranging from $n=8$ (for EW=800) to "indeterminably large" at EW=390 (100% sulfonated).²³ The water uptake reported here for similar samples is much higher, in excess of $n=20$.

Table II: Water uptake of sulfonated polymers.

Sample	Equivalent Weight (g./equiv.)	H ₂ O Uptake (wt. %)	H ₂ O's/SO ₃ H (n)
20% S-PEEK	1520	24	22
30% S-PEEK	1040	34	22
45% S-PEEK	720	72	33
65% S-PEEK	523	149	49
10% S-PES	2400	3.6	4.8
17% S-PES	1444	4.7	3.8
29% S-PES	880	14	6.8
41% S-PES	646	18	6.4
49% S-PES	553	21	6.4
53% S-PES	518	22	6.3
72% S-PES	402	33	7.4
72% S-PPQ	880	14	6.8
178% S-PPQ	404	42	9.4
219% S-PPQ	343	28	5.3
280% S-PPQ	285	51	8.0
4:1 S-DAB/ODA	1904	7.8	8.2
3:1 S-DAB/ODA	1522	9.5	8.0
2:1 S-DAB/ODA	1140	14	8.9
84% S-PBI	447	22	5.4
95% S-PBI	404	16	3.6
110% S-PBI	360	18	3.6
115% S-PBI	348	23	4.4
Nafion®	1100	19	11.5

Although in this case water uptake is being studied on the free acid. The effect of having a sulfonic acid relative to a sulfonic acid salt on water uptake is not clear. The difference in the molecular weights of the S-PEEK samples used in our study and in the referenced one may also account for the different water uptake results. Just as the lower molecular weight may influence

the relative solubility of the materials (see previous section), it may also influence the water uptake properties (see below).

The S-PEEK membranes show unusually high water uptake relative to the other polymers. A plot of water uptake versus equivalent weight makes this very clear (Figure 20). According to corporate literature, water uptake for unsulfonated PEEK is 2.2% indicating some intrinsic affinity. This corresponds to only 0.35 water molecules per repeat unit, however, not enough to explain the difference between S-PEEK and the other sulfonated polymers. With the exception of Nafion[®], all of the other polymers have water uptakes less than $n=10$, and for most of the sulfonated polymers the value of n falls within a fairly narrow range, roughly 5 to 9. This suggests that these waters are all associating with the acid groups. The much higher water uptake of S-PEEK suggests that some of its water is located outside these highly polar regions (see below). All of the S-PEEK samples could be dissolved by heating them in water, with the temperature required for dissolution varying with the equivalent weight. As these membranes were heated in water they went from clear, swollen film to a cloudy gel-like state just prior to dissolution. With careful heating it was possible to isolate the polymer in this gel like state. Once reached, the polymer would remain a gel upon cooling to room temperature in water. These gels were mechanically very unstable and not suited for use in an electrochemical cell.

Figure 20. Equivalent weight versus water uptake for sulfonated polymers.

The factors behind S-PEEK's unusually high water uptake may be related to the microstructure of the polymer. The water taken up by acid containing polymers is normally associated directly with the acid groups. Much work has been done on the microstructure of ion containing polymers. Small-angle x-ray (SAX) done on Nafion[®] have shown that the ions are not evenly dispersed but aggregate together to form clusters.⁵² The microstructure of Nafion[®] consists of two regions

made up by the ion clusters and by the perfluorocarbon polymer backbone. The water associates with the ionic region and even prolonged exposure to boiling water will not drive the perfluorocarbon chains apart, and dissolve the polymer. SAX studies also report the presence of ion clusters in S-PEEK.⁵³ No such studies have been reported for the other sulfonated polymers used in this study. Again, water taken up by S-PEEK will first associate with the ionic regions of the polymer. Upon heating, the water is able to fill in between the organic backbone of the polymer, leading to gel formation and eventually dissolution.

5.1 Conductivity

The conductivity of a sample of each of the five sulfonated polymers was determined at room temperature (20°C). Dry samples of these polymers were equilibrated in water overnight and weighed to determine water uptake. The volume of these water swollen films was also determined using a dial caliper to measure their dimensions. The film was mounted in an electrochemical cell and the resistance was monitored until it stabilized. Conductivity was calculated from the resistance and the dimensions of the film. This same procedure was applied to a sample of Nafion® for comparison.

The water uptake and proton conductivity of the six polymers is shown in Table III. That these values represent proton conductivity and not electrical conductivity is a reasonable assumption because none of the polymers possess uninterrupted conjugation along the polymer chain. This is supported by coulombic efficiency measurements made by comparing the hydrogen evolved in an electrolytic cell to the measured current (as will be discussed later).

Table III. Conductivity data of sulfonated polymers at 20°C.

Sample	Equivalent Weight	# H ₂ O's/SO ₃ H	Conductivity (Ω-cm) ⁻¹
S-PEEK	1332	34	2.9 x 10 ⁻³
S-PES	880	6.8	1.8 x 10 ⁻⁴
S-PPQ	285	8.0	9.8 x 10 ⁻³
S-PBI	447	5.4	3.9 x 10 ⁻⁶
S-PI	1134	8.7	3.8 x 10 ⁻⁵
Nafion®	1100	11.5	9.2 x 10 ⁻²

The range of conductivity values spans more than five orders of magnitude. The lowest value, for the S-PBI sample, is readily explained by cross-linking. This proton conductivity is actually lower than that measured for unsulfonated PBI. This result, along with the total lack of solubility of the sulfonated films, strongly indicates that cross-linking has occurred.

The conductivity of the sulfonated polyimide is also quite low. However, this material is actually the lithium sulfonate, so lithium ion conductivity is being measured and not protonic. Lithium ion conduction occurs through simple ion transport, while proton conductivity involves water as a carrier. The ionic conductivities of H⁺ and Li⁺ in water are 349.6 and 38.7 S cm²/mol. These

differences make comparison of the ionic conductivity of the polyimide with the ionic conductivities of the other polymers invalid.

Attempts to rationalize the conductivity of the other four samples (including Nafion®) can be done by comparing their water uptakes and their acid contents. The relative acid content of the polymers has been compared in terms of their equivalent weights. A better way of looking at this factor is from the perspective of the density of the sulfonic acid groups in the water swollen membrane. This value, $\rho\text{SO}_3\text{H}$, has units of meq/cm^3 , which can be calculated from the sulfonation level, the dry weight and the wet volume. The relevant data for S-PEEK, S-PES, S-PPQ and Nafion® are given in Table IV.

There is not a good correlation between either acid density and conductivity or between water uptake and conductivity if each of these factors is considered singly. The higher conductivity of S-PEEK and S-PPQ in comparison to S-PES can be rationalized by their much greater water uptake and acid density respectively. Comparison of S-PEEK and S-PPQ is difficult because the relative importance of water content and acid density is not known. The difference in their conductivities is dramatic, almost three orders of magnitude, although Nafion's® greater water uptake makes this comparison somewhat difficult. A better comparison can be made with conductivity data for Nafion® found in the literature.

Table IV. Acid density, water uptake and conductivity of sulfonated polymers at 20°C.

Sample	Sulfonic Acid Density (meq/cm^3)	# H_2O 's/ SO_3H	Conductivity ($\Omega\text{-cm}$) ⁻¹
S-PEEK	0.65	34	2.9×10^{-3}
S-PES	1.30	6.8	1.8×10^{-4}
S-PPQ	2.75	8.0	9.8×10^{-3}
Nafion®	1.53	11.5	9.2×10^{-2}

The conductivity of Nafion® 117 with nearly identical water content to S-PES's, roughly 6 waters per acid group, is $3 \times 10^{-2} \text{ S}/\text{cm}$,⁵⁴ still more than two orders of magnitude higher than S-PES. Nafion® is also almost an order of magnitude more conductive than S-PPQ despite the latter's much higher acid content, and Nafion® is a factor of thirty more conductive than S-PEEK despite S-PEEK's much greater water content. The high conductivity of Nafion® in comparison to these three aromatic polymers cannot be explained only in terms of water uptake or acid content.

This greater than expected conductivity of Nafion® can also be seen by comparing it to a series of S-PEEK materials at 20°C (Figure 21). A graph of conductivity versus exchange capacity for the S-PEEK series shows a linear relationship, but Nafion's® conductivity is an order of magnitude above this. The conductivity values in this case are taken from thermoconductimetric analysis curves (see later) with the values at 20°C extrapolated or interpolated from these curves.

Figure 21. Protonic conductivity versus exchange capacity at 20°C.

One explanation for Nafion's® greater conductivity may be found in its microstructure. Nafion®, and other ionomers, which have been studied by small-angle x-ray studies have regions of high ion density, known as clusters. In the case of Nafion®, these highly hydrophilic clusters are surrounded by regions of hydrophobic perfluoroalkyl chains. These clusters have been proposed to form networks, or ion channels, through the material which may greatly increase the rate of proton transport, i.e. conductivity (Figure 22).⁵² Although S-PEEK is reported to possess ion clusters, no detailed descriptions of the microstructures of aromatic based ion containing polymers are available. There is no data to suggest that these materials possess any channel-like morphology which would enhance the rate of proton transfer. The unique morphology of Nafion® is a possible, but not a proven, explanation for its exceptional conductivity.

Figure 22. Model of ion channels in Nafion®.

The greater conductivity of Nafion® compared to the other sulfonic acid containing polymers can be rationalized if the influence of acid strength is considered. The acid dissociation constants of S-PEEK, S-PES and S-PPQ were measured and are compared to Nafion's® (in terms of pKa) in Table 5. Normally, sulfonic acids are referred to as "strong acids". For example, an introductory organic text book states: "Sulfonic acids are strong acids, as strong as typical mineral acids."⁵⁵ A second text states: "Sulfonic acids, ArSO_3H , are related to sulfuric acid and, like sulfuric, are strong acids."⁵⁶ These statements, meant as generalizations, are not true. The simplest aromatic sulfonic acid, benzene sulfonic acid has a pKa of 0.70 (concentration not reported).⁵⁷ Assuming a one molar solution, approximately 36% of the acid groups are dissociated. The pKa's of the sulfonic acid polymers determined here are all much higher, meaning the acids are less acidic. The sulfonic acid groups on S-PEEK, S-PES and S-PPQ are all located on rings ortho to an electron-donating ether substituent. This electron donating destabilizes the conjugate base, the sulfonate anion, relative to an unsubstituted sulfonate anion. The presence of a second electron donating ether substituent in the S-PEEK molecule lowers the acidity even further. Even more dramatic examples of this are known in the literature. For example, m-aminobenzenesulfonic acid has a pKa of 3.73 in water.⁵⁷ These pKa's reported in Table V translate into 3.9%, 7.1% and 6.9% of the acid groups being dissociated at equilibrium for S-PEEK, S-PES and S-PPQ respectively. When this percentage is factored in, the actual ion density in these polymers drops significantly (Table 5).

In contrast to the aromatic sulfonic acids, Nafion® truly is a strong acid. Its acidity is comparable to the super-acid triflic acid,⁵⁸ $\text{CF}_3\text{SO}_3\text{H}$, which has a pKa of -5.1.⁵⁹ To put this value in perspective, an acid that is 99% dissociated has a pKa of -2 and one that is 99.9% dissociated has a pKa of -3. Therefore Nafion® is essentially 100% dissociated and its ion density is virtually the same as its sulfonic acid density. The significance of this difference in acidity between Nafion® and the aromatic sulfonic acids can be seen by comparing their ion densities in Table V. These values assume that the dissociation of the acid in a membrane is the same as in a dilute

Table V. Ion densities and pKa's of sulfonated polymers at 20°C.

Sample	Sulfonic Acid Density (meq/cm ³)	pKa	Ion Density (meq/cm ³)
Nafion [®]	1.53	see text	1.53
S-PEEK	0.65	2.80	0.025
S-PES	1.30	2.27	0.092
S-PPQ	2.75	2.29	0.189

solution (see below). Nafion's[®] ion density ranges from one to two orders of magnitude greater than the aromatic sulfonic acids. This is directly reflected in the conductivities of these materials. Although the water content of the materials is also clearly important, much of Nafion's[®] superior conductivity can be attributed directly to its greater ion density, and this is directly related to its greater acidity.

One final point worth mentioning is the measured pKa's of the sulfonic acids and their relation to the acids in a polymer membrane. The pKa's in Table V were measured as dilute solutions (10^{-3} - 10^{-2} M in acid). In contrast, the sulfonic acids in the membrane are solvated by water molecules ranging from roughly 7 to 30 H₂O's per acid group. Weak acids dissociate less (have a higher pKa) in more concentrated solutions,⁶⁰ so the acid dissociation constants may actually be lower in the membranes than reported here. Therefore the relative acid strengths of the polymers becomes even more significant. Recommendations related to the above discussion of acid strength will be made at the conclusion of this dissertation.

5.3 Thermoconductometric Analysis:

The change in conductivity as a function of temperature was investigated for the sulfonated polymers. This study, which has been termed thermoconductometric analysis (TCA), was done to provide information on the relative conductivity of the different polymers at different temperatures and to provide a measure of the temperature limits of each polymer.

Initially these experiments were run by suspending the conductivity cell in the reactor above the water. Thus the moisture was supplied by steam. This method was abandoned because the polymer film began to lose water above 100°C, resulting in a loss of conductivity. Successful experiments were performed by submerging the cell in water. A summary of these experiments is given in Table VI.

The $T_{\max}$ values in Table 6 represent the temperature at which maximum conductivity was obtained and $\sigma_{\max}$ is that maximum conductivity. For all of the S-PEEK and S-PES samples, $T_{\max}$ represents the temperature

Table VI. Summary of thermoconductiometric analysis.

Sample	$T_{\max}$ ($^{\circ}\text{C}$) ¹	$\sigma_{\max}$ (S/cm) ²	E_a (kcal/mol) ³
S-PEEK (20%)	112	0.023	4.03
S-PEEK (30%)	109	0.023	4.84
S-PEEK (45%)	92	0.021	3.24
S-PEEK (65%)	82	0.034	2.32
S-PES (18%)	120	0.008	2.53
S-PES (28%)	127	0.065	5.65
S-PES (41%)	110	0.037	2.52
S-PES (53%)	63	0.020	2.93
S-PPQ (91%)	180 ⁴	0.130	3.82
Nafion [®]	169 ⁴	0.250	1.87

- 1 Temperature of maximum conductivity
- 2 Maximum conductivity
- 3 Activation energy from Arrhenius plot
- 4 Experiment stopped before failure occurred

just prior to complete failure of the membrane. During the experiments this failure was evident because the resistance went from the lowest value recorded during the experiment to greater than the maximum measurable by the impedance bridge (1100 k Ω); the conductivity peaked and then dropped off scale. In these cases, no membrane remained in the Teflon cell at the conclusion of the experiment. The S-PPQ and Nafion[®] samples did not undergo complete failure. These experiments were stopped at 180 $^{\circ}\text{C}$ in order to avoid damaging the Teflon cell. These two membranes were intact after the experiment.

The complete failure of the S-PEEK and S-PES membranes suggests either significant chemical decomposition or simple dissolution. No evidence of charred polymer was found which would indicate chemical decomposition, and it would be very surprising for a high temperature polymer to undergo decomposition at these temperatures. $T_{\max}$ for the S-PEEK series and the S-PES series generally decreases with increasing sulfonation level which suggests that they are simply dissolving in the water with increasing acid content causing dissolution to occur at lower temperatures. This line of reasoning is supported by the water uptake studies discussed earlier.

Figure 23. Conductivity verses temperature and saturated vapor thermogravimetric analysis of 30% S-PEEK.

Thermogravimetric analysis (TGA) done under saturated vapor conditions confirm that S-PEEK does not undergo significant decomposition at the failure temperatures seen in these experiments. These TGA experiments will be discussed in detail in chapter six, but one example is given here to illustrate the point. For 30% S-PEEK, T_{max} is 109°C by TCA, but no significant weight loss is seen until 200°C is reached in the TGA study (Figure 23). Although T_{max} does not provide information about chemical stability, it does set an upper working temperature limit for the membranes that underwent complete failure. In order to be run at higher temperatures these materials would need to be made more resistant to dissolution. Chemical cross-linking would accomplish this, but the only reasonable functionality for this is the sulfonic acid group, so cross-linking would require a trade-off between conductivity and resistance to solubility.

The maximum conductivities of the polymers recorded during the TCA runs have a narrower range than do the conductivities measured at room temperature (Table 4). In both cases Nafion® is the most conductive and S-PES is the least, but at room temperature Nafion® is 511 times more conductive than S-PES while the difference in their σ_{max} values (using the least conductive S-PES sample) is only a factor of 31. A second example is that while at room temperature Nafion® is about ten times more conductive than S-PPQ, their maximum conductivities differ by only a factor of two. All of the aromatic materials show a greater increase in conductivity per unit increase in temperature than does Nafion®. This is directly reflected in the activation energies as will be discussed below. In practical terms this means that higher operating temperatures will make the aromatic materials more competitive with Nafion® from a conductivity standpoint. This data does not indicate if electrochemical cells can be run at these temperatures however.

The activation energies (E_a) in Table 6 were obtained from the slopes of the Arrhenius plots which are plots of the log of conductivity versus reciprocal temperature in degrees Kelvin. The Arrhenius equation: $\log \kappa = \log A - E_a/2.30RT$ represents the equation of the trendline for these data plots with the slope of the line being $-E_a/2.3R$ where R is the gas constant. The activation energy can be easily solved for once the slope of the line is known. Arrhenius plots are included for the S-PEEK series (Figure 24), the S-PES series (Figure 25) and for S-PPQ and Nafion[®] (Figure 26). The computer generated trendlines used in calculating the activation energies are not included for purposes of clarity.

Physically E_a represents the energy barrier to proton transport through the membrane. The value obtained for Nafion[®] of 1.87 kcal/mol is in reasonable agreement with the literature value of 2.25 kcal/mol.⁶¹ The energy barrier to proton transport should decrease with increasing ion density, so the activation energies should decrease with increasing acid content. This trend is generally seen in the S-PEEK series, but not in the S-PES one.

Figure 24. Arrhenius plot of S-PEEK conductivity versus temperature data.

Figure 25. Arrhenius plot of S-PES conductivity versus temperature data.

Figure 26. Arrhenius plot of S-PPQ and Nafion® conductivity versus temperature data.

Because Nafion[®] is the most conductive of the materials, it is reasonable to assume that it would have the smallest energy barrier to proton transport and therefore the smallest activation energy. This is in fact the case. However, the other materials don't follow this expected behavior. The S-PEEK samples show increasing conductivity with increasing acid content (see Figure 21), but their activation energies do not decrease accordingly. Based on this it is important to consider just how good a measure of activation energy this method provides. In order to provide a good value for the activation energy using Arrhenius plots, the changing variable in question, conductivity, must vary only with temperature. If other variables are present the value becomes suspect. For the aromatic materials two other variables are also present in these experiments. The first variable is water content. The water uptake of the membranes, particularly of the S-PEEK's and S-PES's increases dramatically with temperature. As discussed previously, this uptake is sufficient to dissolve the polymer. Since water is the proton carrier in these materials, increasing the temperature, and therefore the water content of the membrane, will increase the conductivity values. The second variable is ion content. The acidity of a weak acid increases with temperature by roughly an order of magnitude per 100°C, so as the temperature increases so will the ion content of the film. This will have a strong influence on the conductivity measurements and therefore on the measured activation energies.

These effects likely did not influence the activation energy determined for Nafion[®]. Nafion[®] is fully ionized at room temperature, so an increase in temperature will have no effect on the ion density. Nafion[®] also does not swell to the point of dissolution, but seems to reach a maximum water uptake after boiling in water for several hours. Samples swelled in boiling water retain this swelling when cooled to room temperature.⁶² Since the Nafion[®] membrane was pretreated in this way prior to being placed in the conductivity cell, increasing the temperature during the experiment likely did not increase the water uptake. The lack of water content and acidity effects make the slope of the Arrhenius plot for Nafion[®] a more reliable measure of the activation energy associated with proton transport. If both acidity and water content are increasing with temperature in the TCA's of the aromatic materials then the E_a 's determined for them are greater than the true values. This suggests that Nafion's[®] low E_a relative to the other materials may not be solely due to its superior proton conductivity.

5.4 Current - Voltage Behavior

The current-voltage behavior of an electrochemical cell is a measure of the performance of that cell. In an electrolytic cell, performance is evaluated by the current density generated at a given voltage. In a water electrolysis cell, this current density is directly related to the amount of hydrogen produced. The intent of the work presented in this section is not to demonstrate that superior water electrolysis cells can be made using the aromatic electrolyte materials. That task would involve optimizing the entire membrane electrode assembly and would require a significant engineering effort. The most important information presented in this section is the coulombic efficiency of water electrolysis cells containing the aromatic electrolyte materials. The significance of this data will be made clear as the data is presented. Additionally, current-voltage curves generated for S-PEEK as a function of temperature and acid content will be presented and compared to the current-voltage behavior of Nafion[®].

Coulombic efficiency compares the measured cell current to the output of hydrogen in the following way. The number of moles of hydrogen produced over a given time period can easily be determined from its volume by the ideal gas law. The number of moles of electrons flowing through the cell over this same period of time can be determined from the current since a coulomb is equal to an amp/sec and there are 96,500 coulombs/mol. Equating the moles of electrons to the moles of hydrogen produced (remembering that two moles of electrons are required for each mole of hydrogen) yields the coulombic efficiency, with the actual value being moles H_2 /(2 x moles electrons).

Figure 27. Current-voltage behavior and coulombic efficiency of 20% S-PEEK at 80°C (x = current - voltage plot, + = coulombic efficiency).

The coulombic efficiency of 20% S-PEEK at 80°C is presented over a range of voltages in Figure 27. Over a wide potential range this efficiency is in excess of 95%. The key information that this provides is that the flow of current is accounted for almost exclusively by the flow of protons. As mentioned earlier, this is as expected based on the structure of S-PEEK, but it is important as evidence that the conductivity results presented earlier are the result of proton conductivity. The coulombic efficiencies of other materials show similar results. A sample of S-PES and one of S-PPQ had coulombic efficiencies of 100% and 93% respectively at 3.0 volts.

Figure 28. Water electrolysis current-voltage curves at 80°C.

The electrolytic current-voltage (I-V) curves for Nafion® and S-PPQ at 80°C are shown in Figure 28. These curves are shown to illustrate the typical features of electrolytic I-V curves. Initially, the curves show a rapid increase in voltage with little increase in current density, the current in this region is limited by the activation barriers of the electrochemical reaction. Next, the curves become linear, and efficiency losses are due to resistance across the polymer membranes. Finally, the curves begin to curve upward as the current becomes limited by the rate of diffusion of electroactive species to the electrode surface. Nafion® exhibits higher current densities than S-PPQ in this case because the initial activation barrier is overcome at a lower voltage. This may be due to more intimate contact between Nafion® and the electrodes than for the stiffer S-PPQ.

One of the trends that was studied was the influence of acid content on current density. One would expect that increasing the acid content of a specific polymer would increase its current-voltage performance, and this was the case. The current-density at a given voltage increases with increasing acid content for S-PEEK at several different temperatures. This is shown for samples tested at 60°C in Figure 29. This same trend was seen in the S-PES samples tested.

Figure 29. Current-voltage behavior of S-PEEK membranes at 60°C.

A direct relationship between current density and temperature was expected and seen in the samples tested. The applied potential acts as a driving force for proton transport, so if this force, the voltage, is held constant, the effect of temperature can easily be determined. As expected, increasing the temperature also increased the current density. Figure 30 depicts this relationship at two different voltages for 30% S-PEEK. Note that the y-axis is current and not current density. The drop in current above 90°C indicates that the membrane is beginning to fail due to solubility in the near boiling water.

Figure 30. Temperature versus current plots for 30% S-PEEK.

5.5 Summary

The water uptake of the sulfonated polymers was measured at room temperature with most of the materials having a value of $n < 10$. All of the S-PEEK membranes were exceptions to this with n values ranging from 22 to 49. The room temperature proton conductivity was measured for the sulfonated derivatives of each of the five candidate polymers and Nafion®. The conductivity of Nafion® ranged from one to nearly five orders of magnitude greater than the aromatic materials. The differences in conductivity could not be rationalized by differences in the water uptake and acid content of the membranes. The microstructure of the polymers may be an important factor as has been suggested previously, but the much greater acidity of Nafion® relative to the aromatic sulfonic acids seems to be the most significant factor.

Conductivity versus temperature experiments were run on materials submerged in water. The rate of increase of conductivity with temperature was determined from Arrhenius plots with Nafion® having the smallest activation energy. This was attributed to the increase in acidity and the increase in water content of the aromatic materials with increasing temperature, both variables that were not present in Nafion®. The S-PEEK and S-PES samples reached maximum conductivity just prior to total failure of the membrane. This failure was due to dissolution of the polymers in the hot water. This failure was not seen in Nafion® or S-PPQ.

Electrolytic current-voltage curves of the membranes showed the expected trends of increasing current with increasing temperature or increasing acid content at constant voltage. Coulombic

efficiency measurements were nearly 100% for all of the materials. This supports the reasonable assumption that the conductivity measurements are due to proton transport.

6.0 THERMAL CHARACTERIZATION

The thermal stability of high temperature polymers in an inert atmosphere and in air has been extensively studied. The thermal stability of sulfonic acid derivatives of these materials is not well studied and the thermal stability of high temperature polymers and their sulfonic acid derivatives in a hydrolytic environment is virtually unknown. The results presented in this section will compare the thermal stability of the sulfonated polymers with their unsulfonated analogues in both an inert atmosphere and in saturated vapor. An analysis of the decomposition products of both sulfonated and unsulfonated materials will also be presented. The saturated vapor experiments were run for 24 hours in a high pressure reactor with excess liquid water so that at a given temperature both liquid and vapor phase water were present. The superheated steam experiments were run for six hours using boiling water to generate the one atmosphere of steam pressure and a tube-furnace to superheat that one atmosphere of steam to the desired temperature.

One important assumption that should be stated is that stability based on weight loss only assumes that volatile components are being evolved. The significance of materials that decompose but do not lose weight or lose very little weight is not considered in these studies.

6.1 Thermogravimetric Analysis

The engineering polymers used in this study were chosen based on their stability in 0.5 atmosphere of steam under both oxidizing and reducing conditions.⁵ However, a saturated water environment is required to maintain the conductivity of these sulfonic acid based PEM electrolytes. Therefore knowledge of their chemical stability under these conditions at a range of temperatures is essential. Conventional thermogravimetric analysis cannot be done in a saturated vapor environment because very high pressures are required. The solution to this problem was to determine the weight loss of the polymers after a twenty-four hour exposure to saturated conditions. The weight loss curves were generated by running experiments every 25°C.

The thermogravimetric data from the saturated vapor tests are given for both the unsulfonated (Figure 31) and sulfonated (Figure 32) polymers from 150-225°C. These tables represent average values taken from multiple decomposition experiments. Figure 31 also includes the saturated vapor pressure at each temperature. All of the polymers showed the expected decrease in weight with increasing steam temperature (and pressure) with the only anomaly being found in the data for PEEK in going from 150 to 175°C.

Figure 31. Weight change versus temperature for base polymers in saturated vapor for 24 hours.

Figure 32. Weight change versus temperature for sulfonated polymers in saturated vapor for 24 hours.

In most cases the weight loss of the sulfonated polymer was greater than that of its unsulfonated analogue at a given temperature. This is not surprising given that aromatic sulfonic acids can be rapidly desulfonated in dilute aqueous solutions with the passage of a current of steam.⁶³ What is

significant is that even the unsulfonated polymers showed significant weight loss at temperatures of 200-225°C. This is well below the 300°C minimum stability criteria that was used in selecting these polymers for further study. This indicates that superheated, low-pressure steam stability is not a good predictor of stability under high-pressure, saturated vapor conditions.

For almost all of the materials tested, there is greater decomposition in the sulfonated derivative than in the unsulfonated analogue. The greater weight loss of the sulfonated derivatives can reasonably be attributed to the loss of the sulfonic acid group. The one polymer that does not follow this relationship is PPQ. This polymer has significantly greater weight loss at 200°C and 225°C than does S-PPQ. This difference may be due to the modest amount of cross-linking that occurs during the sulfonation of PPQ with the cross-linking hindering the loss of polymer fragments by requiring a greater number of bonds to be broken in order to completely sever a fragment. However this is not supported by the results of PBI and S-PBI which follow the general trend despite the extensive cross-linking of the sulfonated derivative.

Several of the polymers studied here are made by condensation polymerization, so it is perhaps not too surprising that they would show some hydrolytic susceptibility. The one polymer that stands out in this regard is the sulfonated polyimide (S-PI) (Figure 32). Its very poor resistance to decomposition mirrors the embrittlement seen when the polymer was exposed to moisture at room temperature as discussed in chapter three. This same embrittlement was seen in the S-PI after the saturated vapor decomposition experiments. That the very high weight loss is not due simply to hydrolytic susceptibility of the imide group is evident in that the unsulfonated material does not show this same degree of decomposition (Figure 31).

It is impossible to determine an exact decomposition temperature for these materials based on the weight loss curves because each curve is defined by a small number of points. The temperature at which 5% of the weight was lost was chosen as a basis for comparison between the samples run in saturated vapor and the same samples run in helium (Figures 33 and 34). The 5% weight loss in saturated vapor was determined by interpolation between the plotted points rather than by trying to produce a smooth "least-squares" curve. The 5% weight loss under an inert atmosphere was readily determined from the continuous curves. All of the sulfonated polymers are very hygroscopic, so an initial weight loss was seen due to the loss of water in these curves. The 5% weight loss in these cases was determined excluding the loss of water.

Figure 33. Temperature of 5% weight loss in helium.

Figure 34. Temperature of 5% weight loss in saturated vapor for 24 hours.

Under both sets of conditions the unsulfonated polymers had greater stability than their ionic derivatives; the only exception being for PTFE and Nafion® in saturated vapor. Notice that in using 5% weight loss as the stability criteria, PPQ is more stable than S-PPQ under saturated conditions, but as stated previously, S-PPQ has lower weight loss than PPQ under saturated

conditions at 200°C and 225°C. This illustrates the importance of stating the stability criteria when declaring one material more stable than another.

One significant difference between the inert and vapor conditions is the magnitude of the difference in temperatures at which 5% weight loss occurs between the sulfonated and unsulfonated materials. In helium this difference is in the range of 100-150° C in all but two cases; one of those cases, the polyimide pair, is likely due to the ionomer being tested in the lithium salt form instead of as the free acid. The reason for the exceptional stability of the S-PPQ under both wet and dry conditions may be due to some cross-linking as was stated previously. In contrast, with the exception of the polyimide pair, the greatest difference between a pair of sulfonated and unsulfonated polymers in saturated vapor is 20° C. The range of stability's for the sulfonated polymers is also much different in helium than in saturated vapor. In helium there is a range in excess of 200° C (305° C for Nafion® to 522° C for S-PPQ) among the sulfonic acid polymers, but under saturated vapor the temperature range is only 43° C. This makes clear the harshness of the saturated vapor conditions at the temperatures tested. Note that because of the different time scales involved in the two TGA methods, a direct comparison of stability's is not justified, but a comparison of trends is. Finally, under saturated vapor Nafion® is the best performing of the sulfonated polymers, while under inert conditions it is the worst. It is obvious from Figures 33 and 34 and from the above discussion that polymer stability in an inert atmosphere is not a good predictor of stability under saturated vapor conditions.

Two conclusions can be drawn from the results discussed above. First, polymers that are engineered for their resistance to thermal decomposition do not maintain that resistance under the severe saturated vapor conditions employed in these studies. Both sulfonic acid bearing and unsulfonated polymers showed significant decomposition at temperatures at or below 225°C. Second, and most importantly, none of the polymers tested in this study are suitable for use in a PEM based electrochemical cell run at the moderately high temperatures of 200°C - 300°C that are desirable as discussed previously.

6.2 Superheated Steam Decomposition Analysis

When evaluating the stability of polymeric materials, it is desirable to know how the materials decompose. The nature of their decomposition products is the usual means of obtaining this information. In decomposition studies done in air or in an inert gas these products can be analyzed directly during the TGA experiment by coupling the instrument to an infrared or mass spectrometer. The steam environment of the degradation experiments performed in this study made this approach impossible. Instead, decomposition experiments were run for six hours under one atmosphere of superheated steam as described previously. The results of these experiments are presented below.

6.2.1 General Results

A summary of the superheated steam experiments is given in Table VII. Because the polymers studied are fairly diverse in structure, the details of their decomposition are best treated individually. Therefore, each polymer and its sulfonic acid derivative will be discussed apart from the others. However, some general trends and observations will be made initially.

Table VII. Summary of superheated steam experiments

Polymer	Temperature (° C)	% loss	Decomposition Products
Nafion®	300	22.1	acid + "PTFE like"
PBI	300	2.6	not analyzed
PBI	350	4.3	organics
PBI	400	4.1	not analyzed
S-PBI	300	17.1	acid + organics
PEEK	350	0.4	none detected
PEEK	400	3.0	mild acid + organics
S-PEEK	350	26.1	acid + organics
PES	300	0.4	none detected
PES	350	2.8	organics
S-PES (41%)	300	24.8	acid + organics
PPQ	400	1.3	organics
S-PPQ (132%)	300	11.8	acid
S-PPQ (75%)	350	8.2	acid
S-PPQ (50%)	400	9.4	acid + organics

The most important general statement that can be made from inspection of the data is that the stability's of the sulfonic acid derivatives are significantly lower than that of their unsulfonated analogues. S-PEEK and S-PES, for example, show significant decomposition at 350°C and 300°C respectively while their unsulfonated versions are essentially untouched. This is also true for S-PPQ and to a lesser degree for S-PBI. This general result is more similar to the results from the inert gas TGA's than to the results from the saturated vapor experiments. Additional tube-furnace decomposition experiments done on PES, PPQ and S-PEEK in the absence of any water give results similar to those presented in Table VII (details are given later). Therefore, although these superheated steam experiments do provide new information about the stability and decomposition of aromatic polymers and their sulfonated derivatives, they are not good models for decomposition under saturated vapor conditions.

6.2.2 Nafion®

Nafion® readily decomposed at 300°C, losing almost one-quarter of its weight at this temperature. This weight loss was due to the loss of acid, which was determined by measuring the pH of the condensate in the ice/water trap, and to the loss of a white solid which coated the walls of the glass tube in the tube furnace. This white solid was identified as "PTFE like", meaning some sort of a fluorocarbon, based on common sense and by comparing its IR spectrum to authentic PTFE (Figure 35). The absorbances found from approximately 1250 cm⁻¹ to 1000 cm⁻¹ can be attributed to various C-F stretches while the signals found around 650 cm⁻¹ are attributed to CF₂ or CF₃, although the specific assignments are uncertain.⁶⁴ There are more absorbances in the Nafion® decomposition product than in the PTFE spectrum; this may be due to the presence of C-O-C stretching which would have absorbances within this same range of wavenumbers,⁶⁵ or to the greater structural diversity found in a decomposition product than in a commercial polymer. The presence of any sulfonic acid in the decomposition product is unlikely based on the lack of any absorbances for O-H stretch around 3000 cm⁻¹ or any SO₂ stretch above 1300 cm⁻¹.⁶⁶

Figure 35. Nafion® decomposition products compared to PTFE reference.

6.2.3 PBI and S-PBI

Under superheated steam conditions PBI showed very little decomposition from 300 - 400°C. Gas chromatography/mass spectral analysis (GC/MS) of an organic extract from an experiment run at 350°C did not disclose the structures of any decomposition products. In contrast, S-PBI showed extensive decomposition at 300°C, which can be attributed to the loss of the sulfonic acid based on the presence of acid in the condensate. A small amount of organic soluble material was extracted and analyzed by GC/MS, but again, no definite products could be determined. Despite the lack of definite decomposition products, this study does provide some insight into the inert gas TGA experiments in that it confirms that the lower stability of S-PBI relative to PBI is due to the loss of the sulfonic acid.

6.2.4 PEEK and S-PEEK

The results presented in Table VII show that the presence of sulfonic acid groups on PEEK dramatically effects its thermal stability under superheated steam conditions. While PEEK showed no weight loss at 350°C, S-PEEK lost more than one-quarter of its weight at this temperature. This weight loss is not only due to the loss of acid but also to the loss of organic fragments as will be detailed below.

PEEK began to show decomposition at 400°C giving both acidic and organic decomposition products. The nature of the acid was not determined, but based on the pH of the aqueous condensate, 3.25, it may be carbonic acid derived from the loss of CO₂. GC/MS analysis of the organic extract identified two decomposition products, phenol and 4-phenoxyphenol. Phenol has been identified as the major decomposition product in previous studies,^{67,68} but 4-phenoxyphenol has never been reported as a decomposition product from this polymer. Other previously reported decomposition products such as diphenyl ether, benzophenone and benzoquinone were not detected. The latter two products were identified in a thermo-oxidative degradation study and not under inert conditions.⁶⁷

A greater diversity of decomposition products was found in the organic extract of the ice/water trap condensate from the S-PEEK sample run at 350°C. Table VIII lists these by GC retention time. The four compounds, diphenyl ether, dibenzofuran, 4-phenoxyphenol and 1,4-diphenoxybenzene were all identified by a routine spectral search of the Hewlett Packard software database. All of the mass spectra showed the expected M⁺ molecular ion and were in good agreement with the library spectra. In addition, with the exception of dibenzofuran all of the compounds are straightforward fragments of the S-PEEK structure. The formation of dibenzofuran can be rationalized through a radical or diradical intermediate in which hydrogen has been abstracted, evolving molecular hydrogen and forming the new carbon-carbon bond. Precedence for this is found in a thermal degradation study of 1,4- polyphenylene sulfide in which the analogous dibenzothiophene and molecular hydrogen were detected as decomposition products.⁶⁹ These compounds are the first reported decomposition products from a S-PEEK.

Table VIII. S-PEEK degradation products in 350°C superheated steam.

Retention time	Mol. Weight	Relative Abundance	Structure
16.25	170	4%
17.85	168	38%
20.11*	186	100%
23.62	262	48%

* This degradation product was also found for PEEK at 400°C.

One important observation is that none of the decomposition products have any carbonyl group. Although some bond breaking is obviously occurring at the ether oxygen (as in 4-phenoxyphenol), most of the cleavage is occurring at the ketone group. No evidence of any carbonyl group was found in ^{13}C NMR or IR spectra of either the organic extracts or the aqueous residue. In addition, the IR spectrum of the residue contains no absorbances for any ketone or carbonyl groups (Figure 36). The spectrum of 30% S-PEEK shows the ketone absorbance at 1651 cm^{-1} . This signal is absent in the 83% S-PEEK residue. Other carbonyl derivatives that might arise from cleavage of the ketone, such as a carboxylic acid group, are also absent in this spectrum. This suggests that decomposition is occurring resulting in the clean loss of the

Figure 36. Comparison of IR spectra of 30% S-PEEK and superheated steam decomposition residue of 83% S-PEEK.

carbonyl group, probably as carbon dioxide. Inspection of the two spectra also reveals that the signal arising from the ether linkage at 1219 cm^{-1} in the spectrum of 30% S-PEEK is dominant in the spectrum of the decomposed residue. The slight shift in the position of this signal between the two spectra is due to the different methods that were used to collect them. Discussion of possible decomposition mechanisms is done below.

The spectra in Figure 36 also show the clean loss of the sulfonic acid group during the decomposition. The signals at 1078 cm^{-1} and 1022 cm^{-1} which are obvious in the spectrum of 30% S-PEEK are absent from the spectrum of the decomposed residue of 83% S-PEEK.

The acid decomposition product for S-PEEK (and probably for all of the sulfonic acid bearing polymers) is likely due to simple desulfonation of the aromatic sulfonic acid groups to form sulfuric acid. In order to confirm this for S-PEEK, BaCl_2 was added to the acidic aqueous condensate. This caused a white precipitate to form which was collected by filtration, washed and dried. Its IR spectrum was taken and compared to authentic BaSO_4 which was the presumed precipitate (Figure 37). All of the absorbances from the spectrum of BaSO_4 are also seen in the spectrum of the unknown precipitate. The unknown also has some additional absorbances in the region from $1000 - 900\text{ cm}^{-1}$, but these can reasonably be attributed to impurities from other degradation products perhaps including the barium precipitate of carbonic

Figure 37. IR spectra of presumed BaSO_4 and an authentic sample.

acid, BaCO_3 . Therefore, it can be concluded that the unknown acid is the expected H_2SO_4 .

A key issue regarding the decomposition of S-PEEK is to determine how the presence of a sulfonic acid substituent reduces the stability of the main chain of the PEEK polymer. The reasonable speculation was made that an intramolecular, acid-catalyzed hydrolysis of the carbonyl group might be occurring as the first step in degradation, and two additional experiments were performed to test this hypothesis. First, the decomposition of PEEK was attempted at 350°C using 6M HCl as the steam source to provide a source of both water and acid. Essentially no decomposition of PEEK occurred under these conditions suggesting that simple acid catalyzed decomposition was not the mechanism. The second experiment was run at 350°C on the sodium salt of S-PEEK in order to determine if decomposition would occur in the absence of acid. Substantial decomposition of S-PEEK occurred under these conditions. These two experiments

do not support any acid promoted decomposition, and their results, along with the other PEEK/S-PEEK tube-furnace experiments are summarized in Table IX.

Table IX. Summary of PEEK/S-PEEK six hour tube-furnace experiments.

Sample	Experimental Conditions	Weight Loss (%)
PEEK	350°C steam	0.4
PEEK	350°C steam/acid vapor	0.3
S-PEEK	350°C steam	26.1
S-PEEK (Na salt)	350°C steam	29.7
S-PEEK	350°C inert	29.4

The presence of one atmosphere of superheated steam does not appear to have a significant influence on the decomposition of S-PEEK. A decomposition experiment was run on S-PEEK at 350°C under an inert atmosphere in the absence of steam. The weight loss under these conditions was similar to experiments run under superheated steam conditions (Table IX). This indicates that the one atmosphere of steam is having little influence on the decomposition chemistry of S-PEEK in these experiments.

Since neither acid nor water driven decomposition is implicated in the decomposition experiments discussed above, thermally driven decomposition must be occurring. That some decomposition is occurring by a radical mechanism is suggested by the presence of dibenzofuran as a decomposition product as was discussed previously. Since the presence of the sulfonic acid group on S-PEEK destabilizes the polymer chain relative to PEEK, it is reasonable that thermal decomposition might begin with this functional group. This is consistent with the relative bond strength of a C-S bond relative to a C-C or a C-O bond.⁷⁰ A reasonable mechanism would involve the loss of the sulfonic acid group by homolytic bond breaking to form two radical species which in turn might decompose further. The radical sulfonic acid fragment might reasonably fragment into SO₂ and a hydroxyl radical, the latter of which could then cause further degradation of the polymer. The thermal decomposition of an aromatic sulfonic acid to give SO₂ has been reported for a sulfonated polybenzimidazole. The evolution of SO₂ was detected using TGA/mass spectrometry with the SO₂ being detected from about 375°C - 600°C with a peak evolution occurring around 450°C.²⁹

6.2.5 PES and S-PES:

As is the case for the PEEK/S-PEEK pair, the presence of a sulfonic acid group on PES lowers its stability. Once again this lowered stability is not due only to the loss of the sulfonic acid group

but also to the decomposition of the main chain. At 300°C, no decomposition products were detected from PES, but S-PES decomposed into both acidic and organic fragments.

Previous degradation studies done on polyethersulfones have been done on a polymer made from bisphenol A and 4,4' dichlorodiphenyl-sulfone.^{69,71} To this authors knowledge, no published studies of decomposition products have been done on the PES used in this work or on any S-PES. PES decomposed at 350°C to give a series of organic fragments which were isolated by extraction of the ice/water trap (phenol) or by washing the condensed organics from the inside of the tube (all the others). Table X presents the relevant details.

The structure of phenol was determined by comparison to the available mass spectral database. This database did not provide any reasonable matches for the other compounds, so their structures were deduced from the mass spectrum.

Table X. PES superheated steam degradation products.

Retention Time	Mol. Weight	Relative Abundance	Structure
7.58	94
22.62	326	5%
22.79	310	10%
23.85	344	22%
25.05	340	55%	
31.46	402	100%

The four sulfone containing decomposition products shown in Table 10 are fragments arising from straightforward fragmentation of the polymer. These were identified primarily from their molecular ions. PES is made synthetically by the nucleophilic displacement of an aryl chloride by a phenoxide, so the presence of the chlorinated decomposition product is due to fragmentation at the end of polymer chains. The presence of the chlorine was obvious from the diagnostic 3 to 1 ratio of the molecular ions at m/e 344 and 346 in the mass spectrum.

Additional evidence for the structures indicated in Table X comes from the fragmentation patterns of the mass spectrum. In all cases, these mass spectrum possess daughter ions that are consistent with the proposed structures (Figure 38). Three of the structures, those with molecular weights of 310, 344 and 402, have a daughter ion at $m/e = 217$. This structure arises from the loss of phenoxide fragments to produce the diphenyl sulfone cation. This fragment is not seen in the mass spectrum of the decomposition product with a molecular weight of 326, but the analogous hydroxylated daughter ion at $m/e = 233$ is. All five structures have a daughter ion at $m/e = 185$. One possible structure that could explain this mass is Ph-S-Ph^+ , but no evidence for this sort of fragmentation is found in the spectrum of the analogous diphenyl sulfone. A better explanation may be that this ion results from the loss of an Ar-SO fragment via rearrangement of the sulfone. This fragmentation is consistent with the mass spectrum of diphenyl sulfone which has as its base peak a daughter ion at $m/e = 125$ which is consistent with a structure of Ph-SO^+ ion.⁷² The postulated structure for this daughter ion is shown in Figure 38 as well.

The structure of the decomposition product with a molecular weight of 340 is not obvious. It is clearly not a simple fragment of the polymer chain. As stated above, its mass spectrum does have many of the same daughter ions found in the spectra of the other decomposition products. However, no reasonable structure has been postulated for this material.

Figure 38. Postulated structures of daughter ions from PES decomposition.

Two of the decomposition products found for PES were also found for S-PES. These were the compounds with molecular weights of 344 and 402 (see Table X). No other decomposition products were identified.

Based on inspection of the PES decomposition products there is no clearly preferred site for polymer chain breakage. There are decomposition products arising from polymer chain cleavage at both the ether and the sulfone linkages. This is in contrast to PEEK/S-PEEK where there seems to be a preference for cleavage at the ketone linkage.

As was the case for the PEEK/S-PEEK pair, sulfonation lowers the stability of the polyethersulfone polymer chain. While PES showed a modest amount of decomposition at 350°C and essentially none at 300°C, S-PES showed substantial decomposition at 300°C and even at 250°C. Some of this weight loss can be attributed to loss of the sulfonic acid, but there is also polymer chain decomposition as evidenced by the decomposition products discussed above. As was done for PEEK/S-PEEK, two decomposition experiments were performed to determine the influence of acid in the decomposition process. Heating PES at 300°C in the presence of steam generated from 6M HCl had no effect on its stability. Heating the sodium salt of S-PES at 300°C resulted in substantial decomposition, indicating that acid was not necessary for decomposition. Additionally, decomposition of PES at 350°C in the absence of any steam resulted in modest decomposition. These experiments which are summarized in Table XI demonstrate that neither acid nor steam are the crucial factors in the decomposition of these polymers. Decomposition is thermally driven as was the case for the PEEK/S-PEEK pair.

Table XI. Summary of PES/S-PES six hour tube-furnace experiments.

Sample	Experimental Conditions	Weight Loss (%)
PES	300°C steam	0.4
PES	300°C steam/acid vapor	0.9
S-PES	250°C steam	11.7
S-PES	300°C steam	24.8
S-PES (Na salt)	300°C steam	5.9
PES	350°C steam	2.8
PES	350°C inert	4.3

6.2.6 PPQ and S-PPQ:

Superheated steam degradation experiments were performed on PPQ and S-PPQ. These represent the first attempt to analyze decomposition fragments from this class of polymers. These experiments revealed that the presence of the sulfonic acid group did not reduce the stability of the polymer chain (see Table VII). At 400°C a 1.3% weight loss was measured from PPQ. This amount was sufficient to allow identification of organic decomposition products (see below). In contrast, S-PPQ underwent significant decomposition at 300°C and 350°C, but no organic decomposition occurred. The greater weight loss at 300°C (11.8%) than at 350°C (8.2%) is due to the greater sulfonic acid content of the sample run at the lower temperature. For 132% S-PPQ, 15.5% of its initial weight is sulfonic acid and for the 75% S-PPQ, 9.4% is sulfonic acid.

The 11.8% weight loss of the 132% S-PPQ corresponds to 76% of the total acid content (assuming that all of the loss is due to loss of sulfonic acid), and the 8.2% weight loss of the 75% S-PPQ is 87% of the total acid. Therefore, the data does support greater weight loss with increasing temperature.

The 50% S-PPQ sample run at 400°C lost 9.4% of its weight, but its total acid content makes up only 6.5% of its weight. Therefore organic decomposition must also be occurring. This was confirmed by the isolation of an organic soluble fraction, but no structures could be identified by GC/MS. The 400°C temperature required to yield organic decomposition is the same temperature that was necessary to bring decomposition of the unsulfonated analogue.

Gas chromatography/mass spectral analysis of the decomposition products from PPQ revealed a number of straightforward monomer fragments (Table XII). Based on the weight of the molecular ions, a reasonable structure can be postulated for each of the organic fragments. That the postulated structures are in fact the correct ones is based on two arguments. First, formation of the postulated structures requires less bond breaking than does formation of any alternate structures that can be imagined. Decomposition to form these alternate structures would require the breaking apart of the fused aromatic quinoxaline ring system which is unlikely to occur before the breaking of carbon - carbon single bonds. Second, a published mass spectrum is available for one of the postulated structures. The tabulated, published mass spectrum for 2,3 diphenylquinoxaline (MW = 282) is consistent with the spectrum obtained in this study.⁷³ These two arguments present a strong case for the postulated structures being the correct ones.

Table XII. PPQ organic decomposition products from GC/MS experiments.

Retention Time	Molecular Weight	Relative Abundance	Postulated Structure
16.74	206	90%
21.19*	282	45%
24.05	298	100%
28.20	374	23%
29.87	388	24%

* Structure of this decomposition product confirmed by comparison to a published spectrum of the material.

Only one reasonable structure is possible for the last entry in the table (MW = 388). This decomposition does involve the destruction of the quinoxaline ring system, but its mechanism is reasonable because it involves the hydrolysis of the tertiary aromatic amines to produce the ortho substituted diamine. This hydrolysis is the reverse of the condensation reaction used in the synthesis of the polymer.

With the exception of the ortho diamine decomposition product described above, the nature of the decomposition products suggests thermally driven polymer degradation as the primary decomposition mechanism. As a test of this, decomposition of PPQ at 400°C was done in the

absence of any steam and resulted in 1.8% weight loss. This is actually slightly greater than the 1.3% weight loss observed under superheated steam, but it clearly demonstrates that the one atmosphere of water is not having a significant influence on the decomposition.

6.2.7 Concluding Remarks

The decomposition analyses presented above represents significant new information about the influence of a sulfonic acid functionality on the stability of aromatic polymers. It does not provide any information about decomposition of these polymers under saturated vapor conditions. Saturated vapor decomposition analysis is presented in the following section.

6.3 Saturated Vapor Decomposition Analysis

Initially, 225°C was chosen as the temperature for the saturated vapor decomposition experiments in order to ensure adequate decomposition. Because of inadequate decomposition, this temperature was raised to 250°C. S-PEEK, S-PES and S-PPQ were analyzed because these were the most promising candidates in the study. Their unsulfonated analogues were also tested for comparison.

As a control, all of the materials were heated at 225°C under inert conditions to confirm that the high pressure steam conditions were responsible for the observed decomposition. All of the materials showed minimal weight change with one exception. The S-PEEK (90%) lost a substantial portion of its weight at this temperature. A 46.5% S-PEEK was tested in order to evaluate the effect of a lower sulfonation level, and it did not lose any weight, although it did become embrittled. This result is at odds with the inert TGA results presented earlier, and an explanation for this difference is not clear.

All attempts to analyze the decomposition products by GC/MS were unsuccessful; no materials were analyzed by this method presumably because the decomposed organic fragments were not sufficiently volatile. Instead, the decomposition products were analyzed by IR, ¹H NMR and ¹³C NMR with the goal being to understand the decomposition by evaluation of functional group changes. In addition, comparisons were made between the starting materials and their residues remaining after the decomposition experiment by IR in order to determine changes in the functional groups or changes in their distribution.

Comparison of the PEEK residue from a saturated vapor experiment at 250°C with unmodified PEEK by IR did not show discernable changes between the two spectra. Some organic decomposition product was analyzed by ¹H NMR which confirmed the presence of aromatic material, but its quantity was not sufficient for collection of a ¹³C NMR spectrum. Analysis of this material by IR was also inconclusive.

The decomposition products and residue of 83% S-PEEK from a 225°C experiment under saturated vapor were analyzed by NMR and IR spectroscopy. Comparison of the IR spectrum of

the decomposition residue to unmodified 30% S-PEEK showed two key differences (Figure 39). First, the loss of the sulfonic acid group was detectable. Two absorbances at 1078 cm^{-1} and 1021 cm^{-1} which are present in the spectrum of 30% S-PEEK are absent in the spectrum of the decomposed residue. A second piece of evidence showing the loss of sulfonic acid is the splitting of the aromatic signal at just less than 1500 cm^{-1} to give a new absorbance at 1468 cm^{-1} . This splitting, which is caused by sulfonation of the diether bearing aromatic ring,²⁴

Figure 39. Comparison of the IR spectrum of S-PEEK with S-PEEK residue following saturated vapor decomposition.

is present in the spectrum of 30% S-PEEK but absent in the spectrum of the residue and in the spectrum of PEEK. That the sulfonic acid would be lost due to desulfonation in a saturated vapor environment is no surprise.

The second key difference between the spectra is the presence of two absorbances at 1723 cm^{-1} and 1687 cm^{-1} in the spectrum of the decomposition residue. These peaks are not found in the spectra of PEEK or S-PEEK, and they are found in the region typically associated with carbonyl compounds. The signal at 1687 cm^{-1} is characteristic of aromatic carboxylic acids,⁷⁴ and the signal at 1718 cm^{-1} can also be ascribed to a carbonyl derivative, although its assignment is uncertain. These two signals are important because they provide spectroscopic evidence for the hydrolysis of S-PEEK's diaryl ketone group under saturated vapor conditions.

Analysis of the S-PEEK's organic decomposition products by IR and NMR did not provide any conclusive information. Proton NMR of the crude mixture revealed a mixture of aromatics as well as a resonance at 12.7 ppm , indicating an acidic group. Carbon NMR showed the mixture to be primarily two compounds, one major and one minor with no carbonyl groups. This mixture

was chromatographed using reverse-phase preparative thin-layer chromatography with 2:1 methanol:water as the eluent. Analysis of the major product by IR and NMR did not confirm the presence of any acid groups or other distinctive functionality.

Analysis of PES and S-PES decomposition products by IR and NMR did not reveal any structural information either. Comparison of the IR of 29% S-PES with the spectrum of its decomposed residue showed a reduction in the sulfonic acid content of the residue based on a reduction of the relative peak intensity of an absorbance at 1024 cm^{-1} in the decomposed residue (Figure 40). The shoulder at 1468 cm^{-1} just below the aromatic absorbance at 1484 cm^{-1} was also smaller in the spectrum of the decomposed residue. This shoulder is not present in the spectrum of PES and is probably due to sulfonation as was the case for S-PEEK.

Figure 40. IR spectrum of 29% S-PES and its decomposed residue.

An analysis of PPQ and S-PPQ yielded the same type of information. Aromatic decomposition products were produced by saturated vapor decomposition, but no useful functional group information was gained. A comparison of the infrared spectrum of S-PPQ with that of its decomposed residue (Figure 41) showed the loss of sulfonic acid as part of the decomposition. The key evidence for this is the loss of the absorbance at 1084 cm^{-1} in the spectrum of the decomposed residue.

Figure 41. Comparison of S-PPQ film before and after decomposition.

6.4 Summary

The thermal stability of the five aromatic polymers and their sulfonated derivatives were investigated under both inert and saturated vapor conditions. Under inert conditions the sulfonic acid derivatives were less stable than their underivatized analogues. This lowered stability ranged from only a few degrees in the case of PPQ/S-PPQ to greater than 150°C for PES/S-PES. Under these conditions the sulfonated high temperature polymers were from 36°C to greater than 200°C more stable than Nafion®.

None of the polymers tested under saturated vapor conditions were stable at temperatures above 200°C. In most cases the unsulfonated polymers were more stable than their sulfonated derivatives, but usually only by a few degrees. The aromatic based polymers did not have superior stability to Nafion® under these conditions. The most important conclusion from this work is that the aromatic polymers are not suitable for use as proton exchange membrane electrolytes in cells run at high temperature under water-saturated conditions.

Decomposition analysis of the polymers was done under one atmosphere of superheated steam. New decomposition products were reported for PEEK and S-PEEK as well as for PES/S-PES and PPQ. The presence of the sulfonic acid group destabilized the polymer chain in both S-PEEK and S-PES, but the destabilization was not due to acid catalyzed decomposition or effected by the presence or absence of steam. The decomposition of these polymers appears to be thermally driven at one atmosphere of steam.

Decomposition analysis of PEEK, PES, PPQ and their sulfonated derivatives under saturated conditions was done using spectroscopic methods. Evidence for desulfonation of all of the polymers was found by comparing the infrared spectrum of the sulfonated polymers to their decomposed residues. An infrared absorbance characteristic of an aromatic carboxylic acid group was present in the decomposed residue of S-PEEK. This offers evidence for the hydrolysis of the diaryl ketone functionality of this polymer.

7.0 CONCLUSION

The primary objectives of this research were to synthesize a series of sulfonic bearing aromatic polymers, characterize them as proton exchange membrane electrolytes and investigate their thermal stability under saturated steam conditions. The key results in each of these areas have been summarized at the end of the appropriate chapters. The methanol permeability was also investigated and summarized in its own chapter. This section will again summarize the key findings of this research, but it will also discuss the questions that were not answered and offer some specific recommendations for further work.

The sulfonated derivatives of five high-temperature aromatic based polymers were prepared. The most important result arising from this work is the sulfonation of PPQ as an already cast film by a method which has been termed the "soak and bake" method. This represents not only the first report of the direct sulfonation of a polymer film, but also the first report in the open literature of the synthesis and characterization of a S-PPQ. Spectroscopic evidence suggests that the site of sulfonation is on the diether-substituted aromatic ring, but further work is needed to confirm this. This could be done by synthesis of appropriate model compounds and detailed NMR analysis. The applicability of the soak and bake method to other PPQ's or to other nitrogen-bearing polymers is also a potentially fruitful area of study.

The unusually poor hydrolytic stability of the sulfonated polyimide is a second area that deserves further study. The preferred explanation for this is that the sulfonic acid salt is sterically hindering thermal imidization, and hydrolytic degradation is occurring at the uncyclized polyamic-acid sites. This hypothesis could be investigated by attempting thermal imidization on a series of model compounds bearing substituents of varying steric bulk. Additionally, the synthesis of a hydrolytically stable sulfonated polyimide remains a worthwhile goal.

In the second area, electrolyte characterization, water uptake, conductivity and electrolytic performance of the sulfonated polymers were determined and compared to Nafion's®. The room temperature conductivities of these aromatic polymers ranged from one to several orders of magnitude lower than Nafion's®. This lower conductivity correlates well with the lower ion density of these polymers resulting from the lower acidity of the aromatic sulfonic acids. This is an important observation because sulfonic acid bearing polymers are used in these applications because they are thought of as strong acids. An important area for investigation based on this observation is the influence of sulfonic acid acidity on polymer conductivity. The poor acidity of

the aromatic sulfonic acids is due to the electron donating substituents located on the sulfonated aromatic ring. The acidity of the sulfonic acids can be varied by varying the substituents on the acid-bearing ring. Therefore, a systematic study of substituents effects on sulfonic acid acidity and polymer conductivity would be very interesting. A second approach would be to synthesize an aromatic based polymer bearing perfluoroalkyl sulfonic acid side chains for evaluation as a PEM. Additionally, evaluating the long term electrolytic performance of these materials is warranted.

In the third area, thermal analysis, the key result is that none of the polymers tested, whether sulfonated or unsulfonated, were stable under saturated vapor conditions at temperatures approaching 200°C. In order to operate a proton exchange membrane electrolyte at these elevated temperatures, a material that has excellent proton conductivity in the absence of water is needed.

Decomposition under one atmosphere of superheated steam was due to thermal degradation of the polymers; this represents the first decomposition product analysis of the PES and PPQ materials. This method was not a good model for the decomposition that occurs under saturated steam conditions. Analysis of sulfonated polymer residues after saturated steam decomposition showed desulfonation of S-PEEK, S-PES and S-PPQ and provided evidence for the hydrolytic degradation of S-PEEK's ketone group into a carboxylic acid.

The research presented in this dissertation shows that sulfonic acid bearing, aromatic based polymers are not suitable for use as PEM's in high temperature water electrolysis or fuel cells, but they are potentially useful as electrolytes in cells run at traditional low temperatures. The key technical issue to address is the low conductivity of these polymers which can be addressed by increasing the acidity of the aromatic sulfonic acid groups. Long term stability in an operating fuel cell also needs to be studied.

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Task 3 Report

Production of Hydrogen By Thermocatalytic Cracking of Natural Gas

Final Report

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Submitted to:

U.S. Department of Energy
Mr. Douglas Hooker
1617 Cole Boulevard
Golden, CO 80401

Submitted by:

Nazim Muradov

Florida Solar Energy
1617 Clearlake Road
Cocoa, FL 32922-5703

PRODUCTION OF HYDROGEN BY THERMOCATALYTIC CRACKING OF NATURAL GAS

Prepared by:

Nazim Muradov
Florida Solar Energy Center
1679 Clearlake Road
Cocoa 32922-5703

June 1999

1.0 SUMMARY

The conventional methods of hydrogen production from natural gas (for example, steam reforming and partial oxidation) are complex, multi-step processes that produce large quantities of CO₂. The main goal of this project is to develop a technologically simple process for hydrogen production from natural gas (NG) and other hydrocarbon fuels via single-step decomposition of hydrocarbons. This approach eliminates or significantly reduces CO₂ emission. Carbon is a valuable by-product of this process, whereas conventional methods of hydrogen production from NG produce no useful by-products. Our approach is based on the use of special catalysts that reduce the maximum temperature of the process from 1400-1500°C (thermal non-catalytic decomposition of methane) to 500-900°C. Transition metal based catalysts and various forms of carbon are among the candidate catalysts for the process. This approach can advantageously be used for the development of compact NG reformers for on-site production of hydrogen-methane blends at refueling stations and, also, for the production of hydrogen-rich gas for fuel cell applications.

We extended the search for active methane decomposition catalysts to various modifications of Ni-, Fe-, Mo- and Co-based catalysts. Variation in the operational parameters makes it possible to produce H₂-CH₄ blends with a wide range of hydrogen concentrations that vary from 15 to 98% by volume. We found that Ni-based catalysts are more effective at temperatures below 750°C, whereas Fe-based catalysts are effective at temperatures above 800°C for the production of hydrogen with purity of 95% v. or higher. New reactor configurations to determine the catalyst activity have been designed, fabricated and tested; they included fixed bed, tubular and pulse reactors. The catalytic pyrolysis of liquid hydrocarbons (pentane, gasoline) over Fe-based catalyst was conducted. We observed the production of a hydrogen-rich gas (hydrogen concentration up to 97% by volume) at a rate of approximately 1 L/min.mL of hydrocarbon fuel.

1.0 INTRODUCTION

1.1 Background

All conventional options for hydrogen production from NG (e.g. steam reforming (SR), partial oxidation, autothermal reforming) involve CO₂ production at some point in the technological process chain, therefore, the main problem remains: how to produce hydrogen from NG without CO₂ emission. There are basically two alternative approaches to eliminating CO₂ emissions from methane use in hydrogen production:

- SR of NG with subsequent scrubbing of CO₂ from synthesis gas
- decomposition of methane into hydrogen and carbon

SR of NG is the most widely used among all present-day processes for hydrogen production. It is a complex multi-step process. The reforming reaction is a strongly endothermic, high temperature (800-870°C) process. Because of the energy intensive stages of SR process, the usage of NG as a fuel is almost equal to its usage as a chemical feedstock. As a result, the production of every cubic meter of hydrogen is accompanied by the emission of 0.5 cubic meter of CO₂. CO₂ can be removed from flue gas by several conventional methods, however, the real problem is what to do with accumulating volumes of CO₂ that are not released into the atmosphere. Several proposals have been discussed in the literature (Nakicenovic 1993) on CO₂ disposal (e.g. in the deep ocean, etc.), however, ecological consequences of the proposed solutions are not clear.

1.2 Thermal Decomposition of Methane

The thermal decomposition (TD) of methane is another option for CO₂-free production of hydrogen from NG.

There is a very valuable by-product of TD process, pure carbon, while SR produces no useful by-products. Unlike SR process, TD produces practically no CO₂ emissions. The decomposition of methane can be carried out plasmochemically. In a recent paper, Fulchery et al (1995) advocated a plasma-assisted decomposition of methane into hydrogen and carbon. It was estimated that up to 1.9 kWh of electricity will be consumed per one normal cubic meter of hydrogen produced.

Thermal decomposition of methane is a well known process. The energy requirement per mole of hydrogen produced for TD is somewhat less than that for SR reaction: 37.8 and 41.2 kJ/mole H₂, respectively. The process is slightly endothermic, so only an insignificant amount of hydrogen produced could be used as a source of the thermal energy for the process.

Figure 1 depicts the thermodynamic data on the decomposition of various hydrocarbons (from methane to pentane) that constitute natural gas. It can be seen that the enthalpy of methane decomposition reaction is significantly higher than that of other hydrocarbons due to the strong C

- H bond in the methane molecule. Equilibrium curves for methane decomposition reaction at 1 and 10 atmospheres are shown in Figure 2. Equilibrium H_2 - CH_4 mixtures containing 47-90 and 90-98% by volume of hydrogen can be produced at the temperature intervals of 500-720 and 720-900°C, respectively. As discussed in the literature (Kelley et al 1980) the gaseous mixtures containing 20% v of hydrogen could be used as an ecologically acceptable transportation fuel without any changes in end use devices. Hydrogen rich gas (90-98% v.) could advantageously be used in fuel cells.

1.3 Thermocatalytic Decomposition of Methane

Attempts have been reported in the literature on the use of catalysts for the cracking of methane and light hydrocarbons. For example, Pohleny et al (1966) and Callahan (1974) used various refractory materials and metal oxide based catalysts for the catalytic decomposition of methane at 800-1100°C. The carbon produced was then burned off the catalyst surface. In this regard, these processes exhibited no significant advantages over the conventional processes (for example, SR) because of high operational temperatures and large CO_2 emissions.

Our approach is based on the use of special catalysts that reduce the maximum temperature of the process from 1400-1500°C (thermal non-catalytic decomposition of methane) to 500-900°C. Transition metal based catalysts and various forms of carbon are among candidate catalysts for use in the process. This approach can advantageously be used for the development of the compact NG reformers for on-site production of hydrogen-methane blends at refueling stations and for the production of hydrogen-rich gas for fuel cell applications. The Table illustrates the process characteristics for hydrogen production by conventional processes and decomposition of NG.

Table. Process Characteristics for Producing Hydrogen by Conventional Processes and Decomposition of Natural Gas

Process Characteristics	Steam Reform.	Partial Oxidat.	Thermal Decompos.	Plasmo-chemical Decompos.	Catalyt. Decomp.
Commercial Availability	+	+	+	-	-
Typical Capacity $10^3 \text{ m}^3/\text{h}$	12-120	36-120	N/A	-	-
Number of Steps	3(4)	3	1	1	1
Need for H_2 Purification	+	+	-	-	-
Special Requirements	Steam	Oxygen	-	Electricity 1.1-2 kWh/ $\text{m}^3 \text{H}_2$	-
Catalyst	+	-	-	-	+
Fuel Flexibility	Low	High	Moderate	Low	High
Tolerance to Sulfur in a Feedstock	Very low	High	High	Moderate	Moderate
Useful By-product	-	-	Carbon	Carbon	Carbon
CO_2 Emission	+	+	-	-	-
Efficiency*, %	78.5	80	N/A	95	92.8
Cost**, \$/1000 m^3	67.1	109.2	N/A	N/A	58.0***
Capacity of small scale units, $10^3 \text{ m}^3/\text{h}$	0.1-5.9	0.02-4.0	N/A	2.0	-
Power Density, kW/L	6.4	0.7 (el.)	N/A	~4	5.3

* - total efficiency

** - based on $118 \times 10^3 \text{ m}^3/\text{h}$ capacity (Steinberg 1988),

*** - after carbon credit taken

2.0 EXPERIMENTAL

2.1 Materials and Methods

The gases: methane (99.0%), nitrogen (99.999%) and hydrogen (99.999%) were used without further purification. Pt(1%) on alumina pellets was provided by Aldrich. Alumina-supported (9-16 mesh) Ni- and Fe-based (6-9% w) catalysts were prepared according to the procedure described by Richardson (1989). NiO-MoO₃/alumina catalyst was provided by Haldor Topsoe, Inc. The reduction of metal oxide catalysts into metallic form was carried out in the stream of hydrogen at 650°C. Several types of catalytic reactors were used in this work, continuous flow (packed bed and tubular) and pulse. Tubular reactors were made out of quartz, ceramic (alumina), stainless steel and metallic nickel.

2.2 Experimental Set-up and Analysis

Figure 3 depicts the schematic diagram of the experimental set-up used for the catalytic decomposition of methane in fixed bed and tubular reactors. The experimental unit for the liquid hydrocarbons decomposition consisted of a syringe pump for metering and delivering of the hydrocarbon feedstock, a preheater for the evaporation of liquid fuel, a catalytic reactor, a flowmeter for metering the rate of hydrogen production and the analytical system (GC) for the product gas analysis. The products of methane decomposition/oxidation were measured gas-chromatographically (SRI 8610, N₂-carrier gas, TCD, silicagel column, and Varian 3000, He-carrier gas, FID, Hysep D_B column).

3.0 RESULTS AND DISCUSSION

3.1 Thermocatalytic Decomposition of Methane Using Fixed Bed Reactor

We studied thermocatalytic decomposition of methane over various catalysts and supports in a wide range of temperatures, 200-900°C, and space velocities from, 200 to 1500 h⁻¹, at atmospheric pressure. Preliminary tests were performed on the selection of materials for the catalyst support and catalytic reactor. It was found that among materials tested (quartz, ceramics, stainless steel) quartz demonstrated the least activity in the methane decomposition reaction at temperatures up to 1000°C. Stainless steel (SS) demonstrated noticeable catalytic activity at 750°C and higher. The activated alumina (9-16 mesh) was used as a catalyst support.

It was observed with all catalysts tested that at given pressure and space velocity the hydrogen production rate is a function of the temperature. Figures 4 and 5 depict the maximum concentration of hydrogen in the hydrogen-methane mixture produced in the presence of different catalysts at 750 and 850°C, respectively. It was demonstrated that Ni-based catalysts are more active than Fe-based catalysts at 750°C; and conversely, Fe-based catalysts are more active than Ni-catalysts at 850°C and higher temperatures. Pt/alumina demonstrated moderate activity at 750°C. Unfortunately, no steady state hydrogen production was observed with all the catalysts

tested. Figure 6 depicts the kinetic curves of hydrogen production over alumina-supported Fe, Fe₂O₃ and Pt catalysts at 750°C. We observed initial surge of hydrogen yield in the presence of Fe/Al₂O₃ catalyst which was followed by gradual decrease in the hydrogen production rate. In the case of iron oxide catalyst, there was a distinct induction period of 4-5 min. Apparently, the induction period corresponds to the reduction of iron oxide into metallic iron. GC analysis indicated that during the induction period the effluent gas was rich with carbon oxides. The Pt/alumina catalyst demonstrated quite different behavior. The maximum of the hydrogen yield was observed at the very beginning of the reaction followed by steep decline in the hydrogen concentration in the product gas. The shape of the kinetic curves of hydrogen production in the presence of alumina-supported NiO, NiO-MoO₃ and CoO-MoO₃ catalysts were identical to that of iron oxide, except the induction period was shorter. In the case of Ni-based catalysts the picture was more complicated because of the catalyst disintegration after 20-30 min into the run.

As Figure 7 shows, the hydrogen concentration in the effluent gas in the presence of Ni/alumina slightly dropped during the first 5 min and then continuously increased until reactor was clogged by carbon. Similar behavior was demonstrated by NiO/catalyst except that there was short induction period corresponding to the reduction of NiO into metallic nickel. To prevent reactor clogging, we diluted Ni/alumina catalyst with bare alumina pellets of the same size in a ratio of 1:1 by weight. Figure 8 depicts the kinetic curve of hydrogen production in the presence of diluted Ni/alumina catalyst at 750°C. The catalyst activity drastically dropped during first 10 min, followed by slow decline in hydrogen production rate over several hours.

It was found that newly-reduced Ni/alumina and Fe/alumina catalysts exhibited very high activity in the methane decomposition reaction. For example, in the presence of Ni-catalyst the hydrogen was detected in the effluent gas at the temperature as low as 200°C. At 250°C the concentration of hydrogen in the hydrogen-methane mixture reached approximately one percent. The breakthrough temperature for the methane decomposition in the presence of Fe/alumina catalyst was also 200°C. Unlike Fe/alumina, Fe₂O₃/alumina catalyst became active at temperatures higher than 600°C. Below this temperature the reduction of ferric oxide to metallic iron by methane is a very slow process. These experimental results supported the assumption that the induction period corresponds to the reduction of metal-oxide form of the catalyst into metallic form. Once the active metallic form of the catalyst was produced, the effective decomposition of methane on the catalyst surface with formation of hydrogen and carbon began. The carbon blocks the active sites on the catalyst surface which results in a limited reduction of the catalyst activity. Each catalyst is characterized by the maximum and steady state rate of hydrogen production as well as the time to reach the steady state.

Surprisingly, activated carbon demonstrated relatively high initial activity in methane decomposition reaction at temperatures above 800°C. As it is shown on Figure 9, hydrogen concentration in the effluent gas dropped from 78 to 60% v. during the first 10 minutes of the reaction and after several hours reached the minimum value. The data on the hydrogen production in the presence of activated alumina are also included in Figure 9. Alumina has negligible catalytic activity towards methane decomposition, however, as the process proceeds hydrogen yield increases due to the catalytic effect of carbon deposits on the catalyst surface. Hydrogen production rate reaches maximum and then slowly decreases over several hours and

eventually stabilizes. The catalytic activity of various modifications of carbon is well documented. According to Tenser (1987), the rate constant of methane decomposition reaction over soot (k_s) is expressed by the following equation:

$$k_s = 1.8 \times 10^{-3} \exp(-272,000/RT) \text{ g cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \quad (\text{at } 700\text{-}950^\circ\text{C})$$

3.2 Decomposition of Methane in a Tubular Reactor

We conducted a series of experiments on the decomposition of methane in a tubular reactor for the temperature range of 800-870°C. The tubular reactors were made out of quartz, ceramic (alumina), stainless steel and metallic nickel. The objective was to study the effect of carbon removal from the catalyst surface on its catalytic activity. Figure 10 depicts the results of the tubular reactor experiments. There was no or negligible yield of hydrogen using quartz and alumina reactor at 850-870°. Stainless steel tubes demonstrated relatively low catalytic activity at space velocities of 1500-2000 h⁻¹ and 870°C. Nickel tube demonstrated the highest activity among the tested tubular reactors. After the first experimental run in the Ni reactor at 800°C, we mechanically removed carbon from the inner wall of the reactor, subjected the catalyst to methane flow at the same conditions (2nd run) and repeated the procedure one more time (3rd run). The results indicated that carbon can be removed from the reactor without effecting the catalytic activity. We observed that the rate of the catalyst deactivation was much higher for tubular reactors than for fixed bed reactors packed with alumina-supported catalysts. This can be explained by the effect of catalytic surface area.

Figure 11 summarizes our findings on the catalyst activity tests. Newly prepared or regenerated Ni- and Fe-based catalysts demonstrated the highest catalytic activity in methane decomposition reaction. The maximum hydrogen concentrations in the effluent gas in the presence of alumina-supported Ni- and Fe-catalysts at the range of temperatures of 100-900°C are fairly close to the equilibrium values of hydrogen concentration in H₂-CH₄ mixtures which is an indicative of very efficient catalyst. Experimental results indicate that Ni-based catalysts are suitable for the production of the hydrogen-methane blends with the hydrogen concentrations up to 85-90% v. at moderate temperatures 750°C and below. Fe-based catalysts can be used for the production of hydrogen with purity up to 95% and higher at temperatures of 800°C and higher.

3.3 Catalytic Pyrolysis of Liquid Hydrocarbons

The objective of this series of experiments was

- to study the catalytic decomposition of high alkanes, including pentane which is a minor component of natural gas
- to develop a process for the production of hydrogen-rich gas via single step decomposition of liquid hydrocarbon fuels (e.g. gasoline)

Figure 12 depicts the results of pentane decomposition (pyrolysis) over Fe/alumina catalyst at 880°C. Hydrogen-rich gas (H_2 concentration above 95% v.) was produced during the first 10 min of the process, followed by a steady decline in the hydrogen concentration. After 25 min, we observed the formation of ethane and ethylene. The yield of the hydrogen-rich gas reached up to 960 mL/min and, over one hour, dropped to 750 mL/min per mL of pentane.

Similar results were obtained with gasoline as the feedstock. The results of the catalytic pyrolysis of gasoline are shown in Figure 13 (a and b). After the first run, the carbon (coke) was burned off the catalyst surface by passing air through the reactor at 800°C. After the reactor was purged with nitrogen to remove air, the gasoline vapors were introduced into the reactor (2nd run). The procedure was repeated one more time (3rd run). The results of the 2nd and 3rd runs were similar to that of the 1st run. Figure 13b depicts the yields of hydrogen-rich gas during the three runs and it can be seen that the catalyst activity remains approximately at the same level after the three decomposition-regeneration cycles.

4.0 CONCLUSIONS

- The catalytic activity of various modifications of Ni-, Fe-, Mo-, Co- and carbon-based catalysts for methane decomposition reaction was determined. Variation in the operational parameters (temperature and residence time) makes it possible to produce H_2 - CH_4 blends with a wide range of hydrogen concentrations that vary from 15 to 98% by volume.
- New reactor configurations to determine the catalyst activity have been designed, fabricated and tested. They included: fixed bed, tubular and pulse reactors.
- We found that Ni-based catalysts are more effective at temperatures below 750°C, whereas Fe-based catalysts are effective in a wide range of temperatures up to 900°C and above for the production of hydrogen with purity of 95% v. or higher. It was demonstrated that the induction period of hydrogen production corresponds to the reduction of metal oxide to the metallic form of Ni- and Fe-catalysts.
- The catalytic decomposition of liquid hydrocarbons (pentane and gasoline) over Fe-based catalysts was conducted, resulting in the production of a hydrogen-rich gas with the hydrogen concentration up to 97% by volume at a rate of approximately 1 L/min.mL of hydrocarbon fuel.

5.0 FUTURE WORK

Optimize the process for the high yield of hydrogen and catalyst long term stability. Develop methods for efficient separation of carbon from the catalyst surface. Determine the catalytic activity of various forms of carbon in methane decomposition reaction.

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- Figure 1. Thermodynamics of hydrocarbon decomposition reaction
- Figure 2. Equilibrium data for methane decomposition reaction
- Figure 3. Schematic diagram of continuous flow thermocatalytic system for methane decomposition
- Figure 4. Maximum hydrogen concentration in the effluent gas at 750°C using different catalysts
- Figure 5. Maximum hydrogen concentration in the effluent gas at 850°C using different catalysts
- Figure 6. Kinetic curves of hydrogen production in the presence of alumina-supported Fe- and Pt- catalysts
- Figure 7. Methane decomposition over Ni-based catalysts at 600°C using fixed bed reactor
- Figure 8. Methane decomposition over Ni/alumina catalyst at 750°C
- Figure 9. Catalytic decomposition of methane over activated carbon and alumina at 850°C
- Figure 10. Methane decomposition using tubular reactors
- Figure 11. Methane decomposition over Ni- and Fe-catalysts
- Figure 12. Catalytic pyrolysis of pentane over Fe/alumina catalyst at 880°C
- Figure 13. Catalytic pyrolysis of gasoline over Fe/alumina at 850°C.
a- products concentrations, b- gas production rate.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13 (a).

Figure 13 (b).