DEVELOPMENT OF HIGHER TEMPERATURE MEMBRANE AND ELECTRODE ASSEMBLY FOR PROTON EXCHANGE MEMBRANE FUEL CELL DEVICE BASED ON SPEKK BLENDS

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Summary

Research performed with sulfonated poly (ether ketone ketone) polymer (SPEKK) has provided a better understanding of the polymer design relative to its performance. Experimentation performed during sulfonation, membrane fabrication, testing methods, and membrane electrode assembly (MEA) fabrication, have lead to the understanding that sulfonated poly (ether ketone ketone) polymer can be synthesized with high levels of proton conductivity and that conductivity performance appears less sensitive to low humidity conditions than Nafion[®]. These findings are significant in the advancement of proton exchange fuel cell devices, since Nafion does not perform well at 120°C operation temperatures. The SPEKK may be better suited for the demands of the wide range of operating conditions typical to portable fuel cell devices.

SPEKK based MEAs were not fully demonstrated upon completion of this contract as originally planned in the scope of work. Dimensional instability of the sulfonated polymer made it difficult to thoroughly characterize membrane performance, and made MEA optimization infeasible. The dimensional issues in SPEKK membranes were not sufficiently overcome by complex experimental strategies including crosslinking and reinforcing, but were improved to the extent that limited MEA testing could be completed.

Overall, the work funded by this project led to a greater understanding of SPEKK design for proton exchange membranes (PEM) and that the molecular structure of the existing grades of poly (ether ketone ketone) polymer must be re-engineered if SPEKK membranes with a stable dimensional structure are to be adequately achieved. Membrane stability remains the largest technical obstacle in the further advancement of SPEKK membrane development, but there is high probability of success if PEKK can be optimized.

Comparison of Actual Accomplishments with Goals and Objectives

The project objective was to demonstrate technical feasibility of MEAs based on Oxford Performance Materials, Inc. (OPM)'s novel ion-conducting polymer membrane material. Ideally OPM's membrane will enable PEM fuel cells to operate efficiently at temperatures from 80°C to 120°C and thus provide significant system integration benefits including reduced system costs (eliminating \$375/kWe out of stationary fuel cell targets of \$1500/kWe) and increased system efficiency (increasing from 32 to 40%). The main strategy to achieve the objective was to prepare MEAs from membranes based on SPEKK (and it blends), measure critical physical properties, and demonstrate technical feasibility by testing SPEKK-based MEAs at operation temperatures up to 120 °C. To meet these objectives, OPM proposed to develop testing capabilities for evaluating membrane conductivity and MEA power output.

Membranes prepared from SPEKK blends were evaluated at temperatures up to 105°C with some success, but only when converted as MEA. The technical feasibility of SPEKK-based MEAs was demonstrated on a preliminary basis. However, experimental membranes and prototype MEAs never reached the level of optimization required to fully understand their full performance potential.

FINAL STATUS OF PROJECT GOALS AND OBJECTIVES

The main project goal was to demonstrate SPEKK-based MEA feasibility at 120°C based on 100 hours operation of an optimized MEA in a fuel cell test stand. Fabrication of operational MEAs for testing was delayed under this program as a result of experimental difficulties in compounding dimensionally stable membranes. At completion of the project, significant advancement was made in stabilizing the membranes, allowing fabrication and short term power output testing of preliminary MEAs. Additional development of the SPEKK membrane and MEA construction is needed before ideal power output and long-term stability can be achieved.

Experimental Hypothesis

Over the past decade, fuel cell researchers have investigated aromatic sulfonated hydrocarbon ionomers for their potential as alternatives to Nafion. The alternative ionomers appear to have a similar proton transport system to Nafion through an interconnecting network of sulfonic acid substituents. Although Nafion and SPEKK appear to share the same conductivity/water content relationship, SPEKK appears to utilize moisture more efficiently than Nafion, and therefore enjoys potentially better performance at lower humidity. However, the utility of the sulfonated polymers as membrane materials has typically been limited by inadequate membrane strength as the membranes swell as they absorb water.

The focus of this project was to improve the dimensional stability of SPEKK based hydrocarbon membranes and develop better performing MEAs than Nafion based MEAs operating at 120°C. The main hypothesis of the work was that a polymer blend, having a spinodal-type nano-structure morphology, would have improved membrane strength, as well as improved ion transport mechanism as compared to single phase sulfonic acid functional polymers. This improved ion transport mechanism may require less water than a conventional ionomer to achieve high proton-conductivity as a result of complexing between the two polymers in the interfacial regions. It was hypothesized that membranes requiring less moisture to achieve comparable proton conductivity may operate more efficiently at 120°C and low humidity operating conditions.

The working project was designed as a series of seven sequential tasks with associated goals for demonstrating the interfacial complexing concept (see Table 1).

It was anticipated that a high performance membrane composition would be identified, and that an optimized MEA could be fabricated for performance testing and evaluation of durability after 100 hours of operation.

Table 1: Project Summary	
Task	Goal
1. SPEKK Material Selection	Identify the optimum SPEKK polymer for blending work (Target: > 0.1 S/cm at 120°C, 30% RH)
2. SPEKK Blend Processing	Develop blend processing techniques to prepare mechanically stable films
3. SPEKK Blend Characterization	Characterize conductance versus temperature, relative humidity, and fractional polymer content
4. MEA Feasibility	Perform electrochemical cyclic voltammetry of PT in SPEEK MEA environment. Demonstrate mechanically stable interfaces after thermal/humidity cycling.
5. MEA Optimization	Optimize catalyst/SPEKK blend/porosity volumetric ratios.
6. Pt Loading	Evaluate electrode performance versus Pt content
7. Durability	Evaluate selected MEAs in single cells for 100 hours.

Summary of Results

Task 1: SPEKK Materials Selection

The main goal of Task 1 was to identify the optimum SPEKK polymer for blending work. The SPEKK materials utilized in this investigation were synthesized via an oleum process from commercially available grades of OXPEKK[®] polymer, OXPEKK-C having 80/20 terephthaloyl (T) to isophthaloyl (I) monomer ratios and OXPEKK SP having ratios of 60/40.

Figure 1: Terephthaloyl and Isophthaloyl Monomers

The PEKK was sulfonated by electrophilic substitution in the ortho position next to the ether groups with a theoretical maximum two sulfonic acid groups per one repeating unit (see Figure 2).

Figure 2: Sulfonation

Predictable levels of sulfonation were achieved by examining the sulfonation kinetics relative to temperature, reactant concentrations, and time of reaction. The reaction kinetics for sulfonation followed a square root dependence (see Figure 3).

Figure 3: Effect of Reaction Time on Sulfonation Level

Activation energies ranging from 71 to 76 kJ/mol were found based on reaction temperatures from 16 to 74°C. Only free SO₃ was found sufficiently reactive towards PEKK to result in sulfonic acid group formation. Models based on the assumption that all active sites in PEKK are of equal reactivity can describe the first 50% of sulfonation. When volume to volume ratios of concentrated sulfuric acid to fuming sulfuric acid lower than 55/45 were used, a simple pseudo first-order model described the reaction in this region. For higher ratios, the SO₃ groups cannot be assumed to be in excess since the initial SO₃ concentration was significantly reduced by its reaction with water present in concentrated sulfuric acid. In this case a second order model was needed. The validity of this model and its parameters were checked by simulating the effect of the initial SO₃ concentration. After the first 50% of reaction, a retardation effect became apparent, originating from the deactivation of the sulfonate groups neighboring the remaining active sites. The complete sulfonation reaction was described by two consecutive reactions. The addition of the second sulfonate group in the same repeat unit was an order of magnitude slower than the addition of the first sulfonate group. This affected the distribution of these groups along the polymer backbone for different sulfonation levels. This effect might be important for the application of SPEKK as a proton-

exchange membrane material. Decreasing the ratio of terephthaloyl (T) to isophthaloyl (I) in PEKK from 80/20 to 60/40 resulted in a three-fold increase in sulfonation rate, which could be related to the higher flexibility of the 60/40 copolymer. The ion exchange capacity (IEC) was confirmed by neutralizing the SPEKK with sodium chloride, then titrating with sodium hydroxide to determine the ion exchange capacity in milliequivalents per gram. Glass transition temperature increased with increasing IEC (see Figure 4).

Figure 4: Glass Transition Temperature vs. IEC

The thermal properties of each of the SPEKK polymers was characterized thermally (see Figure 5). The SPEKK was thermally stable to ~270°C. Desulfonation occurred between 300-390°C. The magnitude of that weight loss step correlated quantitatively with the sulfonation level.

Figure 5: Thermal Stability of SPEKK

A series of SPEKK polymers were synthesized with ion exchange capacities (IEC) ranging between 1.0 and 2.5. The SPEKK polymers were soluble in N-methylpyrrolidone, and dimethyl acetamide. Membranes were formed by preparing solutions of 5 weight percent polymer in the desired solvent and casting onto glass. The membranes were air dried at 60°C overnight, then vacuum dried at 120°C for 3 days. The average water uptake was characterized for membranes cast from SPEKK at IECs between 1.3 and 2.5 (see Figure 6). At 25°C there was ~20% by weight average water uptake at 98% relative humidity, and slightly higher average water uptake when immersed in water with approximately 6 moles of water per sulfonic acid group.

Figure 6: Water Uptake of SPEKK

The conductivity performance for SPEKK was evaluated for polymers with IEC 1.3 to 2.5 (see Figure 7). IEC 1.6 appears to have comparable conductivity to Nafion 112 at 25°C, 98% RH.

Figure 7: Proton Conductivity and Water Uptake

The room temperature proton conductivities of hydrated SPEKK membranes increased exponentially with sulfonation level. This is due to the increase in the concentration of sulfonic acid sites, which form the locus for proton transport, and the increase in water uptake which plays an important role in increasing the mobility of protons through the membrane.

As the SPEKK membrane became hydrated, it underwent a change from a glassy to a visco-elastic material. The swelling accompanying this change was illustrated by immersing membranes in water at different temperatures. Equilibrated water contents are shown in Figure 6 for different IEC's up to 90°C. Excessive swelling occurred from an IEC of 1.4 meq/g above 60°C. The increase in total water uptake and concomitant decrease in glass transition temperature of higher IEC membranes causes this onset to move to lower temperatures (see Figure 8).

Figure 8: Water Uptake vs. Temperature, SPEKK IEC 2.1

When compared with Nafion, the SPEKK with IEC 1.2 and below had similar water uptake to Nafion. SPEKK with IEC 1.4 and higher had an extremely high affinity for water at temperatures above 80°C.

With a range of SPEKK materials to choose from of varying proton conductivity and dimensional stability, a significant amount of effort was required to identify a highly proton conductive and dimensionally stable membrane composition that could be used to fabricate MEA that could be characterized at temperatures above 80°C. SPEKK with IEC at 2.0 or above was highly proton conductive, but swelled to the extent that the membrane did not stay intact during conductivity testing. SPEKK with IEC near 1.3 was dimensionally stable at elevated temperature and humidity conditions, but had much lower proton conductivity than required for the PEM application.

Ultimately, SPEKK polymers were evaluated at IECs over the range of 1.3-3.5. Initially, polymers with IECs 1.7-2.1 were selected for the blending experiments based on conductivity. IEC 1.7 had the minimum conductivity expectations for the membrane, and had significantly lower water absorption than higher IEC polymers. SPEKK with IEC 2.0 had both high conductivity and a high degree of water- uptake.

In the process of testing the SPEKK membranes, it was observed that that SPEKK became completely water soluble when the IEC exceeded the 2.0-2.5 range. Conductivity experiments conducted in a steam environment (99C, 99% RH, 1 ATM) indicated that SPEKK with IEC as low as 1.3 become gelatinous.

SPEKK polymers having IECs between 1.7 and 2.0 were preferred for further experimentation in subsequent tasks.

Task 2: SPEKK Blend Processing

The main hypotheses of this task were:

1. SPEKK can be blended with other complimentary aromatic-hydrocarbon polymers to create an intermolecular complex that will promote ion conductivity at much lower water content than required for Nafion or SPEKK alone.
2. The SPEKK membranes can be dimensionally stabilized by blending SPEKK with stable, complimentary polymers.

Approaches:

1. The interphase study was approached by blending high IEC SPEKK with polyetherimide (PEI), polyethersulfone (PES), and low IEC SPEKK polymers. The polymers selected for the study had similar solubility parameters compared with SPEKK, and membranes could be cast from solutions of blended polymer. The objective was to prepare membranes having a co-continuous morphology with maximized interfacial area.
2. SPEKK polymer solution was cast into a polyether ether ketone reinforcing mesh substrate to provide mechanical support and a controlled interfacial morphology. The resulting reinforce composite membranes would have high mechanical strength and improved dimensional stability.

Interphase Study – SPEKK compounds synthesized from OXPEKK SP were utilized for the interphase studies. Binary polymer blends containing SPEKK and 15% General Electric Ultem 1000 polyetherimide or BASF Ultrason E6020P polyethersulfone were fabricated from dimethyl acetamide solutions based on cloud point studies (see Table 1). The solvent selection and casting temperature were used to design the membrane morphology. The primary goal was to investigate the effect of blend morphology on the conductivity and dimensional stability of the membrane. The morphology of the blends was manipulated by key variables including ion exchange capacity (IEC) of SPEKK, SPEKK morphology (crystalline or amorphous), choice of blending polymer and its MW

and morphology, choice of the solvent system for film casting, and casting temperature/drying rate (see Table 2 and diagram below).

The blends were cast from NMP and DMAc. The solubility of the SPEKK/PEI mixtures decreased with increasing IEC, a possible result of strong ion-dipole interactions. In contrast, SPEKK/PES/NMP and SPEKK/PES/DMAc mixtures were miscible for all studied compositions and sulfonation levels (IECs between 1.5 and 3.5 meq/g).

Membranes were fabricated by solution casting 5% by weight polymer blend in solutions of either N-methyl-2-pyrrolidone (NMP) or dimethyl acetamide (DMAc). Typically, the solvent was allowed to evaporate for about 1 day at 60°C, after which the films were dried at 120°C under vacuum for 3 days.

Binary Blend Morphology and Conductivity

The SPEKK/PEI blends cast at 60°C exhibited a two-phase morphology (see Figure 9). DSC analysis indicated that the two phases in the SPEKK/PEI were essentially the pure components. This is in agreement with the fact that phase separation goes to completion during casting from the ternary SPEKK/PEI/solvent mixture. On the other hand, and in agreement with the ternary solution behavior, homogeneous SPEKK/PES blends can be obtained by solution casting from DMAc, as indicated by the micrograph in Figure 9 for an 85/15 weight to weight blend. All blend compositions, 80/20 through 50/50, and sulfonation levels, 1.7 to 3.5 meq/g, result in similar images for solution cast membranes. Note that no specific interactions were found from spectroscopic analysis of both blends, confirming that the ternary solution behavior determines the final cast polymer blend morphology.

Figure 9: TEM Micrographs of Blends of SPEKK

(IEC = 1.7 meq/g) with 15 wt% PEI (*left*) and with 15 wt% of PES (*right*); both blends were cast from DMAc solutions at 60°C and stained with lead nitrate.

The effect of PEI content on particle size, conductivity and water uptake is summarized in Figure 10 (*left*). Adding the non-conductive polymer reduced the water swelling of these PEMs, but at the expense of a drop in conductivity of the SPEKK/PEI blends. High-temperature annealing of the films after casting had no noticeable effect on the morphology, which may be due to low molecular mobility in the blend.

A second strategy for controlling the morphology was to vary the temperature during casting. The effect of casting temperature is shown in Figure 10. Properties of SPEKK(IEC = 2 meq/g) / PEI Blends (*right*). Smaller particle sizes were obtained by increasing the casting temperature. This is possibly the combined result of postponed phase separation due to the UCST behavior of the ternary blend and faster solvent evaporation resulting in a frozen-in morphology. Note that the particle size does not significantly affect the conductivity or swelling, indicating a lack of SPEKK-PEI entanglement in the blends.

Figure 10: Properties of SPEKK (IEC = 2 meq/g) / PEI Blends

Cast at 60°C (*left*) and for 15 wt% PEI (*right*); water content and conductivities were determined at 25°C and 98% R.H.; brackets: range of smallest to largest particles

In contrast, SPEKK/PES blends gave stable homogeneous films with no phase separation. Homogeneous blends offer significant advantages in regard to membrane integrity, as illustrated for a range of sulfonation levels and blend compositions in Figure 11. Adding 15 wt% PES already decreases the water content at 90°C below 20 H₂O/SO₃H, while the pure SPEKK (IEC = 1.7 meq/g) exhibits excessive swelling. Note that adding the same amount of PEI still results in a high water content of 60 H₂O/SO₃H, indicative for the bad adhesion between SPEKK and PEI. Water soluble SPEKK's (IEC >2.4 meq/g) are rendered insoluble by adding 50% PES. The intimate SPEKK/PES entanglement clearly enhances the robustness of these membranes. An optimum combination of IEC and PES fraction has to be found, however, since adding the non-conductive PES reduces proton conductivity.

Figure 11: Proton Conductivity and Water Content

25°C, 98% R.H. at 90°C of SPEKK/PES membranes: for SPEKK with IEC = 1.7 meq/g as a function of wt% PES (*left*) and effect of IEC for 50/50 SPEKK/PES blends (*right*)

Membrane Casting Experiments

Membranes were cast from a SPEKK, *N*-methyl-2 pyrrolidone (NMP) solution onto a flat glass plate and oven dried. Membranes that were cast from SPEKK had an increasing tendency to adhere strongly to glass as the IEC increased from 1.7 to 2.0 or greater. These membranes were difficult to remove from the glass intact without using steam to partially dissolve the membrane at the glass interface. Experiments were undertaken to find a suitable reinforcing material as a means of improving the cohesion of water softened membranes for high IEC SPEKK. The reinforcing concept was first explored using a solution infiltration technique. The infiltration technique was performed using 5 wt% solution IEC 2.0 SPEKK in NMP. Several substrates were explored including polyether ether ketone (PEEK) mesh cloth, filter paper, and woven glass filter elements. In all cases, the composite membranes were easier to remove from the casting base than the neat SPEKK 2.0. The PEEK reinforcing mesh with approximately 60% void space was selected for advanced experimentation since a commercial supply of PEEK or SPEKK mesh is not yet available. Initially, the PEEK reinforced composite structures were not stable at elevated temperature and humidities and the SPEKK membrane

migrated out of the mesh. Successful composite structures were later fabricated by crosslinking the reinforced SPEKK composites which substantially reduce the flow of SPEKK.

A series of casting procedures were examined for impregnating the mesh fiber with 2.0 IEC SPEKK. A solution of 5 wt % SPEKK 2.0 in 1.5% wt glycerin in acetone and water 50/50 was preferred over NMP based solutions because they were easier to cast and the resulting membranes were easier to remove from the casting plate. The membranes were cast into a PEEK mesh that was mounted to a flat glass substrate. Multiple castings were used, air drying in between each, until the mesh void space was completely filled with dried polymer and a continuous reinforced composite was achieved. The composite was then crosslinked at 120°C in a nitrogen atmosphere to improve dimensional stability and structural durability.

An improved membrane fabrication process was developed for IEC 2.0 SPEKK to improve the poor dimensional stability while maintaining proton conductivity. Typically, most membranes have been cast from NMP at a weight percent solution of SPEKK. The solution is cast onto a flat glass plate, air-dried for 24 hours then oven dried. However, alternative casting solutions were investigated for the purpose of improving both the casting process and the membrane performance.

The reinforced SPEKK membranes were more dimensionally stable than non-reinforced membranes and could be handled and cut with shears without cracking. However, excessive handling suggested that improvements might be required to the interfacial bonding of the reinforcement and the SPEKK.

Task C: SPEKK Blend Characterization

The goals and objectives of this task were:

1. To set up a complete membrane and MEA testing laboratory at Oxford Performance Materials, Inc. by purchase and installation of new testing equipment.
2. To characterize the SPEKK blended membranes for conductivity and physical properties.

Membrane and MEA Testing Laboratory

OPM had planned to set up a working laboratory space and furnish it with new testing equipment that could be used with certainty to obtain data. This goal was partially met through the purchase and installation of a used bench top work-space and ventilated hood and several pieces of used testing equipment. The used equipment included ovens, a multimeter, potentiometer, fuel cell test stand and miscellaneous fixtures for measuring membrane conductivity. The used equipment was originally believed to meet the requirements for membrane and MEA testing. However, there were substantial delays in laboratory work since modifications and upgrades were required for operation of the equipment. In some cases, the used test equipment never really enabled full testing capability, particularly with respect to membrane conductivity and MEA performance. For example, characterization of membrane conductivity was not possible at low relative

humidity. Also, the used MEA test stand did not have computer control to facilitate continuous data collection, nor the ability to apply a specified current load to the test MEAs.

Characterize SPEKK Blended Membranes

The blend membranes were characterized using transmission electron microscopy (TEM), atomic force microscopy (AFM), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). A frequency response analyzer (Solartron SI 1260) combined with a potentiostat (Solartron SI 1287) was used to measure the proton conductivity of hydrated membranes. Single cell performance curves of the membranes were determined using a membrane-electrode-assembly (MEA) at 80°C and 1 atm. Gases for the anode and cathode side were hydrogen and oxygen, respectively.

A resistance testing fixture was fabricated of PTFE and provided for a 1 cm spacing between the (inner) pickup electrodes, as well as large area contacts for the (outer) current supply electrodes. Sample geometry was typically 5 mm width by ~50 micron thickness. Pickup electrodes were fixed at 1 cm distance. The fixture is usable in either the 2 point or 4 point method of resistance measure. Measurements were made with a Pro-Tek LCR meter at 100Hz.

Compositions of pure SPEKK and SPEKK blends were tested. Pure SPEKK exhibited poor mechanical properties in a saturated steam environment, except at the lowest sulfonation levels. At an IEC of 1.3, SPEKK absorbed water from the steam environment and gradually turned to gel, partially flowing from the test fixture. A conductivity of 180 mS/cm was recorded before the sample lost integrity. In contrast, SPEKK with an IEC of 1.1 survived testing intact, with little more than the contact marks from the electrodes as visible evidence that the sample had ever been tested. This sample achieved a conductivity of 95 mS/cm.

As an example, the fuel cell performance of SPEKK with an IEC of 1.7 meq/g is compared to its 85/15 blend with PES. Although lower performance is found for the latter PEM, the stability has been improved significantly (over 50h for the blend compared to about 10h for the parent SPEKK).

Preliminary results show that phase separated morphologies can be obtained when SPEKK is neutralized to its Zn or Mn-salt prior to solution casting. The introduction of additional parameters like counter-ion and extent of neutralization might be valuable for morphology control. Blends with defined morphology can be re-acidified to obtain useful PEM materials.

Task 4: MEA Feasibility

The objectives of this Task were to prepare MEAs from the most promising membrane materials as determined by Task 3 Characterization of SPEKK Blends. The membranes were to be fabricated as traditional MEAs using a typical MEA construction (see Figure 12).

Figure 12: Proton Exchange Membrane Fuel Cell Components

Electrochemical cyclic voltammetry of platinum in a SPEEK, MEA environment was to be performed to demonstrate mechanically stable interfaces after thermal/humidity cycling. The primary goal was to produce a functioning MEA that could be characterized at elevated temperatures so that data could be collected to demonstrate the feasibility of SPEKK as an advancement over Nafion based membranes. As part of this study, OPM worked with the University of Connecticut to understand basic fabrication techniques so that operational MEAs could be fabricated.

Four major accomplishments were realized under this Task were as described following:

Qualify OPM Test Stand and Testing Parameters for MEA – Two new 5 cm² heated fuel cell test fixtures were purchased from Electrochem. Qualification testing performed on a commercially available Nafion based MEA from the Fuel Cell Store. Initial testing revealed operational issues in the test station. The initial 2 channel load bank demonstrated limited functionality as built. Its dynamic range was seriously limited by resistor ranges, which precluded observations at higher current/lower voltage conditions. Also, resolution near the end of travel of the adjustment resistor suffered due to the mechanical limitations of the device. The initial load bank limiting resistor was re-sized on the High Current channel, thereby doubling the maximum (resistor limited) current. Resolution was improved by a factor of 25. A replacement panel voltmeter was ordered from the same vendor, thereby minimizing difficulty in making the upgrade. Replacement resistors were ordered from the same vendors, again minimizing difficulty in making the upgrade.

The OPM fuel cell test stand was certified for use by evaluating a commercially purchased Nafion based MEA. Start-up MEA testing was operated on H₂ and air between 70 and 85°C using a commercially available Nafion based MEA made by Golden Energy Fuel Cell. The MEA active area was advertised as 5 cm² but careful measurement showed the true area was actually only ~4.5 cm². Typical MEA characterization data, such as performance curves, the catalyst, and catalyst loading

were not provided by the manufacturer. A preliminary series of performance curves for this Nafion based MEA is shown in Figure 13.

Figure13: Performance of Nafion MEA in OPM Test Stand

The areal resistive component of these performance curves was quantified by measuring the slope of each curve in its most linear portion, as shown in Figure 14. MEA Resistance (in actuality, these areal resistances also include some cathode mass transfer polarization, making them somewhat higher than purely resistive values). These initial measurements showed lower voltages and higher resistance than typical Nafion performance (i.e., JECS, Vol 151, A623, Si, Kunz & Fenton). The lowest resistance of these tests was over 9-fold higher than typical published resistance measurements for similar Nafion based MEAs. This finding was consistent with a large fraction of the MEA being non-functional. The working hypothesis was poor contact between the MEA and current collector, caused by insufficient compressive force.

A later series of experiments showed the importance of adequate compression force on obtaining low resistance. The compression force was gradually increased by reducing the Teflon spacer gaskets used to prevent gas leaks from the test fixture. The strategy was to progressively undersize the total (anode and cathode) spacer gap relative to the combined thickness of the two gas diffusion media = 29.1 mil (see Figure 14). The gaskets are located at the periphery of the MEAs active area and seal the uncatalyzed membrane against the flat land of the current collector. The gas diffusion media have a high porosity and undergo compression as the spacer gap is reduced. This improves the electrical contact between the current collectors, gas diffusion media and MEA's catalytic layer. At some point, a very narrow gap can be undesirable. Insufficient gasketing can potentially cause leaks. In addition, over-compression of the gas diffusion media can hamper diffusion of gaseous reactants into the catalytic layer.

Figure 14: MEA Resistance

The second series of performance curves, made using the same MEA, now at 85-90°C under similar humidification and feed gas flow rates, but with differing spacer thicknesses, is shown in Figure 15. The change was from a total 28 mil thickness down to a 24 mil thickness.

Figure 15: Effect of Compression on MEA Performance

These areal resistances are plotted vs. total gasket thickness in Figure 16. The resistance decreases monotonically as the gap is reduced to from 28 to 26 and 24 mils. Further gap decrements might further decrease resistance although the incremental benefits appear to be decreasing.

Figure 16: Resistance vs Gasket Spacing

These polarizations approach those some typical Nafion based MEAs in the literature. Since a manufacturer's performance curve was not supplied for comparison, we do not know whether this is a high performance MEA. It may have been designed as a more robust sample MEA to demonstrate fuel cell performance in science class experiments. In such situations, a slightly higher resistance has the advantage of showing representative MEA performance curves while not requiring large and dangerous amounts of H₂ gas. A final series of start-up experiments showed the effect of temperature on the performance curve for Nafion. Temperature was progressively increased from 80 to 120°C. Data was taken at several combination of anode and cathode pressure and humidification. Performance curves at near ambient pressure are plotted in Figure 17, showing that as the temperature increased from 80 to 120°C, the resistance also progressively increased from about 0.5 to 3 ohm-cm².

Figure 17: The Effect of Temperature on Nafion MEA Performance

Testing revealed that proper compression of the MEA against the current collectors and proper control of both humidifiers is critical to obtaining peak performance from an MEA.

Catalyst and GDL Application Development – An air brush technique was used to apply catalyst to SPEKK membranes and carbon decal gas diffusion layers. Initially a laboratory prepared NMP-based ink containing SPEKK and platinum (Pt) on carbon was air brush applied. The ink was later switched to a commercially supplied suspension of 25% Nafion and 20% Pt on XC-72 in methanol because the OPM-prepared ink had problems with the carbon settling out of solution. Typically, 100 or more air brush coats of ink were required to deposit 0.1 mg/cm² of platinum. The reproducibility of this technique was low from membrane to membrane given the large number of coats required, variation in hand applied spray patterns, and the tendency of high IEC SPEKK membranes to swell and distort with methanol exposure leading to increasing damage by the spray velocity.

A decal technique for gas diffusion layer (GDL) was also developed. Commercially supplied carbon paper supplied by Toray was solvent welded to the surface of the membrane with a thin layer of SPEKK solution. The carbon paper was then infiltrated with catalyst ink using the air brush technique. A heat lamp was used to expedite the evaporation of the methanol vehicle from the ink before there was sufficient buildup to attack the membrane materials. This decal technique appeared to result in an intimately mixed layer near to the membrane.

Commercially available catalyst and gas diffusion layers were evaluated as a means of circumventing the difficulties associated with the air brush technique to hopefully improve membrane to membrane reproducibility. However, since these layers were based on Nafion binders, rather than SPEKK binders, they did not function well with our experimental membranes.

The crosslinked composite reinforced membranes were used to prepare MEAs for evaluation in the fuel cell test stand. The MEA was prepared by sandwiching membrane between two gas diffusion electrodes (GDE)s. The GDEs were fabricated by impregnating Toray TGP-H 090, 280 micron thick carbon paper with custom formulated catalyst inks. These inks contained E-Tek 20% platinum catalyst dispersed on XC-72 carbon, a polymer binder, and a volatile vehicle. The catalyst appeared to have a concentration gradient throughout the thickness of the carbon paper. A commercial GDE, E-Tek GDE LT 120E-W was also evaluated in the MEA construction, assuming that it may provide better performance and reproducibility than the custom GDE. Six GDE constructions were fabricated and tested (see Table 3).

Overall, the results obtained from the OPM fabricated GDE's appeared to provide as consistent performance as the commercial GDEs. However, in general, SPEKK based MEAs fabricated with the Nafion based GDEs did not generate current. Only GDEs containing SPEKK binders resulted in MEA current output. In all test configurations, the GDE fused to the SPEKK membrane during in cell testing of the MEAs. Conversely, Nafion membranes suffer electrode delamination during MEA operation.

Table 3: GDE Constructions				
	GDE	Membrane	Vehicle	Result
1	Nafion/ E-Tek 20% pt catalyst	Reinforced	Methanol	High open circuit voltage, no measurable current
2	Nafion/ E-Tek 20% pt catalyst	Commercial 1.3 IEC SPEKK	Methanol	High open circuit voltage, no measurable current
3	SPEKK 2.0 IEC/ E-Tek/ SPEKK blend	Reinforced	Acetone/ Water	High open circuit voltage, excellent current output, SPEKK migration in membrane and at cathode
4	Crosslinked SPEKK 2.0 IEC/ Toray GDL/ E-Tek	Reinforced	Acetone/ Water	High open circuit voltage, excellent current output, SPEKK migration in membrane
5	E-Tek Elat GDE LT 120E-W	Reinforced		No measurable current
6	E-Tek Elat GDE LT 120E-W	Commercial 1.3 IEC SPEKK		Similar open circuit voltage to custom GDE no measurable current

As MEAs fabricated with SPEKK containing GDEs were evaluated, the SPEKK appeared to migrate from the center of the GDE towards the outer edges of the MEA. This migration of binder within the GDE contributed to a very limited MEA service life. Further development of the MEA lead to a new design with crosslinked GDE to minimize the migration of SPEKK from the GDE. Once this design feature was incorporated into the test matrix, the MEAs became stable enough to characterize current density in a fuel cell test stand. The MEAs fabricated from composite membranes had greatly improved handling and survivability over those with monolithic membranes. However, the composite membranes did not produce as much voltage per current density as some of the monolithic structures.

Develop Preliminary Test Data for Experimental MEAs – MEA feasibility appears largely dependent on the dimensional stability of the SPEKK membrane at elevated temperature. Experiments reported previously indicated that SPEKK materials with ion exchange capacity (IEC) 2.0 have good conductivity, but swell excessively in the presence of moisture. SPEKK with IEC below 1.5, are more dimensionally stable, but have reduced conductivity (see Figure 18).

Figure 18: Water Uptake and Conductivity vs. IEC

The SPEKK of most interest to this evaluation is IEC 2.0 SPEKK because of its high conductivity. This material was fabricated as MEA and its performance was evaluated at 73°C and 75% relative humidity with good reproducibility (see Figure 19).

MEA performance testing became problematic for the IEC 2.0 SPEKK membranes as the testing temperature was increased above 73°C because the membrane appeared to dissolve. Blends of SPEKK with other polymers were similarly not stable. Significant improvements in membrane stability were made by crosslinking the SPEKK membranes prior to MEA fabrication. The membrane swelling and dissolution was substantially minimized by the crosslinking process, some additional development was required to enable characterization at temperatures above 80°C. The emphasis of this work was to advance the development of reinforced composite structures by developing a crosslinked structure for improved dimensional stability and durability.

Figure 19: MEA Performance Curves for SPEKK (IEC 2.0)

Composite MEA testing was performed at elevated temperatures, 105-140°C, with the main focus above 100°C so as to eliminate the presence of liquid water. Dry test conditions were enabled by using feedline heaters operating at 120°C independently of the humidifiers and cell.

Several trials were run with SPEKK-based MEAs in cell. Most typically the cell temperature was set at 120°C with the humidifiers set at approximately 5-10 % relative humidity. PTFE gaskets were used to seal the cells. A cross pattern was used to tighten the bolts closing the fixture. Ceramic fiber non-woven insulating cloth was used to help maintain cell temperature.

The in-cell testing results of the reinforced MEAs were encouraging. A poly ether ether ketone (PEEK) mesh reinforced MEA had 870 mV open circuit (O/C) voltage, filter paper reinforced MEAs had O/C voltages of 725 mV, and glass filtration paper had O/C voltage of 500mV. The dimensional sensitivity of the IEC 2.0 SPEKK in the presence of small amounts of water was problematic in the MEA test cell and, in all cases, the MEAs failed after a couple of minutes in the test cell. Membrane reinforcements including poly ether ether ketone (PEEK) mesh, filter paper, and glass filtration paper were an advancement over non-reinforced membranes which were essentially destroyed in the test cell before open circuit voltage could be measured.

Research emphasized optimization on the SPEKK infiltration techniques with the objective of uniformly dispersing the SPEKK throughout the reinforcing structure.

Results of the early in-cell MEA testing appeared to suggest that the water formed at the cathode may be absorbed by the membrane, causing the membrane to plasticize and lose dimensional stability. This hypothesis is based on the location of the membrane failure which occurred at the point of the first closure of the current loop where significant amounts of water are first created in an active cell. It appears that the water created at the cathode is sufficient and available to plasticize non-reinforced IEC 2.0 SPEKK, to the point where the SPEKK is able to flow out of the matrix and into the surrounding gasket area. This phenomena was seen in all high IEC SPEKK membranes to some degree. However, in MEAs that were poor conductors because of reinforcement, the water absorption was less significant and possibly a result of less available water due to lower current flow. Failure could be forced in these same low conducting MEAs by increasing proton conductivity of the membrane by infiltrating it with several drops of candidate water replacement liquid for 24 hours at 40°C before operation at 140°C. The failure location of the MEA with enhanced proton conductivity was also at the first closure of the current loop and thereby appeared to confirm the water absorption hypothesis.

It was encouraging that SPEKK seems able to scavenge available water from a hot, dry environment before it boils and is exhausted from the cell. It is also encouraging that the MEA was able to produce sufficient water to plasticize itself, in spite of the very low humidity in the test cell (approximately 5-10% RH). Further, the use of high boiling water replacement liquids to enhance proton conduction seems to provide another path to operating at elevated temperatures. New experimental strategies need to be engineered to protect the membrane from dissolution by water created at the cathode.

Composite MEA testing was performed at dry cell test conditions between, 105-140°C, with the main focus above 100°C. The hydrogen feed was heated to 120°C and cell humidifiers were set at approximately 5-10% relative humidity. PTFE gaskets were used to seal the cells and a cross pattern was used to tighten the bolts closing the fixture. Ceramic fiber non-woven insulating cloth was used to help maintain cell temperature.

Significant progress was made in fabricating a SPEKK-based membrane having improved dimensional stability. However, equipment limitations prevented conductivity evaluation of the stabilized membranes. MEAs fabricated from the improved composite membranes allowed for detailed testing at several temperature and humidity profiles. Results developed at 105°C demonstrate membrane activity at low relative humidity conditions.

The measured cell output of the crosslinked MEAs was lower than desired because of the approximate 40% membrane volume containing the non-proton conducting PEEK reinforcing mesh. However, the data collected from these MEAs can be used to determine the ability of SPEKK to proton conduct at operating temperatures above 80°C at low humidity. Promising results will provide justification for advanced molecular design of a new grade of improved SPEKK that will remain dimensionally stable at high ion exchange capacities and high proton conductivity.

The dimensionally stable MEAs based on crosslinked reinforced composite SPEKK membranes and crosslinked SPEKK GDEs were evaluated in a test matrix of operating conditions over the range of 25-105°C at relative humidities between 25% and 100%. Comparing current density performance, it appears that the MEA performance was dynamic. The response of the MEA to changes in relative humidity appeared to decrease as the cell operating temperature was increased above 80°C. Overall, the best cell potential was measured when the cell was operated at 50% relative humidity (see Figure 20). Surprisingly, the measured cell potentials of the MEAs operating at 25% RH and 75% RH both slightly underperformed those at 50% RH. As the cell temperature was increased to 80°C or above, the measured differences were less significant.

For example, at 60°C, the MEA cell potential improved approximately 200 mV as the humidity was increased from 25% to 75% RH (see Figure 21).

A similar, but smaller difference between cell potential at 25% RH and 75% RH was seen at 95°C with the optimum cell output occurring at 50% relative humidity (see Figure 22).

Figure 20: SPEKK MEA Performance* vs. Humidity & Temperature

Figure 21: SPEKK MEA Performance at 60°C vs. Humidity

Figure 22: SPEKK MEA Performance at 95°C vs. Humidity

However, as the test temperature was further increased to 105°C, the cell output appeared to be less dependent on humidity and the performance of the MEA appeared equivalent at operating humidities of 25% and 50% relative humidity (see Figure 23).

Figure 23: SPEKK MEA Performance at 105°C vs. Humidity

Select MEA Configuration for Optimization – The crosslinked reinforced MEA composites appeared to be the most durable and therefore have the most promise for optimization. However, at this point in the development, it appears that the molecular structure of PEKK should be improved, pre-sulfonation, before substantial effort is made in this area. The main reason for this conclusion is the fact that highly conductive SPEKKs synthesized by sulfonating OXPEKK-C and OXPEKK-SP are too soluble for practical use long term as membranes. Ideally, an improved grade of PEKK should be developed with higher molecular weight and lower polydispersity so that once sulfonated, it will resist solubilization. A successful new grade of polymer may or may not require blending or reinforcing strategies to achieve a durable membrane for PEM fuel cells.

Task E: MEA Optimization

The objectives and goals of this task were to optimize the MEA construction. However, the SPEKK membrane stabilization lagged behind the allotted project schedule, and there was not sufficient time under this project to undertake this task. Primarily, the available quantities of SPEKK polymer and stability of the membranes were not sufficient to enable substantial MEA optimization work. MEAs that were evaluated under Task D of this research were of insufficient development to allow definitive evaluation of SPEKK as a high temperature membrane. Methods for preparing and applying gas diffusion layers and anode and cathode components of the MEAs need to be further developed at OPM before SPEKK can be evaluated fully.

Task F: Platinum Loading

The objective of this task was to evaluate electrode performance vs platinum catalyst content with the objective of developing an effective level to be used in MEAs that will undergo durability testing. The objectives of this task were not completed under this contract as a result of the difficulties in stable membrane development and subsequent delay in progress on Task D: MEA Feasibility. Experimental development of a stable membrane lagged behind the originally proposed project schedule, thereby precluding advancement on MEA Optimization.

Task G: Durability

The objective and goals of this task were to evaluate optimized MEAs in single cells for 100 hours, plotting polarization vs time. The goals of this task were not completed as a result of the delayed progress on Task D: MEA Feasibility.

Conclusions

The interfacial complexing concept was never fully proven under this contract as a result of the insurmountable dimensional stability issues associated with the existing high IEC SPEKK polymers. Overall, membrane structures prepared from blends of SPEKK with other polymers enjoyed improved dimensional stability, but remained difficult to characterize at temperatures above 80°C. At these lower temperatures, the conductivity of the polymer blends typically was lower than neat SPEKK itself.

Crosslinked, reinforced composite membrane structures were sufficiently dimensionally stable to operate for several hours at elevated temperatures. During this evaluation, the MEAs fabricated from the composite type membranes appeared to maintain proton conductivity at elevated temperatures and low humidity. The level of the SPEKK performance at elevated temperature and low humidity appears comparable to the performance of the MEA at 60°C and high humidity. Given these results, further design of SPEKK is warranted to synthesize and improved grade of SPEKK having higher molecular weight for inherent dimensional stability at IECs of 2.0 or greater. Successful work in this direction should eliminate the need for a reinforcing matrix, and will help to improve the proton conductivity of the membrane to useful levels.

PUBLICATIONS & PRESENTATIONS

1. "Polymer Blends Based on Sulfonated Poly(ether ketone ketone) and poly(ether sulfone) as Proton Exchange Membranes for Fuel Cells", S. Swier, V. Ramani, J.M. Fenton, H.R. Kunz, M.T. Shaw, R.A. Weiss, Journal of Membrane Science, February 2005.
2. Heteropolyacid/Sulfonated PEKK Composite Membranes for PEFC and DMFC Applications," V. Ramani, S. Swier, M. Shaw, H. Kunz and J. Fenton, Paper L1-0405, 205th Meeting of the Electrochemical Society, May 12, 2004.
3. "Proton-exchange membrane materials based on blends of poly(ether ketone ketone) and poly(ether imide)", S. Swier, J. Gasa, M. T. Shaw and R. A. Weiss, APS Meeting, Montreal/Canada (March '04).
4. "Influence of Electrolyte and Electrode Composition on PEFC Performance in Sulfonated PEKK Systems", V. Ramani, S. Swier, R. A. Weiss, M. T. Shaw, H. R. Kunz, J. M. Fenton, 206th Meeting of the Electrochemical Society, Honolulu, HI, Oct. 2004.

COLLABORATIONS & NETWORKS FOSTERED

- University of Connecticut
- Fumatech GmbH

Appendix A

Final Task Schedule

Final Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
A	Material Selection	12/31/03	10/31/04	10/31/04	100%	Completed.
B	SPEKK Processing	02/29/04	08/81/04	09/30/04	100%	Completed.
C	SPEKK Characterization	04/30/04	10/30/04	12/31/04	100%	Completed.
D	MEA Feasibility	09/30/04	06/30/05	09/30/05	100%	MEA stability an issue
E	MEA Optimization	03/32/05	canceled	TBD	0%	Deferred Pending Completion of "D"
F	Platinum Loading	06/30/05	canceled	TBD	0%	Deferred Pending Completion of "D"
G	Durability	09/30/05	canceled	TBD	0%	Deferred Pending Completion of "D"

Appendix B

Final Spending Schedule

Final Spending Schedule

Project Period: 09/06/03 to 09/30/05

Task	Approved Budget	Final Project Expenditures
Task A- Material Selection	\$18,392	\$43,658
Task B- SPEKK Processing	\$45,145	\$67,613
Task C- SPEKK Characterization	\$47,375	\$104,920
Task D- MEA Feasibility	\$135,436	\$265,921
Task E- MEA Optimization	\$49,605	\$2,125
Task F- Platinum Loading	\$27,200	\$330
Task G- Durability	\$21,707	\$47
Total	\$344,860	\$484,614
DOE Share	\$250,000	\$250,000
Cost Share	\$94,860	\$234,615

Appendix C

Final Cost Share Contributions

Final Cost Share Contributions

Funding Source	Approved Cost Share		Final Contributions	
	Cash	In-Kind	Cash	In-Kind
Oxford Performance Materials, Inc.	\$39,360	\$55,500		\$234,615
Total	\$39,360	\$55,500		\$234,615
Cumulative Cost Share Contributions				\$234,615

Appendix D

Energy Savings Metrics

One Unit of Proposed Technology:

One 55 gallon drum of number 2 oil equals 7.8 million BTUs

One Unit of Current Technology:

One 55 gallon drum of number 2 oil equals 7.8 million BTUs

Discussion of Energy Savings:

The values in the following table are theoretically derived and based on published DOE projections of fuel saved by switching 10% of the US automobiles to PEM fuel cell.

Energy Savings Metrics

Type of Energy Used	A	B	C=A-B	D	E=CxD
	Current Technology (Btu / yr / drum)	Proposed Technology (Btu / yr / drum)	Energy Savings (Btu / yr / drum)	Estimated Number of Units in U.S. by 2010 (drums)	Energy Savings by 2010 (Btu / yr)
Oil / Gasoline	17.7B	15.4B	2.3B	6.1M	35.4B
Natural Gas					
Coal					
Electricity (@ 10,500 Btu / kWh)					
Other Energy 1 (Explain)					
Other Energy 2 (Explain)					
Other Energy ...n (Explain)					
Total Per Unit	17.7B	15.4B	2.3B	6.1M	35.4B