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Executive Summary:

The goal of this work was to develop a composite proton exchange membrane utilizing 1) readily available, low cost materials 2) readily modified and 3) easily processed to meet the chemical, mechanical and electrical requirements of high temperature PEM fuel cells. One of the primary goals was to produce a conducting polymer that met the criteria for strength, binding capability for additives, chemical stability, dimensional stability and good conductivity. In addition compatible, specialty nanoparticles were synthesized to provide water management and enhanced conductivity. The combination of these components in a multilayered, composite PEM has demonstrated improved conductivity at high temperatures and low humidity over commercially available polymers. The research reported in this final document has greatly increased the knowledge base related to post sulfonation of chemically and mechanically stable engineered polymers (Radel). Both electrical and strength factors for the degree of post sulfonation far exceed previous data, indicating the potential use of these materials in suitable proton exchange membrane architectures for the development of fuel cells. In addition compatible, hydrophilic, conductive nano-structures have been synthesized and incorporated into unique proton exchange membrane architectures. The use of post sulfonation for the engineered polymer and nano-particle provide cost effective techniques to produce the required components of a proton exchange membrane. The development of a multilayer proton exchange membrane as described in our work has produced a highly stable membrane at 170°C with conductivities exceeding commercially available proton exchange membranes at high temperatures and low humidity. The components and architecture of the proton exchange membrane discussed will provide low cost components for the portable market and potentially the transportation market. The development of unique components and membrane architecture provides a key element for the United States: 1) to transition the country from a fossil fuel based energy economy to a renewable energy based economy, and 2) to reduce our dependence on foreign oil. Developments of this program will serve as an important step toward continuing PEMFC technology and ultimately the broad-based commercial availability of this technology and its benefits.

Objective 1. Tasks 1-9

Objective 1, Task 1 (Q1)

Obtain baseline high temperature polymers including polycarbonate, polysulfone, polyethersulfone, polyetherimide and Parmax poly(p-phenylene) materials and develop basic mechanical, physical and conductivity profiles.

A number of potential baseline polymers were obtained, and their basic physical, mechanical and thermal profiles (Table 1), their chemical stability profiles (Table 2), and their solubility profiles (Table 3) were developed. A fuel cell test station (Model 2006-S-C) and associated apparatus from Fuel Cell Technologies was installed, benchmarked and used to perform through-plane proton conductivity measurements. The Fuel Cell Test Station is capable of generating electrochemical impedance spectra (EIS). This sophisticated test differentiates between all of the major sources of loss in a fuel cell, because it can evaluate time- and frequency-dependent phenomena. In EIS, conductivity is obtained from the bulk specimen resistance, R , as Z' tends to a minimum at infinite frequency. Through-plane conductivity testing (i.e., perpendicular to the surface of the film) was carried out at 70°C / 80% RH.

Table 1. Thermal and mechanical properties of baseline polymers.

Material	T _g (DSC) / °C	Inception of major weight loss (TGA) / °C	Storage modulus at RT (DMA) / MPa	Storage modulus at 170°C (DMA) / MPa
Nafion N-117*	Ill-defined	330 (1st) 400 (2nd)	600	3.3
Dow Calibre 302-15 PC	147	398	2050	Very low above T _g
Solvay Udel P- 3500 LCD- MB7 PSU	184	450	2250	250
Solvay Radel A-100-700 PES	218	425	1700	1000
GE Ultem PEI	216	450	2800	100
Parmax 1200 CK	155	406	8000	50
Daikin EFEP*	Ill-defined	325	3	Very low

* An elastomer material.

The behavior of the baseline polymers was studied in Fenton's reagent (for peroxide stability), in concentrated sulfuric acid (98%), and in 38% sulfuric acid (maximum proton conductivity) for 8 hours at room temperature (Table 2). Visual inspection showed no changes in the polymers, with the exception of PSU, PES, and PEI which dissolved in concentrated sulfuric acid.

Table 2. Visual inspection of stability of baseline polymers after 8 hours at room temperature.

Material	Fenton's reagent	98% H ₂ SO ₄	38% H ₂ SO ₄
Calibre PC	No change	No change	No change
Udel PSU	No change	Dissolved	No change
Radel PES	No change	Dissolved	No change
Ultem PEI	No change	Dissolved	No change
Parmax 1200 CK	No change	No change	No change

Table 3. Solubilities of baseline polymers and nano-additives.

Polymers and nano-additives	Isopropylacetate	NMP	DMAc	CH ₂ Cl ₂
POSS(Ph) ₈	No	No	No	No
Phosphazene(OPh) ₆	Yes	Yes	Yes	Yes
Sulfonated POSS	No	Sparingly	No	No
Sulfonated phosphazene	No	Sparingly	Yes	Sparingly
Calibre 302-15 PC	No	Yes	Sparingly	Yes
Udel P-3500 LCD-MB7 PSU	No	Yes	Yes	Yes
Parmax 1200 CK	No	No	No	No
Parmax 1201	No	No	No	Yes
Ultem PEI	No	No	No	Yes
Radel A-100-700 PES	No	Yes	Yes	Yes
BPS-40	No	No	Yes	No

The Wright Patterson AFB sulfonated polythioether sulfone (SPTES) polymer (see Dang, T.D.; Bai, Z.; Dalton, M.J.; Fossum, E., *Polym. Prepr.*, **2004**, 45(1), 22-23) and non-sulfonated Solvay Radel A-100 polyethersulfone (PES) were initially shortlisted for film formulation experiments with nano-additives. PES was selected because of its high modulus at high temperature, good solubility properties and reasonable stability to acid and peroxide. After it was demonstrated that films cast from non-sulfonated Radel A-100 and sulfonated nano-additives had zero proton conductivity, the program focused exclusively upon sulfonated baseline polymers. An account of the sulfonation (modification) of Solvay Radel A-100 PES and also of Solvay Radel R-5000 polyphenylsulfone (PPSU) is given under Task 2.

Characterization data for a series of partially sulfonated SPTES polymers supplied by Akron Polymer Sysms is given in Table 4, and a TGA (nitrogen, 10°C/min) of the 55/45 material appears in Figure 1. DSC showed the SPTES 55/45 material to have a T_g of 214°C.

Table 4. SPTES polymer characterization data.

Sample	Sulfonation level, NMR (d ₆ -DMSO)	Molecular mass, SEC (NMP)	Through-plane conductivity (S cm ⁻¹)	Intrinsic viscosity
Akron Polymer X4	50% sulfonation 14.9 wt.% SO ₃ H	Mn=45,220 Mw=69,630 Mw/Mn=1.54	Not done (Pin holes)	1.4
Akron Polymer X7	50% sulfonation 14.9 wt.% SO ₃ H	Mn=30,670 Mw=55,220 Mw/Mn=1.80	Not done (Pin holes)	1.2
Akron Polymer 55/45	45% sulfonation 13.6 wt.% SO ₃ H	Mn=70,780 Mw=101,100 Mw/Mn=1.43 Bimodal	0.059	NA

Figure 1. TGA of sulfonated polythioether sulfone (SPTES 55/45).

A series of 100% sulfonated SPTES polymers was also prepared at MMI (Figure 2), and characterization data for these is given in Table 5. These reactions were carried out in NMP at 100 to 180°C in the presence of potassium carbonate. Yields were greatly improved by precipitating the crude product out of acetone (rather than methanol, as per the literature method). Since this is a condensation polymerization, high purity monomers were essential in order to achieve high molecular masses. Although 4,4-thiobenzenethiol monomer was commercially available, it was necessary to purify it by recrystallization from hexane. The sulfonated sulfone monomer (see Figure 2) was prepared by sulfonation, and was then purified by salting out followed by successive recrystallizations from methanol-water. The monofunctional endcapping agent 4-fluorobenzophenone was used in order to reduce the dark color of the product caused by very low levels of deeply colored impurities. NMR spectra of SPTES in d₆-DMSO showed a good match to literature data. Although the molecular weight values in Table 5 are significant, they fall below the literature values in the 50,000 to 100,000 range, and thus low quality, flaky films were obtained when the SPTES sample was cast from ~20% solids in DMAc.

Figure 2. Synthesis of the SPTES polymer.

Table 5. 100% sulfonated SPTES polymer preparations.

Synthesis	Scale (g)	Molecular mass, SEC (NMP)	Inherent viscosity (NMP, dL g ⁻¹)
Uncapped	20	Mn = 13,800 Mw=15,700 Mw/Mn=1.14	0.300
Capped	35	Mn = 16,000 Mw=23,800 Mw/Mn=1.49	0.297
Capped	13	Mn = 11,000 Mw=14,600 Mw/Mn=1.33	0.281

Objective 1, Task 2 (Q1)

Evaluate modifications to the polymers necessary to achieve temperature, %RH, and conductivity targets. Synthesize modified baseline high temperature polymers.

Sulfonated Radel A-100 Polyethersulfone (PES)

Radel A-100 PES was modified by sulfonation, and was evaluated as a baseline polymer to carry nano-additives. Two sulfur trioxide sulfonations of Radel A-100 PES were developed. In the first method, a 4 wt.% solution of sulfur trioxide in dichloromethane was added to a 20 wt.% solution of PES in dichloromethane and stirred at room temperature. The quantities were such that a sulfonated PES with 7.6 wt.% SO₃H content (i.e., comparable to Nafion) would be generated if the reaction went to completion. After 2 hours, the sulfonated polymer had precipitated out of solution and the sulfur trioxide was consumed (as indicated by an absence of fuming on exposure to air/normal humidity). A light brown clear film of the product was cast from NMP. In the second method, a 20 wt.% solution of Radel A-100 PES in NMP was similarly sulfonated, and the solution was stirred at room temperature for 24 hours. Both of these methods

could be readily scaled up to 100 g batches. ^1H NMR showed that sulfonation occurred on the more activated OPhO units, rather than on the less activated OPhSO₂ PES units (Figure 3). Calculated estimates from ^1H NMR integrals showed that Radel A-100 contains a 2.6 to 1 molar ratio of conventional to OPhO-type repeat units. 17% of all repeat units (conventional and OPhO) had been sulfonated and the polymer contained 3 wt.% SO₃H groups. SEC in NMP with 0.1 M sodium nitrate gave Mn = 49,110, Mw = 69,880, and Mw/Mn = 1.42.

Figure 3. Sulfonation of Radel A-100 (PES) and of Radel R-5000 (PPSU).

Sulfonated Radel R-5000 Polyphenylsulfone (PPSU)

Since the structure of Radel A-100 was such that high sulfonation levels and high proton conductivities were difficult to achieve, an alternative Radel polymer that could be more readily sulfonated was selected, namely, Radel R-5000 polyphenylsulfone (PPSU) (Figure 3). Two sulfonation methods for Radel R-5000 were evaluated. The first method used sulfur trioxide as a sulfonating agent, and the second method used chorisulfonic acid as a sulfonating agent.

Radel R-5000 was sulfonated by reacting 20 wt.% solids solutions of Radel in NMP with an appropriate quantity of sulfur trioxide in dichloromethane. A number of Radel R-5000 / sulfur trioxide sulfonations were attempted with various target sulfonation levels. Table 6 shows the relationship between target and obtained sulfonation levels measured from ^1H NMR spectra. Owing to the decrease in NMP solubility as the sulfonation level increases, it was found that sulfonation levels above 12 wt.% could not be obtained using the NMP/sulfur trioxide method. In order to determine if sulfonation levels could be successfully controlled below 12 wt.%, a sulfonation with a target of 5 wt.% SO₃H was attempted, but this gave a product containing only 2 wt.% SO₃H (Table 6).

Table 6. Target and actual sulfonation levels in sulfur trioxide/NMP sulfonations of Radel R-5000.

Target sulfonation level, wt.% SO ₃ H (from reaction stoichiometry)	Actual sulfonation level, wt.% SO ₃ H (from ¹ H NMR)
31	10
21	12
12	11
5	2

In parallel to this work, a study of an alternate chlorosulfonic acid-acetic anhydride sulfonation method (see Cui, W.; Socza-Guth, T.; Frank, G., Celanese Ventures GmbH, **2004**, *US Patent 6790931 B2*) was carried out. All sulfonated Radel materials prepared using these two methods were characterized for sulfonation level (by ¹H NMR) and for proton conductivity. Films were cast from formulations of these materials with sulfonated POSS and sulfonated phosphazene nano-additives, and these films were also characterized for proton conductivity. It was found that pure S-Radel films, and also S-Radel/S-POSS films and S-Radel/S-phosphazene films would only conduct protons above a threshold sulfonation level of ~17 wt.% SO₃H. Since the maximum sulfonation level possible using the sulfur trioxide method was below this threshold (Table 6), the chlorosulfonic acid method was selected.

The series of sulfonated Radel R-5000 batches prepared using the chlorosulfonic acid-acetic anhydride sulfonation method was characterized for sulfonation level (by ¹H NMR in d₆-DMSO), for molecular mass (by SEC in NMP), and for through-plane proton conductivity at 70°C / 80% RH (Table 7). Bimodal mass distributions were obtained for two sample batches of sulfonated Radel R-5000 prepared by Akron Polymer Systems, AP7 and AP11 (Table 7), suggesting that chain scission had occurred under the sulfonation conditions they used.

Table 7. Sulfonation level, molecular mass, and conductivity data for batches of sulfonated Radel R-5000.

Sample	Sulfonation level, (wt.% SO ₃ H) from NMR (d ₆ - DMSO)	Molecular mass, SEC (NMP)	Through-plane conductivity (S cm ⁻¹)
Sulfonated Radel R-5000 Akron Polymer AP7	15.9	Mn=10,870, Mw=15,280 Mw/Mn=1.41 (bimodal)	0.002
Sulfonated Radel R-5000 Akron Polymer AP11	17.0	Mn=9,620, Mw=12,920 Mw/Mn=1.34 (bimodal)	Dissolved during 3% peroxide pre- treatment
Sulfonated Radel R-5000 Akron Polymer X43	15.7	Mn=27,910, Mw=43,740 Mw/Mn=1.57	0.019

Sulfonated Radel R-5000 Chemsultants #5A	7.6	Mn=29,730, Mw=40,540 Mw/Mn=1.36	0
Sulfonated Radel R-5000 Chemsultants #5B	12.4	Mn=30,000, Mw=40,000 Mw/Mn=1.33	0
Sulfonated Radel R-5000 Chemsultants #6	12.2	Mn=36,980, Mw=47,340 Mw/Mn=1.28	0
Sulfonated Radel R-5000 Chemsultants #7	17.6	Mn=33,190, Mw=46,240 Mw/Mn=1.39	0.002
Sulfonated Radel R-5000 Chemsultants #8	17.4	Mn=31,230, Mw=42,200 Mw/Mn=1.35	0.065
Sulfonated Radel R-5000 Chemsultants #9	17.8	Mn=27,010, Mw=37,270 Mw/Mn=1.38	0.031 0.038
Sulfonated Radel R-5000 Chemsultants #10	17.5	Mn=22,340, Mw=30,200 Mw/Mn=1.35	0.036
Sulfonated Radel R-5000 Chemsultants #11	17.4	Mn=31,480, Mw=43,550 Mw/Mn=1.38	0.019
Sulfonated Radel R-5000 Chemsultants #12	18.5	Mn=32,610, Mw=44,700 Mw/Mn=1.37	0.038 0.020

Objective 1, Task 3 (Q2)

Synthesize novel ionic nanoparticles including POSS nanoparticle materials that contain sulfonic acid functional groups, POSS nanoparticle materials that contain phosphonic acid functional groups, phosphazene nanoparticle materials that contain sulfonic acid functional groups, and phosphazene nanoparticle materials that contain phosphonic acid functional groups.

Sulfonic acid POSS (S-POSS) was prepared via a one-step aromatic electrophilic sulfonation of octaphenyl POSS using an excess of chlorosulfonic acid (Figure 4), and the resulting brown solid was characterized by IR, ^1H NMR, ^{13}C NMR and MALDI-TOF mass spectrometry. The asymmetric SO_3 band at $\sim 1150\text{ cm}^{-1}$ and the symmetric SO_3 band between 1000 and 1100 cm^{-1} characteristic of aromatic sulfonic acids (see Ghosh, A.K.; Ramachandran, V.; Hanra, M.S.; Misra, B.M., *J. Macromol. Sci. Pure Appl. Chem.*, **2002**, A39(3), 199-216) were observed in the IR spectrum. An asymmetric SiOSi band at $\sim 1050\text{ cm}^{-1}$ and a symmetric SiOSi band at $\sim 800\text{ cm}^{-1}$ associated with POSS were also observed. The S-POSS compound had markedly different solubility characteristics to the starting octaphenyl POSS reagent. S-POSS was soluble in water, while octaphenyl POSS was not. Four peaks were observed in the aromatic region of the ^1H NMR spectrum with chemical shifts, integrals, doublets and coupling constants consistent with the four non-equivalent protons of a *meta*-disubstituted phenyl group carrying a sulfonic acid

group and the electron-withdrawing and *meta*-directing POSS substituent. Four strong ArCH peaks were also observed in the aromatic region of the ^{13}C NMR spectrum. In contrast, the starting octaphenyl POSS reagent is a mono-substituted phenyl compound with three non-equivalent aromatic proton environments and three non-equivalent ArCH carbon environments.

Figure 4. Preparation of sulfonated POSS (S-POSS).

The corresponding phosphonic acid half ester of POSS (P-POSS) was prepared in a three-step synthesis (Figure 5). In the first step, octaphenyl POSS was brominated using bromine and iron in a literature method described elsewhere (see Brick, C.M.; Tamaki, R.; Kim, S.G.; Asuncion, M.Z.; Roll, M.; Nemoto, T.; Ouchi, Y.; Chujo, Y.; Laine, R.M., *Macromolecules*, **2005**, 38, 4655-4660). The NMR and mass spectra showed that the desired product had been obtained. In the second step, octabromophenyl POSS was phosphonated (see Allcock, H.R.; Hofmann, M.A.; Wood, R.M., *Macromolecules*, **2001**, 34, 6915-6921, and Lafitte, B.; Jannasch, P., *J. Polym. Sci. Part A, Polym. Chem.*, **2005**, 43, 273-286) using diphenylchlorophosphate and butyl lithium under the rigorously anhydrous and oxygen-free conditions necessary for the use of pyrophoric reagents. The MALDI-TOF mass spectrum showed a distribution of products ranging from a POSS carrying one phosphonic ester group to a POSS carrying five phosphonic ester groups. This material was soluble in chloroform. In the third step, the phosphonic ester precursor POSS (PE-POSS) was hydrolyzed to the desired phosphonic acid half ester P-POSS product following a literature method using sodium hydroxide in THF (see Allcock, H.R.; Hofmann, H.R.; Ambler, C.M.; Morford, R.V., *Macromolecules*, **2002**, 35, 3484-3489) which was subsequently modified, and found to give improved yields if wet THF was used and/or water was added to anhydrous THF. The expected asymmetric and symmetric POSS bands were observed in the IR spectrum, plus a number of bands characteristic of a phosphonic acid half ester, i.e., a POH stretch band at 944 cm^{-1} , a P=O stretch at 1087 cm^{-1} , acid salt bands at 2700 and 2100 cm^{-1} , and a distinctive HOP=O band at 1630 cm^{-1} associated with species in which one P=O is combined with one POH (such as phosphonic acid half esters, phosphinic acids, or phosphonous acids). Since both the phosphonic ester precursor (PE-POSS) and the phosphonic half ester product (P-POSS) contain disubstituted POSS phenyl groups and phosphonic ester phenyl groups, the ^1H and ^{13}C NMR spectra of these materials were very similar and the aromatic regions were complex owing to the numerous aromatic protons and carbon atoms present. However, it was possible to assign the spectra using the ^1H and ^{13}C NMR spectra of the model compounds diphenylphosphate and triphenyl phosphate to distinguish POSS-aromatics from P-O-aromatics. P-POSS was soluble in methanol.

Figure 5. Preparation of phosphonic acid POSS (P-POSS).

Sulfonated phosphazene was prepared in a two-step synthesis from hexachlorophosphazene (Figure 6). The molecular ions for both the precursor and the final S-phosphazene product were observed in the mass spectra.

Figure 6. Preparation of sulfonated phosphazene (S-phosphazene).

Sulfonic acid POSS (designated S-POSS). Octaphenyl-POSS (69.8 g, 67.5 mmol) was added to chlorosulfonic acid (250 mL, 3.76 mol). The reaction solution was stirred overnight at room temperature. Unreacted chlorosulfonic acid was removed by vacuum distillation. Deionized water (400 mL) was added to dissolve the crude product. The volume was reduced to 100 mL under reduced pressure. The crude product was washed three times with anhydrous tetrahydrofuran (1.5 L). The product was then dried under reduced pressure to give a brown solid in quantitative yield.

Phosphonic ester POSS (designated PE-POSS). Octabromophenyl POSS (87.09 g, 5.3 mmol) was dissolved in tetrahydrofuran (1 L) and cooled to -78°C in a dry-ice slush bath. Butyl lithium (27.45 g, 0.429 mol) was added to the solution followed by diphenylchlorophosphate (115.4 g, 0.429 mol). The solution was allowed to warm to room temperature overnight. Deionized water (200 mL) was added and the solvents were removed under reduced pressure. The crude product was washed three times with water (200 mL) and then with hexane (200 mL). The product was dried under reduced pressure. Yield = 118 g, 78%.

Phosphonic acid half ester POSS (designated P-POSS). Hydrolysis of the diphenyl phosphonic acid ester was performed using a two-phase solution of tetrahydrofuran (200 mL), sodium hydroxide (75 g, 1.9 mol), and deionized water (150 mL). The mixture was stirred for two days and then allowed to separate. The organic layer was decanted off and dried. Concentrated hydrochloric acid (200 mL, 37 wt.%) was added to the crude product and stirred overnight. The

acid was decanted off, the product was dissolved in acetone (100 mL), and the solution was filtered. The product was then dried under reduced pressure. Yield = 12 g.

Preparation of sulfonated phosphazene precursor. Sodium hydride (25.8 g, 1.07 mol) was mixed under dry nitrogen with tetrahydrofuran (250 mL, 3.1 mol) and cooled in an ice/water bath. Phenol (100.0 g, 1.06 mol) in solution with tetrahydrofuran (250 mL, 3.1 mol) was slowly added to the stirring mixture. Once the addition was complete, a solution of hexachlorocyclotriphosphazene (61.5 g, 0.177 mol) in tetrahydrofuran (250 mL, 3.1 mol) was added slowly. The mixture was brought to reflux and heated overnight. A white precipitate was removed by reduced pressure filtration. The precipitate was washed with anhydrous tetrahydrofuran. The filtrate was collected and then dried under reduced pressure. The resulting white crystalline solid was redissolved in acetone (200 mL, 2.72 mol), which formed a suspension that subsequently precipitated in deionized water (1.5 L, 83 mol). The resulting white crystalline precipitate was filtered off under reduced pressure. The product was then recrystallized in hexane-toluene (1.5:1 v/v, 250 mL). The resulting needle-shaped crystals were dried. Yield = 83 g.

Preparation of sulfonated phosphazene (designated S-phosphazene). Hexaphenoxycyclotriphosphazene (36.30 g, 5.23 mmol) was dissolved in dichloromethane (200 mL, 3.1 mol), cooled in an ice/water bath, and chlorosulfonic acid (70 mL, 1.05 mol) was added. The reaction was allowed to warm to room temperature overnight. The mixture was allowed to separate. The organic layer was collected and vacuum distilled to yield a red oil. Water (200 mL, 11.11 mol) and methanol (200 mL, 5 mol) were added to dissolve the oil. The resulting mixture was then filtered. The red solution was dried under reduced pressure to give a red oil. Yield = 104 g.

Objective 1, Task 4 (Q2)

Synthesize selected mixed surface POSS nanoparticle materials and/or selected mixed surface phosphazene nanoparticle materials that bear sulfonic acid functional groups that impart conductivity, but that also contain compatibilizing groups that may aid in subsequent polymer matrix dispersibility and solubility.

In order to study the effect of long (C_{18}) alkyl chains on the solubility of sulfonated POSS, and on the additive dispersion and morphology of an S-PPSU-POSS membrane, a POSS compound carrying both C_{18} alkyl groups and sulfonic acid groups was prepared in a two-step synthesis (Figure 7). In the first step, octaphenyl POSS was alkylated in a Friedel-Crafts reaction. Initially a literature method for the Friedel-Crafts alkylation of benzene with *t*-butyl chloride and aluminum chloride at 0°C was used (see Fieser, L.F.; Fieser, M., *Reagents for Organic Synthesis*, John Wiley and Sons, Inc., New York, 1967, Volume 1, p. 26), but ^1H NMR showed that only one-third of the POSS phenyl groups had been successfully alkylated. The method was then modified. The molar excess of aluminum chloride to octaphenyl POSS was increased from 1.5-fold to 5-fold, the reaction time was extended from a few minutes to three days, the temperature was raised from 0°C to room temperature, and a fully alkylated product was obtained. The MALDI-TOF mass spectrum of this material had a distribution of peaks at 252 mass unit intervals (corresponding to the octadecyl group). The peak at the center of the distribution with the highest intensity was at 2820, corresponding to a structure with seven alkyl groups per POSS (target mass of 2797 plus sodium). The high mass side of the distribution went up to 3575, corresponding to a structure with ten alkyl groups per POSS (target mass of 3552 plus sodium) and demonstrating that a small fraction of the phenyl rings had been dialkylated. The ^1H and ^{13}C

NMR spectra suggested *meta*-substitution had occurred as expected. This material had good solubility in chloroform.

In the second step, the alkylated POSS product (A-POSS) was sulfonated using sulfuric acid in dichloromethane. Since alkylated octaphenyl POSS is more activated to electrophilic aromatic substitution than octaphenyl POSS (owing to the inductively electron-donating nature of the alkyl group), a more mild sulfonating system than the chlorosulfonic acid used above for octaphenyl POSS was selected. In the sulfonated alkylated POSS (SA-POSS) IR spectrum, SO_3 and SiOSi bands were observed (as per the S-POSS discussion above) plus methyl and methylene symmetric and asymmetric stretch bands in the 2800 to 2900 cm^{-1} region associated with the octadecyl groups. The ^1H and ^{13}C NMR spectra suggested that tri-substituted phenyl groups were present (i.e., carrying a POSS group, an alkyl group, and a sulfonic acid group). There were three peaks in the aromatic region of the ^1H NMR spectrum corresponding to three non-equivalent aromatic proton environments, and three strong peaks in the aromatic region of the ^{13}C NMR spectrum corresponding to three non-equivalent ArCH carbon atoms. However, the spectra did not contain sufficient information to determine whether the sulfonic acid groups were *ortho* or *para* (or both) to the POSS substituent. This material was water soluble.

Figure 7. Preparation of sulfonated alkylated POSS (SA-POSS).

Alkylated POSS (designated A-POSS). 1-Chlorooctadecane (169.8 g, 0.587 mol) in solution with dichloromethane (600 mL) was mixed under nitrogen with octaphenyl POSS (76.45 g, 74.0 mmol). Aluminum chloride (20 g, 15 mmol) was added in four parts over a 10-minute period. The mixture was stirred initially at 0°C and allowed to warm to room temperature over 3 days. 100 mL of water was added, resulting in a pale precipitate. The crude product was extracted into ethyl acetate from water. The ethyl acetate was removed under reduce pressure. THF was used to dissolve the crude product, which was filtered through a short column of flash column chromatography silica. The volume of the filtered solution was reduced to about 100 mL and the solution was precipitated into acetone (1.5 L). The acetone solution was decanted off and discarded. Chloroform was used to dissolve the material, which was dried under reduced pressure to produce an oil. Yield = 154.2 g, 68%.

Sulfonic acid alkylated POSS (designated SA-POSS). Alkylated POSS (73.31 g, 24.3 mmol) was dissolved in dichloromethane (300 mL) and cooled in an ice-water bath. Sulfuric acid (21 g, 11 mL, 0.214 mol) was added to the solution and stirred overnight at room temperature. Dichloromethane was removed under reduced pressure and the resulting oil was added to dry methanol (1.2 L) and formed a precipitate. The precipitate was dissolved in chloroform and then dried under reduced pressure. Yield = 75.81 g, 82%.

Objective 1, Task 5 (Q2)

Characterize all synthesized nanoparticle materials by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, FTIR, SEC-MALLS, MALDI-TOF MS, and assess their solubility characteristics.

Sulfonated POSS (designated S-POSS) has the following spectra: IR: ν (cm^{-1}) 3070 (OH of SO_3H), 2330 ($\text{SO}_3\text{H}-\text{H}_2\text{O}$), 1718, 1590, 1470, 1446, 1395, 1298, 1132 (SO_3 asym), 1081 (SO_3 sym), 1023 (SiOSi asym), 991, 806 (SiOSi sym); ^1H NMR (D_2O): δ_{H} (ppm) 7.54 (dd; *ArH meta* to POSS), 7.81-7.83 (2dd; *ArH para* to SO_3H , *ArH para* to POSS), 8.03 (dd; *ArH ortho* to SO_3H and POSS); ^{13}C NMR (D_2O): δ_{C} (ppm) 122.5 (*ArCH*), 128.4 (*ArCH*), 130.0 (*ArCH*), 143.2 (*ArCH*); MALDI-TOF MS: m/z 1698 (Calc. 1697, molecular ion plus sodium).

Phosphonic ester POSS (designated PE-POSS) has the following spectra: ^1H NMR (CDCl_3): δ_{H} (ppm) 7.2 (m; *ArH*). ^{13}C NMR (CDCl_3): δ_{C} (ppm) 120.1 (*POArCH*), 125.1 (*POArCH*), 127.9 (*POSSArCH*), 129.6 (*POArCH*), 134.1 (*POSSArCH*), 150.5 (s; *POArCO*); MALDI-TOF MS: m/z 1287 (Calc. 1287, mono-substituted molecular ion + Na, $\text{POSSPh}_7(\text{Ph}(\text{PO}(\text{OPh})_2)_2)$, 1543 (Calc. 1543, disubstituted molecular ion + 2Na, $\text{POSSPh}_6(\text{Ph}(\text{PO}(\text{OPh})_2)_2)_2$, 2258 (Calc. 2253, penta-substituted molecular ion + 5Na, $\text{POSSPh}_3(\text{Ph}(\text{PO}(\text{OPh})_2)_5)$).

Phosphonic acid half ester POSS (designated P-POSS) has the following spectra: IR: ν (cm^{-1}) 3067 (*ArH*), 3040 (*ArH*), 2700 (*POH*), 2100 (*POH*), 1630 (*HOP=O*), 1584, 1487, 1196 (SiOSi asym), 1087 (*P=O*), 944 (*POH*, str), 753 (SiOSi sym). ^1H NMR (CD_3OD): δ_{H} (ppm) 6.87-6.91 (m; *ArH*), 6.95-6.97 (m; *ArH*), 7.05-7.10 (m; *ArH*). ^{13}C NMR (CH_3OD): δ_{C} (ppm) 120.5 (*POArCH*), 122.7 (*POSSArCH*), 124.7 (*POArCH*), 127.8 (*POSSArCH*), 129.9 (*POArCH*), 133.9 (*POSSArCH*), 152.4 (*POArCO*).

Sulfonated phosphazene precursor compound has the following spectra: ^1H NMR (D_2O): δ (ppm) 6.91-7.17 (m; *ArH*); ^{13}C NMR (D_2O): δ (ppm) 121.0 (*ArCH*), 124.8 (*ArCH*), 129.4 (*Ar-CH*), 150.6 (*ArCO*); MS (LC): m/z 694 (Calc. 695, molecular ion).

Sulfonated phosphazene (designated S-phosphazene) has the following spectra: IR: ν (cm^{-1}) 2924 (OH of SO_3H), 1460, 1429, 1375 (asym SO_2), 1301, 1133, 1021, 1120 (sym SO_2); ^1H NMR (D_2O): δ (ppm) 7.13-7.16 (d; *ArCH meta* to SO_3H), 7.62-7.64 (d; *ArCH ortho* to SO_3H); ^{13}C NMR (D_2O): δ (ppm) 120.5 (*ArCH*), 127.5 (*ArCH*), 138.6 (*ArCO*), 153.7 (*ArCSO}_3\text{H}*); MS (EI positive mode): m/z 1305 (Calc. 1305, sodium salt).

Alkylated POSS (designated A-POSS) has the following spectra: ^1H NMR (D_2O): δ_{H} (ppm) 0.87 (t; CH_3), 1.42 (m; CH_2), 7.01 (s; *ArH ortho* to POSS), 7.11 (m; *ArH meta* to POSS), 7.56 and 7.67 (m; *ArH ortho* and *para* to POSS). ^{13}C NMR (D_2O): δ_{C} (ppm) 19.7 (CH_3), 26.1 to 31.8 (various CH_2), 37.1 (ArCH_2), 127.2 (*ArCH*), 130.2 (*ArCH*), 131.7 (*ArCH*), 133.6 (*ArCH*). MALDI-TOF MS: (m/z) 2820 (Calc. 2820, hepta-substituted POSS, molecular ion plus sodium), 3072 (Calc. 3073, octa-substituted POSS, molecular ion plus sodium).

Sulfonated alkylated POSS (designated SA-POSS) has the following spectra: IR: ν (cm^{-1}) 3068, 3049, 3005 (*ArH*), 2951, 2924, 2843 (CH_2 and CH_3), 2726, 2676 ($\text{SO}_3\text{H}-\text{H}_2\text{O}$), 1681, 1596, 1429 (Si-Ph , sym) 1378, 1156 (SO_3 asym), 1118 (SiOSi asym), 788 (SiOSi sym). ^1H NMR (D_2O): δ_{H} (ppm) 0.86-0.90 (t; CH_3), 1.27-1.40 (m; CH_2), 1.52-1.59 (m; CH_2), 2.48 (CH_2Ar), 7.05-7.81 (3m; *ArH*), 9.54 and 11.05 (SO_3H). ^{13}C NMR (D_2O): δ_{C} (ppm) 14.5 (CH_3), 20.1 to 32.6 (various CH_2), 37.4 (ArCH_2), 127.3 (*ArC*), 128.5 (*ArCH*), 132.1 (*ArCH*), 133.4 (*ArC*), 134.0 (*ArC*), 134.7 (*ArCH*).

The stability of model and sulfonated nano-additives (Table 8) was studied in Fenton's reagent, in concentrated sulfuric acid (98%), and in 38% sulfuric acid (maximum proton conductivity), for 8 hours at room temperature. Thermal stability was studied by TGA (Table 9) in order to obtain an upper temperature limit for film preparation techniques.

Table 8. Stability of sulfonated nano-additives after 8 hours at room temperature.

Material	Fenton's reagent	98% H ₂ SO ₄	38% H ₂ SO ₄
S-POSS	Dissolved	Dissolved	Dissolved
S-Phosphazene	Dissolved	Dissolved	Dissolved

Table 9. TGA data for sulfonated nano-additives.

Material	Onset of mass loss (°C)	Mass loss fraction (%)
S-POSS	208	85
S-Phosphazene	145	92

Objective 1, Task 6 (Q3)

Characterize all polymer-ionic nanoparticle blend formulations by SEM to assess the efficiency and extent of mixing and dispersion, and any salient morphological features.

S-POSS and S-Phosphazene Study

A TEM study of the morphology of the following three films was carried out:

1. 25% Sulfonated POSS, 75% sulfonated Radel R-5000 batch #4 (17 wt.% SO₃H)
2. 20% Sulfonated phosphazene, 80% sulfonated Radel R-5000 batch #4 (17 wt.% SO₃H)
3. 100% Sulfonated Radel R-5000 batch #4 (17 wt.% SO₃H) control

Both the pure sulfonated Radel control film, and the sulfonated phosphazene-containing film (see Figure 8) showed no discernible domain structure. In contrast, the sulfonated POSS formulation showed 1 to 10 µm sized particles of sulfonated POSS in a continuous Radel matrix phase (Figure 9). In order to confirm that the features in the 25% sulfonated POSS, 75% sulfonated Radel batch #4 film were POSS particles rather than voids, additional SEM evaluations were conducted. The film was cryo-fractured in liquid nitrogen, and the resulting film was mounted on an SEM stub and coated with carbon in a vacuum evaporator to control charging. The fracture surface was examined at 5 kV to produce SEM images (see Figure 10), and an X-ray map was produced that showed the presence of silicon (POSS) in the 1 to 10 µm sized domains, and the absence of silicon in the continuous matrix phase (Figure 11). The POSS minor phase has a glassy, hard appearance relative to the matrix material.

Figure 8. TEM micrograph of 20% sulfonated phosphazene, 80% sulfonated Radel R-5000 (Chemsultants batch #4, 17 wt.% SO_3H). Scale bar 0.2 μm .

Figure 9. TEM micrograph of 25% sulfonated POSS, 75% sulfonated Radel R-5000 (Chemsultants batch #4, 17 wt.% SO_3H). Scale bar 2 μm .

Figure 10. Freeze fracture SEM cross section image through a film of 25% sulfonated POSS, 75% sulfonated Radel R-5000 (Chemsultants batch #4, 17 wt.% SO_3H).

Figure 11. Silicon X-ray map of freeze fracture cross section of Figure 10 above.

Three Layer Study

A TEM study was carried out on cross sections of the following four samples microtomed at -100°C, perpendicular to the film surface:

1. Single layer of sulfonated Radel (batch #8)
2. Trilayer of sulfonated Radel (batch #8)
3. Trilayer of batch #8 / 20% sulfonated POSS and 80% batch #8 / batch #8
4. Trilayer of batch #8 / 20% sulfonated phosphazene and 80% batch #8 / batch #8

No evidence of any interfaces was observed in trilayer samples 2, 3, or 4. 200 to 500 nm features were observed in samples 1 and 4 (Figure 12), but were not present in samples 2 and 3. The darker color of these features suggested that heavy atoms may be present, and they appeared at the edges of domains. These features appeared to be independent of film formulation, position in cross section (close to the film surface versus far from the surface), and mono/trilayer structure, but correlated with whether the films were fresh as cast by Chemsultants (1 and 4) or whether they had gone through the conductivity test pre-treatment process (2 and 3). The features are too small for individual SEM X-ray mapping,. The features were not voids, nor were they associated with residual casting solvent, since samples are exposed to high vacuum during the TEM process.

As in the previous TEM study of S-phosphazene versus S-POSS filled films, no phosphazene features were observed, but 2 to 5 micron POSS domains in a continuous Radel R-5000 matrix (Figure 13) were observed in the central area of the cross section (as expected for a trilayer with POSS in the central layer). Smaller POSS particles (~20 nm) were observed in one outer layer of the film (Figure 14), but not in the other. It is conjectured that small POSS particles from the central (second) layer dissolved or diffused into the upper (third) layer during the final (third) stage of film casting.

Figure 12. Features in cross section TEM image of monolayer sulfonated Radel R-5000 batch #8 film. Scale bar, 1 μm .

Figure 13. Cross section TEM image of trilayer sulfonated Radel R-5000 batch #8 / 80% batch #8 and 20% sulfonated POSS / batch #8 film showing 2 to 5 micron POSS domains in the central layer. Scale bar, 5 μm .

Figure 14. Detail of cross section TEM image of trilayer sulfonated Radel R-5000 batch #8 / 80% batch #8 and 20% sulfonated POSS / batch #8 film showing ~20 nm POSS domains in one outlayer. Scale bar, 2 μm .

Five Layer Study

A five layer sulfonated Radel R-5000 / sulfonated POSS film (100% sulfonated Radel R-5000 #12 (18.5 wt.% SO_3H) / 10% sulfonated POSS / 20% sulfonated POSS / 10% sulfonated POSS / 100% sulfonated Radel R-5000) was studied by TEM. The cross section was microtomed perpendicular to the horizontal surface of the film at -100°C with a target thickness of 90 nm. The five layer structure was clearly visible, with the highest loading of nano-additives visible in the center of the film, intermediate additive loading visible on either side of the center, and additive-free regions visible in the outer layers (Figure 15). Interestingly, nano-additive domain size varied with loading. The sulfonated POSS domains in the central 20% sulfonated POSS / 80% sulfonated Radel R-5000 layer were 500 to 800 nm in diameter while the sulfonated POSS domains in the 10% sulfonated POSS / 90% sulfonated Radel R-5000 layers were 300 to 500 nm in diameter. As with the TEM study of the trilayer sulfonated POSS film (see Figure 14), small (50 nm) POSS domains were observed in one 100% sulfonated Radel R-5000 outer layer but not in the other, and this was attributed to some sulfonated POSS diffusing from the fourth layer into the fifth (outer) layer during the multilayer film casting process.

Figure 15. TEM image of a cross section of a five layer sulfonated Radel R-5000 / sulfonated POSS film. Scale bar, 10 μm .

P-POSS and SA-POSS Study

Cross sections were microtomed perpendicular to the horizontal surface of the film at -100°C with a target thickness of 90 nm.

A single layer 20% phosphonic acid POSS / 80% sulfonated Radel R-5000 Akron Polymer X58 (19.5 wt.% SO_3H) film was studied by TEM. This film had a comparable POSS domain size (500 nm to 2 μm , Figure 16) to single layer and trilayer sulfonated POSS films used in earlier TEM studies. However, the sectioning behavior of the phosphonic acid POSS film was very different from that observed for sulfonated POSS films. Figure 16 shows that the microtome blade has caused some of the nano-additive domains to fail cohesively (i.e., particles split across the middle) rather than adhesively (i.e., where the particle matrix interface fails and the particle is ripped cleanly out of the matrix). This suggests either that the interaction between phosphonic acid POSS molecules in its domain is weaker, or that the interaction between phosphonic acid POSS and the continuous matrix is stronger.

A single layer 20% alkylated sulfonic acid POSS / 80% sulfonated Radel R-5000 Akron Polymer X58 (19.5 wt.% SO_3H) film was studied by TEM. This film had surprisingly large POSS domains (2 to 5 μm with a few 6 μm outliers (Figure 17). This suggests that the presence of the alkyl groups decreases the dispersion and compatibility of the alkylated sulfonic acid POSS nano-additives with the sulfonated matrix polymer. The sectioning behavior of this film was the same as that observed for other sulfonated POSS films. The large POSS domains extended out to the edge of the film on one side (left hand side of Figure 17) but not on the other side (right hand side of Figure 17). This could be caused by the tendency of non-polar alkyl groups to assemble at the air-solution interface of the film casting solution during film fabrication.

Figure 16. TEM image of a cross section of 20% phosphonic acid POSS / 80% sulfonated Radel R-5000 film. Scale bar, 5 μm .

Figure 17. TEM image of a cross section of 20% alkylated sulfonic acid POSS / 80% sulfonated Radel R-5000 film. Scale bar, 10 μm .

Objective 1, Task 7 (Q3)

Prepare lab scale thin (1-2 micron) multilayer films of potential fuel cell polymer membrane materials based on the various impregnated, ionically doped systems, and carry out proton conductivity measurements.

Conductivity, water uptake, and dimensional stability data for the Chemsultants sulfonated Radel R-5000 batch #8 (17.4 wt.% SO₃H) multilayer film study is shown in Table 10. In-plane conductivity data (appearing in italics) was measured at room temperature and originated from Case Western Reserve University. Conductivity, water uptake, and dimensional stability data for the Chemsultants sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) multilayer film study is shown in Table 11. Table 12 shows the results for a series of single layer films based on the X58 batch of sulfonated Radel R-5000 prepared by Akron Polymer Systems (19.5 wt.% SO₃H) and phosphonic acid POSS or alkylated sulfonic acid POSS nano-additives.

Temperature and relative humidity conditions, and the procedures for measuring water uptake (mass change, %) and dimensional stability (length change, %), are discussed in the following section (see Task 8).

Table 10. Conductivity, mass change, and dimensional stability data for Chemsultants sulfonated Radel R-5000 batch #8 (17.4 wt.% SO₃H) / sulfonated phosphazene and sulfonated POSS multilayer film study.

Composition	Through-plane conductivity (S cm ⁻¹) <i>In-plane conductivity (S cm⁻¹)</i>	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
100% Sulfonated Radel R-5000 #8 (Formulation - 17.4 wt.% SO ₃ H)	0.065 <i>0.050</i>	80°C, anhydrous	-5.21	-2.07
			-5.60	-2.47
		RT, 52% RH	+1.42	0
		RT, 100% RH	+1.45 +4.01 +5.09	+1.65 0 0
Trilayer control film (a) 100% Sulfonated Radel R-5000 #8 (b) 100% Sulfonated Radel R-5000 #8 (c) 100% Sulfonated Radel R-5000 #8 (Formulation - 17.4 wt.% SO ₃ H)	0.003	80°C, anhydrous	-9.1	-2.6
			-9.7	-2.8
		RT, 100% RH	+11.3	+4.7
			+8.6	+3.3
80% Sulfonated Radel R-5000 #8 20% Sulfonated phosphazene (Formulation - 22.2 wt.% SO ₃ H)	0.038	80°C, anhydrous	-11.2 -11.0	-4.7 -3.4
		RT, 100% RH	+10.8 +9.2	+4.6 +3.3

Table 10 (continued). Conductivity, mass change, and dimensional stability data for the Chemsultants sulfonated Radel R-5000 batch #8 (17.4 wt.% SO₃H) / sulfonated phosphazene and sulfonated POSS multilayer film study.

Composition	Through-plane conductivity (S cm ⁻¹) <i>In-plane conductivity (S cm⁻¹)</i>	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
Trilayer film (a) 100% Sulfonated Radel R-5000 #8 (b) 80% Sulfonated Radel R-5000 #8 and 20% Sulfonated phosphazene (c) 100% Sulfonated Radel R-5000 #8 (Formulation – NA)	0.022	80°C, anhydrous	-7.0	-2.7
		RT, 100% RH	+4.5 +1.5	+2.1 +2.3
80% Sulfonated Radel R-5000 #8 20% Sulfonated POSS (Formulation - 21.7 wt.% SO ₃ H)	0.083 0.054	80°C, anhydrous	-5.38 -6.33	-2.96 -3.20
		RT, 52% RH	+2.07 +1.17	0 +1.16
		RT, 100% RH	+7.38 +3.47	0 +2.73
Trilayer film (a) 100% Sulfonated Radel R-5000 #8 (b) 80% Sulfonated Radel R-5000 #8 and 20% Sulfonated POSS (c) 100% Sulfonated Radel R-5000 #8 (Formulation – NA)	0.004 0.050	80°C, anhydrous	-4.56 -4.80	0 -2.62
		RT, 52% RH	+2.23 +1.66	0 +1.62
		RT, 100% RH	+4.45 +5.15	0 +2.56

Table 11. Conductivity, mass change, and dimensional stability data for the Chemsultants sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) / sulfonated phosphazene and sulfonated POSS multilayer film study.

Composition	Through-plane conductivity (S cm ⁻¹)	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
100% Sulfonated Radel R-5000 #12 (Formulation - 18.5 wt.% SO ₃ H)	0.038 0.020	80°C, anhydrous	-4.4 -4.8	-2.5 -1.3
		RT, 100% RH	+9.0 +9.1	+2.8 +2.5
90% Sulfonated Radel R-5000 #12 10% Sulfonated phosphazene (Formulation - 20.8 wt.% SO ₃ H)	0.041	80°C, anhydrous	-6.2 -6.4	-3.4 -3.6
		RT, 100% RH	+7.3 +7.6	+4.6 +2.5
80% Sulfonated Radel R-5000 #12 20% Sulfonated phosphazene (Formulation - 23.1 wt.% SO ₃ H)	0.037	80°C, anhydrous	-6.2 -7.1	-4.9 -3.7
		RT, 100% RH	-2.0 0	0 +2.5
90% Sulfonated Radel R-5000 #12 10% Sulfonated POSS (Formulation - 20.5 wt.% SO ₃ H)	0.068	80°C, anhydrous	-5.4 -6.5	-1.6 -2.8
		RT, 100% RH	+5.4 +6.3	+2.7 0
80% Sulfonated Radel R-5000 #12 20% Sulfonated POSS (Formulation - 22.5 wt.% SO ₃ H)	0.066	80°C, anhydrous	-6.7 -6.7	-3.9 -3.6
		RT, 100% RH	+1.4 +2.4	0 0
Trilayer control film (a) 100% Sulfonated Radel R-5000 #12 (b) 100% Sulfonated Radel R-5000 #12 (c) 100% Sulfonated Radel R-5000 #12	0.022	80°C, anhydrous	-5.1	-3.4
		RT, 100% RH	+7.1	+3.0

Table 11 (continued). Conductivity, mass change, and dimensional stability data for the Chemsultants sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) / sulfonated phosphazene and sulfonated POSS multilayer film study.

Composition	Through-plane conductivity (S cm ⁻¹)	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
Trilayer film (a) 100% Sulfonated Radel R-5000 #12 (b) 90% Sulfonated Radel R-5000 #12 and 10% Sulfonated phosphazene (c) 100% Sulfonated Radel R-5000 #12	0.030	80°C, anhydrous	-6.0 -6.2	-4.8 -4.6
		RT, 100% RH	+10.0 +9.8	+3.9 +4.3
Trilayer film (a) 100% Sulfonated Radel R-5000 #12 (b) 80% Sulfonated Radel R-5000 #12 and 20% Sulfonated phosphazene (c) 100% Sulfonated Radel R-5000 #12	0.025	80°C, anhydrous	-5.7 -5.9	-4.7 -4.0
		RT, 100% RH	+8.8 +7.8	+1.7 +3.4
Trilayer film (a) 100% Sulfonated Radel R-5000 #12 (b) 90% Sulfonated Radel R-5000 #12 and 10% Sulfonated POSS (c) 100% Sulfonated Radel R-5000 #12	0.035	80°C, anhydrous	-6.1 -5.8	-2.0 -3.0
		RT, 100% RH	+15.0 +11.5	+2.6 +3.4
Trilayer film (a) 100% Sulfonated Radel R-5000 #12 (b) 80% Sulfonated Radel R-5000 #12 and 20% Sulfonated POSS (c) 100% Sulfonated Radel R-5000 #12	0.044 0.054	80°C, anhydrous	-6.6 -4.8	-4.9 -3.7
		RT, 100% RH	+9.2 +7.6	+3.2 +3.3

Table 11 (continued). Conductivity, mass change, and dimensional stability data for the Chemsultants sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) / sulfonated phosphazene and sulfonated POSS multilayer film study.

Composition	Through-plane conductivity (S cm ⁻¹)	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
Five-layer film (a) 100% Sulfonated Radel R-5000 #12 (b) 90% Sulfonated Radel R-5000 #12 and 10% Sulfonated phosphazene (c) 80% Sulfonated Radel R-5000 #12 and 20% Sulfonated phosphazene (d) 90% Sulfonated Radel R-5000 #12 and 10% Sulfonated phosphazene (e) 100% Sulfonated Radel R-5000 #12	0.039	80°C, anhydrous	-6.4 -6.3	-3.5 -4.4
		RT, 100% RH	+10.6 +11.4	+2.4 +1.8
Five-layer film (a) 100% Sulfonated Radel R-5000 #12 (b) 90% Sulfonated Radel R-5000 #12 and 10% Sulfonated POSS (c) 80% Sulfonated Radel R-5000 #12 and 20% Sulfonated POSS (d) 90% Sulfonated Radel R-5000 #12 and 10% Sulfonated POSS (e) 100% Sulfonated Radel R-5000 #12	0.030	80°C, anhydrous	-6.4 -7.5	-4.8 -4.0
		RT, 100% RH	+11.4 +13.3	+5.1 +4.2

Table 12. Conductivity, mass change, and dimensional stability data for the Akron Polymer X58 sulfonated Radel R-5000 series of films.

Composition	Through-plane conductivity (S cm^{-1})	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
100% Sulfonated Radel R-5000 (Akron Polymer X58, 19.5 wt.% SO_3H)	0.036	80°C, anhydrous	-5.89	-2.33
		RT, 100% RH	+9.22	+2.66
90% Sulfonated Radel R-5000 X58 10% Phosphonic acid POSS	0.034	80°C, anhydrous	-5.24	-3.99
		RT, 100% RH	+11.99	+3.09
80% Sulfonated Radel R-5000 X58 20% Phosphonic acid POSS	0.059	80°C, anhydrous	-4.63	-3.80
		RT, 100% RH	+10.20	+1.49
90% Sulfonated Radel R-5000 X58 10% Alkylated sulfonic acid POSS	0.072	80°C, anhydrous	-5.30	-3.55
		RT, 100% RH	+14.30	+3.62
80% Sulfonated Radel R-5000 X58 20% Alkylated sulfonic acid POSS	0.042	80°C, anhydrous	-4.91	-3.89
		RT, 100% RH	+14.84	+4.73

Objective 1, Task 8 (Q4)

Evaluate material stability issues: Low and elevated temperature stability under both acidic conditions and oxidizing conditions, dimensional stability of selected polymer/nanoparticle compositions as a function of temperature, under dehydrated and wet states, and as a function of %RH conditions.

Dimensional Stability and Water Uptake

Several humidity chambers were set up (Table 13) in order to condition films prior to studying swelling, water uptake, and dimensional stability. Different relative humidity (RH) environments were also generated using different concentrations of aqueous sulfuric acid.

Table 13. Examples of relative humidity (RH) systems.

System	Relative humidity (%)
Calcium (II) chloride hexahydrate	32.3
Sodium hydrogen sulfate monohydrate	52.0
Ammonium chloride	70.5
Sodium sulfite heptahydrate	95.0

Relative humidity jars were set up to condition materials at 100%, 80%, 52%, 32%, and 3% RH. ASTM test D1042 was selected to measure dimensional changes in films after exposure to specified humidities, and method development was carried out using a model, 7 mil Nafion film (Table 14).

In this method, changes to an arc inscribed on a film are studied by optical microscopy. Samples were equilibrated for 24 hours in the laboratory at room temperature, inscribed with an arc, exposed to the test conditions, and then re-inscribed. The difference between the two arcs was measured with the aid of a microscope, and expansion (or contraction) of the film was quantified as a percent of linear change, L_C , where D_B is the distance between the inscribed arcs, and D_I is the initial inscribed distance.

$$L_C = D_B / D_I \times 100$$

Mass changes over time were tracked in parallel to dimensional changes, and are quoted as a percent increase (or decrease) from the original mass. Duplicate experiments were carried out for each film.

Table 14. Mass change and dimensional stability data for a Nafion 117 control film.

Composition	Test environment	Water uptake (mass change, %)	Dimensional stability (length change, %)
Nafion N-117	80°C, anhydrous	-3.0 -3.4	0 0
Nafion N-117	RT, 100% RH	+15.9 +17.8	10.1 10.7
Nafion N-117	RT, 80% RH	+3.5 +4.7	3.6 4.1
Nafion N-117	RT, 52% RH	+3.2 +2.8	2.5 2.0
Nafion N-117	RT, 32% RH	+0.7 +0.4	1.5 0
Nafion N-117	RT, 3% RH	-2.6 -3.1	-1.0 -1.5

This method was used to measure the dimensional stabilities of a number of 100% sulfonated Radel R-5000 films (Akron Polymer AP7, AP11, and X43, and Chemsultants batches 9 to 12) and in all cases L_c was in the range 0 to +5% in a 100% RH environment, and -1 to -5% in an anhydrous environment (80°C). The dimensional stabilities of a number of SPTES-type polymers (Akron Polymer X4, X7, and 55/45, see Task 1) were also measured and gave L_c values in the range 0 to +3% in a 100% RH environment, and -2 to -4% in an anhydrous environment (80°C).

Dimensional stability data and water uptake data for the two sulfonated POSS multilayer film studies (based on Chemsultants sulfonated Radel R-5000 batches 8 and 12) are given in Tables 10 and 11, respectively, and dimensional stability data for films formulated from sulfonated Radel R-5000 and P-POSS or SA-POSS is given in Table 12.

Leaching

The material that leached out of the 90% sulfonated Radel R-5000 batch #5B / 10% sulfonated phosphazene film (after 24 hrs in deionized water at room temperature followed by drying at 80°C for 2 hrs) was analyzed by ^1H NMR and was shown to be a highly sulfonated ~25 wt.% (i.e., highly water soluble) fraction of sulfonated Radel R-5000. Table 15 shows the leaching data for a selection of other multilayer and single layer films. The material that leached out of the films was isolated and analyzed by ^1H NMR. The NMR spectra had little aromatic content, with the exception of the phosphazene trilayer film, where the leached material was identified as the sulfonated phosphazene nano-additive (having a distinctive pair of doublets in the aromatic region). Obviously the degree to which this is observed will depend on previous washings and treatments the films may have gone through during fabrication and previous analytical tests. Films that had already been treated and tested for conductivity underwent mass losses of 4 to 8% while untreated films underwent larger mass losses of 12 to 18%.

Table 15. Leaching data for selected films (24 hrs in deionized water at room temperature followed by drying at 80°C for 2 hrs). Samples marked with an asterisk denote films that had previously undergone a conductivity test pre-treatment process.

Sample	Leaching (% of initial mass lost)
100% Sulfonated Radel R-5000 Akron Polymer AP7*	8.0
100% Sulfonated Radel R-5000 Akron Polymer AP11	18.1
100% Sulfonated Radel R-5000 #4	17.1
100% Sulfonated Radel R-5000 #8	11.6
100% Sulfonated Radel R-5000 #8* trilayer film	4.4
100% Sulfonated Radel R-5000 #8* 20% POSS trilayer film	6.3
100% Sulfonated Radel R-5000 #8 20% Phosphazene trilayer film	15.6
100% Sulfonated Radel R-5000 #11	16.2

Objective 1, Task 9 (Q4)

Review modified polymers in thin film format and profile physical, mechanical and chemical properties.

Differential Scanning Calorimetry (DSC) of Baseline Polymers

A DSC study (nitrogen, 10°C/min) of the glass transition temperature of various sulfonated Radel R-5000 samples was carried out, and Tg's in the region of 229°C were observed. (Radel R-5000 itself has a Tg of 222°C). It appears that sulfonation does not have a major effect on the glass transition temperature, as expected from the literature (see Blanco, J.F.; Nguyen, Q.T.; Schaetzel, P., *J. Membrane Sci.*, **2001**, 186, 267-279). For comparison, SPTES 55/45, had been shown to have a Tg of 214°C.

Dynamic Mechanical Analysis (DMA) of Baseline Polymers

Storage moduli for sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H), Figure 18, and SPTES 55/45, Figure 19, were measured at 170°C. Sulfonated Radel R-5000 was shown to have superior mechanical properties, having a storage modulus of 884.9 MPa at 170°C versus that for the SPTES 55/45 polymer, having a storage modulus of 167.7 MPa at 170°C.

Figure 18. DMA of sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) showing a storage modulus of 884.9 MPa at 170°C.

Figure 19. DMA of sulfonated polythioether sulfone (SPTES 55/45) showing a storage modulus of 167.7 MPa at 170°C.

DMA of a sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) membrane containing sulfonated POSS (Figure 20), and a sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) membrane containing sulfonated phosphazene (Figure 21) was then carried out.

Figure 20. DMA of 80% sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) / 20% sulfonated POSS membrane showing a storage modulus of 23.3 MPa at 170°C.

Figure 21. DMA of 80% sulfonated Radel R-5000 batch #12 (18.5 wt.% SO₃H) / 20% sulfonated phosphazene showing a storage modulus of 15.0 MPa at 170°C.

It can be seen that the presence of the nano-additive results in some decrease in storage modulus at 120°C, and in a significant decrease in storage modulus at 170°C (Table 16), and that sulfonated phosphazene membranes have a lower storage modulus than the corresponding sulfonated POSS membranes.

Table 16. Storage modulus as a function of temperature for various sulfonated Radel R-5000 batch #12 membranes versus Nafion 117.

Membrane	Storage modulus at 30°C (MPa)	Storage modulus at 120°C (MPa)	Storage modulus at 170°C (MPa)
Nafion 117	600	50	3.3
Sulfonated Radel R-5000 #12 (18.5 wt.% SO ₃ H)	1954	1750	884
80% Sulfonated Radel R-5000 #12 20% Sulfonated POSS	1426	1120	23
80% Sulfonated Radel R-5000 #12 20% Sulfonated phosphazene	1230	625	15
Three layer film (a) 100% Sulfonated Radel R-5000 #12 (b) 80% Sulfonated Radel R-5000 #12 and 20% Sulfonated POSS (c) 100% Sulfonated Radel R-5000 #12	1348	1320	1202

Thermogravimetric Analysis (TGA) of Baseline Polymers

TGA (nitrogen, 10°C/min) was carried out on a sample of sulfonated Radel R-5000 (Akron Polymer X72) (Figure 22). The TGA weight loss profile showed that sulfonated Radel R-5000 had slightly better stability than SPTES 55/45 (see Figure 1), i.e., sulfonated Radel R-5000 retained 82% of its mass at 411°C while SPTES 55/45 retained 82% of its mass at 377°C.

Figure 22. TGA of sulfonated Radel R-5000 (Akron Polymer X72).

Objective 2. Tasks 1-8

Objective 2: Identify new, potential polymer solution casting fabrication processes, alternate process methodologies and new membrane structures (including multi-layer membranes) suitable to produce commercial scale quantities of thin polymer membranes in roll form that offer improved mechanical stability and water management capabilities.

O2 Task 1 - Investigate and evaluate potentially suitable casting sheet carriers to be used in membrane casting trials, Profile temperature capability and release characteristics of various casting sheet materials.

Casting sheet materials were reviewed for the Radel polymer solutions. A 25% by weight Radel polymer solution in DMAC was cast onto each carrier sheet substrate using an Elcometer bird film applicator and dried 15 minutes in a forced air oven at 94° C. The dried films were subsequently dried at 135° C for 30 minutes to remove the remainder of the DMAC solvent. The results are shown below in Table I.

Table I

Material	Wet-Out Radel A-100 in DMAC	Heat Stability	Release Characteristics
PET	good	excellent	excellent
FEP	poor*	poor	excellent
ETFE	poor*	poor	excellent
E-CTFE	good	poor	excellent
PMP	poor	poor	no data
Kapton	good	excellent	poor
S-10	poor	no data	no data
UV-10	poor	no data	no data

Key:

Wet-Out

poor - would not form film, insufficient wet-out even with corona treatment

poor* - wet-out issues resolved using corona treatment

good - no wet-out issues

Heat Stability

poor - substrate wrinkled severely

excellent - stable substrate, no wrinkles or warping

Release

no data - did not evaluate due to extreme wet-out issues

excellent - membrane peeled off without effort

poor - membrane did not release from carrier

Most of the carrier sheet materials were unstable in high heat with exception of PET and Kraton. However, the membrane cast from the solvent based Radel solution did not release from the Kraton material. Therefore, PET is the only carrier sheet material evaluated that exhibited good wet-out, heat resistance and release properties for both solvent and aqueous based membrane

systems. The carrier sheet evaluation was carried out with the initial polymer selection Radel A 100. Later work indicated low conductivity of the sulfonated Radel A and a new Radel selection was made (Radel R 5000). Carrier sheet evaluation using the Radel R 5000 was comparable and PET was selected as the main carrier for future laboratory and plot casting trials.

O2 Task 2 - Identify potential solvents, and diluents for use with modified polymer/nano-particle structures to achieve casting phase solubility and rheology targets.

Base Solubility Studies of unmodified polymers

Radel A-100 NT and Udel P-3500 LCD, initial polymers selected, were dissolved in a variety of solvents to evaluate solubility, rheology and membrane quality. Table II gives the results of the solubility tests performed using a 20% by weight solids solution of each polymer. The polymers were combined with the solvents and mixed on a roller for 24 hours.

Table II

Solvent	Solute	
	Radel A-100	Udel P-3500 LCD
Asahiklin AK 225	NS	NS
Toluene	NS	NS
MEK	NS	C
DMAC/NMP 60/40	GS	GS
DMAC/Asahiklin 60/40	C	C
DMAC/Toluene 60/40	GS	GS
DMAC/MEK 60/40	GS	FS
DMAC	GS	FS
DMF	GS	FS
NMP	GS	FS
TBAC	NS	NS

KEY:

NS - Solute Not Soluble in Solvent

C - Solute Crystallized in Solvent

FS - Solute Fairly Soluble in Solvent (exhibited some polymer gels)

GS - Solute Greatly Soluble in Solvent (completely dissolved)

Solubility data show that both Radel and Udel polymers favor polar aprotic solvents. The Radel A-100 NT polymer was solvated much quicker than the Udel P-3500 LCD with the same solvents or solvent blends. Some of the Udel blends took over 1 week to dissolve and still exhibited gels in the final solution. The viscosities for solutions having acceptable solubility are shown in Table III below.

Table III

Solvent	Viscosity (cps)* @ 25°C 100 rpm, spindle #4	
	Radel A-100	Udel P-3500 LCD
DMAC	556	1262
DMF	398	-
NMP	1344	-
DMAC/NMP 60/40	684	1586
DMAC/Toluene 60/40	346	-
DMAC/MEK 60/40	408	1008

* All solutions 20% solids by weight

Due to leveling effects of the 20% solution of Radel A-100 in DMAC, thickness limitations were encountered when casting membranes. When the solids were raised to 25% and 30%, the solution was more viscous (1535 and 5800 cps, respectively). The 25% solution gave more uniform membranes than the 30% solution, which was much more viscous and developed craters upon drying. Therefore, all membrane work was performed with the 25% solids Radel/DMAC solution.

Solubility study of modified (sulfonated) Radel R 5000 (see Table IV)

The following solvent/diluent study was performed to determine the solubility of sulfonated Radel R 5000 (conductive polymer selected for multilayer composite). This study will also assist rheology work required for the casting of thin PEM cast from the sulfonated Radel R with and without nano-particles.

Table IV

Resin: Sulfonated Radel R5000 Batch 10				
	Boiling Point, °C	Total Sample Mass, g	% Solids	Observations
Solvent	started 5/23/07			5/23,
Asahiklin AK 225	54	2.5	20	No effect on polymer
Toluene	110	2.5	20	Minor swelling
MEK	80	2.5	20	Crystallized
DMAC	166	2.5	20	soluble
DMF	153	2.5	20	soluble
NMP	202	2.5	20	Readily soluble
TBAC	98	2.5	20	No effect on polymer
Diluent				
MeCl ₂	40	N/A	N/A	insoluble
Methanol	65	N/A	N/A	insoluble
Ethanol	78	N/A	N/A	insoluble
Solvent / Diluent	started 5/24/07			5/25,
NMP / Toluene	N/A	2.5	17	

NMP / MEK	N/A	2.5	17	Soluble after stirring, milky
NMP / DMAC	N/A	2.5	17	soluble
NMP / MeCl ₂	N/A	2.5	17	
NMP / Methanol	N/A	2.5	17	soluble
NMP / Ethanol	N/A	2.5	17	soluble
SR-B9	started 5/29/07			
DMAC / Toluene	N/A	2.5	17	
DMAC / MEK	N/A	2.5	17	Soluble after stirring

Solubility study shows that sulfonated Radel R 5000 (S-Radel R) is readily soluble in NMP. Drying characteristics of a 20% solution of S- Radel R in NMP are acceptable for laboratory castings of the polymer. However, prototyping of the polymer in a roll to roll format on a production coater results in low running speeds and undesirable surface characteristics. A blend of NMP/ DMAC and Ethanol was formulated to provide a pin hole free membrane with excellent surface characteristics.

O2 Task 3 – Evaluate rheology and solubility issues related to the modified polymers to develop initial parameter targets for membrane casting.

Modification by Sulfonation of Radel A 100 and Radel R 5000

Radel A-100 NT polyethersulfone was sulfonated using a method described in US patent 6,790,931. The method was modified slightly due to the insolubility of Radel A-100 in sulfuric or chlorosulfonic acid. The method incorporates use of chlorosulfonic acid as the sulfonating agent with acetic anhydride as an activating agent. A 20 gram batch was sulfonated, washed thoroughly with DI water to pH 6 and dried for 48 hours at 60°C. A white material was obtained.

Degree of sulfonation (DS) was determined by titration with a standard (1.0M) NaOH solution using phenolphthalein as indicator. The following equations were used to calculate both the degree of sulfonation and ion exchange capacity (IEC):

Degree of sulfonation (DS) in %:

$$DS = \frac{[0.215 \times \text{Conc. Of NaOH in mol/l}] \times V(\text{NaOH used in ml})}{[W(g) - (0.08 \times \text{Conc. Of NaOH in mol/l} \times V(\text{NaOH used in ml}))]} \times 100$$

Ion Exchange Capacity (IEC):

$$IEC = 1000 \frac{DS_{\text{in decimal form}}}{[215 + (81 \times DS_{\text{in decimal form}})]} = \text{meq/g}$$

Where W = sample mass in grams

The molecular weight of the repeat unit for the Radel A-100 molecule is 215 g/mol per Solvay Advanced Polymers. The constant, 81, is the molecular weight of the sulfonic acid group, -SO₃H. These equations were taken from R. Guan et al, *European Polymer Journal* 41 (2005) 1554-1560.

The sulfonation procedure was repeated twice and results are compared to sulfonated PES in literature as shown in Table IV:

Table V

	Degree of Sulfonation (%)	Ion Exchange Capacity (meq/g)
Sulfonated Radel A-100, Batch 1	17.4	0.76
Sulfonated Radel A-100, Batch 2	16.1	0.71
Sulfonated PES, Guan et al	14.1	0.54
Sulfonated PES, Guan et al	24.9	0.99
Nafion NRE-212	-	0.95

The degrees of sulfonation for both Radel A-100 batches are comparable to those reported in Guan et al. The data also shows that results from the sulfonation procedure are repeatable.

FTIR

FTIR scans of the sulfonated and non-sulfonated Radel material were obtained using a Perkin-Elmer 1600 spectrometer. According to US 6,790,931, new absorption peaks would be seen at 1028 cm^{-1} and 1465 cm^{-1} due to the $-\text{SO}_3\text{H}$ groups on the aromatic rings relative to ortho-ether bridges. Figures 1 and 2 show the FTIR spectrums obtained for Radel sulfonated and non-sulfonated material.

Figure 1. FTIR Spectrum for Non-sulfonated Radel A-100

Figure 2. FTIR Spectrum for Sulfonated Radel A-100

As illustrated in the FTIR spectra, a shoulder has appeared at 1028 cm⁻¹ and 1465 cm⁻¹ for the sulfonated Radel material. This supports the presence of -SO₃H groups in the molecule.

Previous work with the Radel[®] A-100 polyethersulfone polymer was not successful due to the inability to sulfonate the polymer beyond 20% degree of sulfonation. This limitation was most likely due to the hydroquinone co-monomer that is present in the polymer backbone in only 25%. The hydroquinone portion of the molecule is easily sulfonated, therefore, limiting the degree of sulfonation to about 25% maximum. However, in order to have a conductive polymer, the degree of sulfonation must be above 40% to give a proper percolation network. A polyphenylsulfone polymer, Radel[®] R-5000, was chosen as a base polymer for sulfonation. Several batches of Radel[®] R-5000 polyphenylsulfone (Solvay Polymers) were sulfonated using dichloromethane and chlorosulfonic acid. Radel[®] R-5000 is a very chemically resistant material and modifications to the previously used sulfonation process were made. The polymer was dissolved in large quantities of methylene chloride prior to sulfonation in order to promote a homogeneous reaction mixture. The NMR results for each of the batches indicated there were two -SO₃H groups on the biphenyl unit of the molecule. The following Table VI gives the degree of sulfonation data for each of the Radel[®] R-5000 batches. Table 6 shows the relationship between target and obtained sulfonation levels measured from ¹H NMR spectra.

Table VI
Degree of Sulfonation Data

Batch #	Radel R-5000	*Degree of Sulfonation (% repeat Units)	Degree of Sulfonation (Wt. % SO ₃ H)
B2	20 g	27	10.0
B3	20 g	60	20.3
B4	50 g	52	17.0
B5-A	20 g	20	7.6
B5-B	20 g	35	12.4
B-6	50 g	34	12.2
B-7	50 g	52	17.6

*Degree of sulfonation: each repeat unit is di-sulfonated (two -SO₃H groups per repeat unit) occurring on the biphenyl unit

Each batch of material was soluble in NMP at 20% solids and laboratory cast into membranes. The membranes were evaluated for water uptake, mechanical strength and conductivity.

Table IV of this section shows the solubility characteristics of the sulfonated Radel R 5000 and the effects of diluents.

Laboratory Casting of Membranes

Membranes were produced in the laboratory from the sulfonated Radel[®] R-5000 material. A 20% solids solution was prepared and membranes cast onto glass plates. The membranes were subsequently dried at 140°C for 30 minutes. The membranes were 50 microns thick. Analytical results showed that residual NMP solvent in the laboratory cast films was below 0.28%. The membranes were put through a cleaning step involving boiling in 3% hydrogen peroxide, boiling in deionized water and then boiling in 1.0 M H₂SO₄ solution. Membranes made from sulfonated Radel[®] R-5000 batch #3 were completely dissolved during the cleaning step.

Nano-particles were incorporated into the batch S-Radel[®] R-5000 solution and cast into films. The sulfonated octaphenyl POSS nano-particles had been difficult to disperse in the past. However, by dissolving the sulfonated octaphenyl POSS in water first then adding NMP and subsequently removing the water by evaporation proved successful. The sulfonated POSS material stayed suspended after addition to the sulfonated Radel[®] R-5000 solution (see Objective1 Task 2, Table 7, pages 7&8). Sulfonated phosphazene (acid) was also added to the solutions in oil form. Both the POSS and phosphazene nano-particles were added to neat (non-sulfonated) Radel R-5000 solution for comparison.

O2 Task 4 – Evaluate modified polymers to determine process parameters for drying, curing annealing and release of single and multilayer cast membrane films

A three layered membrane was created by solution casting one layer on top of the previous one. Each individual layer was dried for 15 minutes and cooled for 20 minutes prior to casting the next adjacent layer. Figure 3 below illustrates the three layer configuration of the membranes. The outside unfilled layers were approximately 10 microns thick and the nano-particle filled layer in

the center was approximately 30 microns thick. The outer layers were sulfonated Radel only. The filled middle layer contained both the sulfonated polymer and a nano-particle.

Figure 3. Illustration of 3-Layered Membrane

After each layer was dried, the total membrane thickness was measured using a micrometer and the individual layers obtained by subtraction.

Physical Property Measurements

Mechanical strength, water uptake and conductivity testing were performed on each of the lab cast membranes. The following table VII gives the tensile and elongation data for each membrane or composite membranes tested.

Table VII Tensile Strength Data

Sample	Tensile Strength (N/mm ²)	Elongation (%)
Sulfonated Radel R-5000 (batch 8)	33	27
Sulfonated Radel R-5000 (batch 8) + 20% POSS	23	36
3 Layer Sulf. Radel R-5000 (batch 8)/20% POSS/Sulf Radel R (batch 8)	33	23
Sulfonated Radel R-5000 (batch 8) + 20% Phosphazene	23	32
3 Layer Sulf. Radel R-5000 (batch 8)/20% Phosphazene/Sulf Radel R (batch 8)	26	14
Thioether (X-4)	42	7
Thioether (X-7)	39	6
Nafion NRE-212	25	282

Instrument: ChemInstruments TT-1000
Load cell: 25#
Test Speed: 2 inches per minute
Gauge length = 2.0 inches
Sample thickness = 2.0 mil

As reported previously, tensile strength decreases with addition of the nano-particles. However, by creating a three layered composite membrane, the tensile strength is increased due to the synergistic effect of the unfilled outer layers. The thioether samples exhibited great tensile strength but percent elongation is very low. At this time it is not clear how much elongation is desired in a membrane that will function at higher temperatures and low humidity. Dynamic Mechanical Analysis of the three layer membrane composite produced from sulfonated Radel R 5000 and sulfonated octaphenyl POSS have shown a storage modulus at 170C of 1202 MPa. See O1 Task 9: Table 16, pages 34, 35.

Conductivity tests performed on three layer membranes (see Figure 4) using outer layers of neat (unfilled) sulfonated Radel R and a middle layer of 20% sulfonated octaphenyl POSS and 80% sulfonated Radel R 5000 show significant improvement at 90C and 25% relative humidity over single, neat layer conductive polymer (S-Radel R 5000), S Radel R 5000 filled with sulfonated POSS and Nafion®. The S-Radel R 5000 membranes were cast on a Chemsultants, roll to roll pilot coater using PET as the carrier film.

Figure 4. Conductivity Tests

O2 Task 5 - Evaluate potential solution casting methodologies for capability to produce single layer membranes using the candidate polymer structures,. Identify the suitability of gravure, knife over roll, micro-gravure and/or slot die solution casting processes to produce pin-hole free membrane structures in a 1.0+ mil thick layer.

KNIFE OVER ROLL

One gallon samples of the 10% and 25% Radel solutions in DMAC were prepared by the Chemsultants laboratory for use on the ChemDevelopment PC-1 pilot coater. The first casting method attempted was knife over roll (see Figure 5). In the KOR casting method a liquid is applied to a moving web supported by a chromed steel roll. The casting thickness required is obtained by placing a rigid and stationary knife blade, a measured distance above the uncoated substrate (the Gap) and removing the excess liquid by a scraping type action.

Figure 5

The casting thickness obtained is effected by 1) the gap between the knife and uncoated substrate 2) the blade configuration 3) the blade thickness 4) the viscosity of the liquid 5) the web speed 6) the porosity of the substrate and 6) the rheology of the liquid.

Initial drying conditions on the equipment were based on laboratory castings of the 25% Radel solutions at various calipers. The targets for membrane thickness were set at 2.0-4.0 mils dry.

Table VIII shows the 16 casting trials made using the 25% Radel solution and the KOR casting method. KOR membrane casting of the 10% Radel solutions did not produce suitable films and therefore the trials were discontinued.

TABLE VIII
Knife over Roll Castings

Oven 1	Oven 2	Oven 3	Oven 4	Oven 5	speed	gap	solids	caliper
160	206	208	228	229	7	20	25	3.5
173	201	203	225	222	7	12	25	1.5
174	201	203	225	222	7	14	25	2.1
174	201	203	225	222	7	14	25	2.0
112	203	207	225	222	7	14	25	2.0
107	123	131	231	232	7	14	25	1.8
96	112	122	217	214	7	15	25	2.1
93	111	122	218	216	7	18	25	2.8
92	109	120	210	207	7	18	25	2.8
91	112	123	211	209	7	18	25	2.9
91	110	119	196	192	7	18	25	2.7
91	106	114	183	180	7	18	25	2.7
81	91	100	193	192	7	21	25	2.9
80	93	103	204	203	7	22	25	3.7
82	96	106	212	210	7	22	25	4.0
84	99	112	229	228	7	23	25	3.9

*Oven temperatures in degrees Fahrenheit

*Speed in feet per minute

*Gap in thousands of an inch

*Solids in percent of Radel on total weight of solution

*Caliper in mils; 1 mil equals 50 microns

Summary

Sixteen experiments were carried out to cast membranes from 2.0 mils in thickness to 4.0 mils in thickness using the 25% Radel solution and various gap settings. Initial oven temperature settings on the equipment based on laboratory experiments were too high and produced defective films. A gradual decrease in pilot coater oven temperatures produced pinhole free films. All the films produced released easily from the PET carrier sheet.

Using the base Radel polymer and the Knife over Roll methodology will produce acceptable membrane films free of pinholes and other physical or aesthetic defects usually associated with this process. The basic information obtained during these trials will be used to cast the selected "polymer system" designed by MMI and Chemsultants.

GRAVURE PROCESS

A 25% solution of Radel polymer in DMAC was used for the initial gravure pilot coating trials. In the gravure process several physical manipulations can be utilized to apply a liquid solution to a carrier web. Techniques that can be utilized include direct gravure, reverse gravure and offset gravure. Each of these methods can be utilized depending on the rheology of the solution, solids of the solution, caliper required, cell structure, release, web speeds and doctoring (wiping) angle and blade setup.

The gravure process is a very accurate method of laying down coating thicknesses between 0.1 mil and 2.5 mils dry (see Figure 6). The gravure process is based on a recessed cell engraved in a copper plated steel cylinder. The cell can have various widths, depths and structures. The liquid

coating to be applied is usually placed in a container and the engraved gravure cylinder is partially immersed in the liquid. The cylinder spins in the liquid and as it rotates the cells are filled. The filled cells are then pressed against a moving web via a rubber roll that transfers the liquid to the desired web (see Figure 6)

Figure 6

Four gravure pilot coating trials were performed in the second quarter. The gravure technique used was reverse gravure. Reverse gravure typically produces thin, smooth, dry coatings with excellent precision and accuracy (see Table IX).

TABLE IX

Reverse Gravure Castings

Expt	Oven 1	Oven 2	Oven 3	Oven 4	Oven 5	speed	cylinder	solids	caliper
1	79	91	100	194	193	7	TH 24	25	1.4
2	80	93	102	194	192	7	TH24	25	2.1
3	81	94	103	194	192	7	TH24	25	1.5
4	82	96	104	195	193	7	TH24	25	1.9

*Oven temperature in degrees Fahrenheit

*Speed is in feet per minute

*Cylinder: ATH24 is mechanically engraved, triangular shaped groove cell

*Solids in percent

*Caliper in dry mils

O2 Task 6 – Evaluate potential solution casting methodologies for capability to produce multi-layer membranes using the candidate polymer structures. Identify the suitability of gravure, knife over roll, micro-gravure and/or lot die solution casting processed to produce pin-hole free membrane structures in 10-20 micron thick layers.

The following studies have been performed to determine the process for producing thin, cast polymer membranes in single layers. This study will also assist in the production of a multilayer composite where individual layers will vary from 0.25 mils (6 microns) to 2.8 mils (70 microns).

Materials:

*5 mil PET film

*20% solution of Radel R 5000

Trial 1: The following study was performed to determine the various coat weight calipers that would be obtained using two types of engraved cylinders with similar volumes (see Table X). Both mechanically engraved TH cylinders and chemically etched Q type cylinders were used. The solution used was a 25% solution of Radel R 5000 dissolved in NMP.

Table X

Oven settings 1-5 (degrees F)								
<i>sample</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>Line speed, fpm</i>	<i>cylinder</i>	<i>Caliper in mils</i>
1	90	109	126	221	219	10	TH 35	.54
2	90	107	121	221	219	10	16 Q	.60
3	91	109	121	220	219	10	12TH	1.2
4	92	110	121	220	219	10	29TH	.54
5	92	110	122	221	220	10	10Q	1.0
6	93	110	122	221	221	10	16Q	.60
7	93	110	123	221	221	10	25Q	.30
8	93	110	122	221	221	10	45TH	.45

*All coatings were applied to a %5 mil PET film

*Q cylinders are chemically etched cylinders with standard quad cells

*TH - mechanically engraved cylinders with the grooves running diagonally across the cylinder

Summary: Pilot coating trials indicate that target coat weights can be obtained using the gravure process and both a TH and Q engraved cylinders. This data will be helpful in future work to produce multilayered Radel R membranes.

Trial 2: The following gravure pilot coating trial was performed to develop a multilayered membrane. A TH 35 cylinder was used to produce approximately 0.5 mils of coating per pass. The last column in Table XI shows the cumulative coat weight achieved.

Table XI

Oven settings 1-5 (degrees F)								
<i># of passes</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>Line speed fpm</i>	<i>Cylinder</i>	<i>Cumulative caliper in mils</i>
1	85	98	111	188	187	10	TH 35	0.48
2	85	98	111	188	187	10	TH 35	1.02
3	82	97	109	188	188	10	TH 35	1.6
4	82	97	109	188	188	10	TH 35	2.2
5	83	97	109	188	187	10	TH 35	2.8

*The initial coating (pass 1) was applied to a 5 mil PET film. Pass 2 coating was applied over the initial coating on PET carrier film.

*TH cylinder is a mechanically engraved cylinder

Summary: Pilot coating trial 2 (see Table XI) indicates fairly good uniformity of coat weight using the gravure process and a single mechanically engraved cylinder. At this time no attempt was made to change other key variables such as pressure, cylinder speed, web speed, viscosity or percent solids. The cumulative coat weight produce in this trial was 2.8 mils dry. The target will be lowered in future experiments.

Trial 3: A third pilot coating trial was made in an attempt to produce approximately a 2.00 +/- 0.1 mil total film caliper. Again a gravure process was used and the TH cylinder was a TH 65, that is engraved at a lower cell volume than that used in Table XI.

Table XII

# of passes	1	2	3	4	5	Line speed fpm	Cylinder	Cumulative Caliper in mils
1	88	110	121	187	185	10	TH 65	0.25
2	87	110	121	188	185	10	TH 65	0.49
3	88	110	121	188	185	10	TH 65	0.79
4	87	110	122	188	185	10	TH 65	1.03
5	79	106	118	187	186	10	TH 65	1.31
6	80	108	118	189	188	10	TH 65	1.53
7	82	108	121	190	190	10	TH 65	1.85
8	84	109	121	190	189	10	TH 65	2.11

*The initial coating (pass 1) was applied to a 5 mil PET. Pass 2 coating was applied over the initial coating on PET.

*A TH cylinder is a mechanically engraved cylinder.

Summary: Table XII shows the cumulative, dry caliper of 2.11 mils obtained using the gravure process. Good uniformity was attained using a single TH cylinder.

Conclusions

The reverse gravure process was used to develop the data in Tables X, XI & XII. The data indicate that multi-layered membranes for use in fuel cells can be produced using this particular technique.

O2 Task 7 – Develop baseline laboratory procedures for both single layer and multi-layer membrane solution casting, drying, curing, annealing and possible chemical alteration.

Laboratory Casting of Membranes

Membranes were produced in the laboratory from the sulfonated Radel® R-5000 material. A 20% solids solution was prepared and membranes cast onto glass plates. The membranes were subsequently dried at 140°C for 30 minutes. The membranes were 50 microns thick. Analytical results showed that residual NMP solvent in the laboratory cast films was below 0.28%. The membranes were put through a cleaning step involving boiling in 3% hydrogen peroxide, boiling in de-ionized water and then boiling in 1.0 M H2SO4 solution. Membranes made from sulfonated Radel® R-5000 batch #3 were completely dissolved during the cleaning step.

Nano-particles were incorporated into the S-Radel[®] R-5000 solution and cast into films. The sulfonated octaphenyl POSS nanoparticles had been difficult to disperse in the past. However, by dissolving the sulfonated octaphenyl POSS in water first then adding NMP and subsequently removing the water by evaporation proved successful. The sulfonated POSS material stayed suspended after addition to the sulfonated Radel[®] R-5000 solution. Sulfonated POSS readily disperses at levels of 25% based on the weight of the dry base polymer.

Further laboratory casting trials indicated that a smoother, pinhole free polymer membrane made using sulfonated Radel R 5000 and sulfonated octaphenyl POSS resulted from a blend of solvents. The ultimate solvent blend consisted of n-methyl pyrrolidone, dimethyl acetamide and ethyl alcohol. A blend of 55%NMP and 45% DMAC diluted with 25% ethyl alcohol was used in both the laboratory and pilot coating casting trials.

O2 Task 8 – Prepare a design of experiments plan to establish pilot scale roll to roll process parameters for casting, drying, curing, annealing and possible chemical alteration of polymer membranes based on the research results in Objective2, tasks 1-8.

Based on laboratory and pilot coater trial history with (neat) Radel R-5000, initial pilot coater settings and solution mixing parameters were selected for producing membranes using:

- a. sulfonated Radel R-5000 in NMP solvent with 20% solids content
- b. sulfonated Radel R-5000 in NMP at 20% solids with sulfonated POSS nanoparticles added at 20% of the total solution solids

Results from initial trials in March 2007 on multiple pilot coating machines showed that coater PC2 was most able to produce the quality membranes needed for fuel cell testing in terms of cleanliness and the processing of small quantities of resin solution (<100ml). The experimental trials with sulfonated Radel R-5000 with the POSS nano-particles indicated a need to further explore the solvents used to process the polymer system. The initial solvent blend used consisted of primarily NMP, with a very high boiling point (202°C), that produced an unacceptable surface appearance upon drying. Therefore, subsequent work focused on improving the solvent system as described below in the report. The trial was designed and executed as follows:

Trial 1: Sulfonated Radel R-5000 was dissolved in NMP and coated to determine optimal machine settings for high quality film production. The pilot coater trials were run with neat Radel as a control, sulfonated Radel and sulfonated Radel with POSS nanoparticles. Three coating solution orifice settings 8, 10 & 12 microns, were used to obtain the dry film at various thicknesses.

Figure 7. Film thickness as a function of gap setting

The results showed relatively good film quality and thickness control and predictability from the Radel 5000 control. The sulfonated Radel 5000 solution made with NMP showed more variation in film thickness and poor surface quality. The addition of POSS nano-particles further degraded the film appearance. All of the three solutions showed poor film drying at thicknesses near 0.002 inch dry. The film appearance, quality and drying (residual solvent) were improved at thicknesses of 0.001 inch dry or less. An attempt was made to use only the control solution (Radel 5000 / NMP) to determine if a dry film of 0.002" could be produced with acceptable quality. A second step was added to post process the material in order to remove residual solvent. That experiment was completed as follows:

Trial 2. Pilot coater trials were run with neat Radel R-5000 and post cured to determine the oven profile necessary to produce dry membranes and also to determine the minimum and maximum coater gap settings for coating Radel R-5000. These results are listed below:

Table XIII. First Pass vs Second Pass Drying Thickness

Thickness (mils)	
1st Pass	2nd Pass
0.585	0.525
1.245	1.230

Oven conditions: Zone 1 - 220°C, Zone 2 – 214°C, Zone 3 - 165°C
 Lab drying conditions: 265°C (isothermal for 30 minutes)

The results of these trials indicate a need to explore some solvent blending for the equipment and knife-over-roll (KOR) coating process. A thickness of 0.002 inch dry could not be achieved with the existing solvent system. The limits of drying capacity and residence time of this particular machine were reached without producing an acceptable dry film. In addition, the secondary post-drying step did not produce an acceptable film quality in this case.

Initial pilot coater trials also determined that head pressure, i.e. the ability to deliver a steady and minimally variable amount of solution to the coating head orifice, was necessary to produce a consistent film thickness using sulfonated Radel R-5000 polymer solution. The sulfonated Radel polymer solution with the addition of POSS nano-particles produced films with a more consistent thickness variation than the sulfonated Radel R-5000 polymer solution without POSS. We attribute this consistency to the higher viscosity of the POSS solution. However, addition of the POSS nano-particles further degraded the surface appearance of the dry film. The surface quality issues were observed to a lesser degree in laboratory bench top castings under ideal conditions. The defects were amplified in a continuous high temperature drying process.

Based on the results of Trial 2, a solvent study was then initiated to determine if an alternative solvent, solvent blend and/or a solvent/diluent blended polymer solution could be useful in producing consistent high quality membranes from the sulfonated Radel R-5000 polymer solution. It believed that the solvent system should have a boiling point much lower than NMP alone (202°C) for suitable process of membrane films. The alternative solvent study was commenced as follows:

Trial 3. Pilot coater trials were run for initial testing of possible “solvent blends” which could effectively dry the membrane in a suitable time and temperature profile. These results are listed below.

Figure 8. Film thicknesses at same settings for different polymer solutions

Figure 9. Oven temperature profile for selective blends

Coater trials were run using various solvents (NMP, DMAC, DMAC/NMP (40/60) blend & DMF). The DMAC solvent and the 60%/40% blend of NMP and DMAC showed the most promise as possible solvent blends. All alternative solvent systems showed some level of improvement in film surface quality. The results also indicated that larger sample quantities would be required to further clarify which solvent or solvent blends would produce the finest quality dry films on the selected coater system. However, the NMP/DMAC blend was selected for further evaluation as it is most compatible with future additive materials for this system. The idea of adding a diluent to further clarify the solution and dry film appearance was also introduced at this point in the study and was included in the next experimental set as follows:

Trial 4. Previous trials indicated that a NMP/DMAC blend could be used to produce a quality film with the desired surface finish. Pilot coater trials were undertaken to test and evaluate the control solvent, all new solvent blends, and solvent / diluent additions. Research suggested that the addition of a diluent could further drive the solution boiling point lower which could have a desirable effect on the surface finish based on the coating methodology. An inclusive solvent / diluent trial was completed to evaluate all acceptable solvents and solvent / diluent blends. The trials were run under four distinct processing conditions:

1. Low heat (180°F)-fast line speed (1.0 fpm)
2. Low heat (180°F)-slow line speed (0.5 fpm)
3. High heat (280°F)-slow line speed (0.5 fpm)
4. High heat (280°F)-fast line speed (1.0 fpm)

Head pressure and oven profile were kept constant for all runs. The results are listed below in Figures 6-9:

Experiment 1.

Figure10

Experiment 2.

Figure11

Experiment 3.

Figure 12

Experiment 4.

Figure 13

Analysis of the raw data from the 48 experiments listed above revealed a superior solution formulation. Based on the results of these trials, the combination of sulfonated Radel R-5000 (48-52% sulfonation), a solvent blend of 60% NMP & 40 % DMAC (using 20% resin solids) with a diluent of Ethanol (up to 25% of the total solvent content) offered the best surface quality, repeatable and reliable dry film thickness. The cast film was dry enough for handling as it exited the processing oven using the current coater system with the KOR methodology.

It was also decided that because the solvent blending and the addition of a diluent further improved the process, future work should be done to optimize the solvent blend ratio and the diluent level. The experiment was completed as follows:

Trial 5. Pilot coater trials were run using solutions of:

1. 60% NMP & 40% DMAC (baseline)
2. 80% NMP & 20 % DMAC
3. 90% NMP & 10% DMAC

Each mixture was blended with ethanol at 20% of the total solvent weight. The resin content was held constant at 20% solids. Considerations were given to the lab data which suggested that with increased addition of DMAC to the solvent solution, the solubility of the final solution would be compromised. It had not been quantified how much of an effect this would have on the final solutions solids percentage. The results of these trials are listed below.

Figure 14. Film thickness of various blends

The results of this trial indicated that increasing the DMAC percentage in the solvent blend produces improved film surface quality. We attribute this to the lower boiling point of the solvent system and more uniform and complete drying of the membrane.

Milestones and Deliverables

PROJECT Q-1

Milestones:

- 1] Identification of a minimum of two existing and two new high temperature polymers, and suitable modifications capable of achieving the temperature, RH% and conductivity targets completed.
- 2] Identification of suitable casting sheet candidates for use in casting polymer film membranes completed.
- 3] Initial evaluation of solubility and rheology issues related to the modified polymers completed.

Deliverables:

- 1] Complete status report on physical, chemical and mechanical (including release and rheology) properties of the base polymer films selected for study.
- 2] Complete status report of casting sheet and polymer rheology / solubility studies.

Q-1 Deliverables:

- 1-Delivered two potential engineering polymer candidates based on Radel A 100 and Radel R 5000 and sulfonated both polymers.
- 2-Produce an alternative sulfonated polymer of polythioether sulfone
- 2- Delivered a casting sheet carrier for the production of proton exchange membranes with easy release and thermal stability beyond the requirements for drying and or curing the PEM.
- 3- Delivered solubility data for the rheology requirements of casting a modified PEM.

PROJECT Q-2

Milestones:

- 1] Identification, synthesis and characterization of suitable novel ionic and mixed surface nano-particle materials for use as polymer additives with potential to provide target functionalities (ionic transport and water management) completed.
- 2] Analysis and evaluation rheology, solubility and process parameter (casting, drying, curing, annealing and release - from - carrier) of nano-particle modified polymers completed.

Deliverables:

- 1] Complete status report on suitable nano – particles identified and evaluated.
- 2] Complete status report on the solubility, rheology and transport and other properties of the *modified* base polymer films *with and without* additives.

Q-2 Deliverables

- 1-Synthesized a sulfonated octaphenyl POSS, compatible with the conductive polymers utilized. Synthesized a sulfonated phosphazene nanoparticle. Synthesized an alkylated POSS. All nano-particles characterized by H NMR, C NMR, Si NMR, FTIR, SEC-Malls, MALDI-TOF MS
- 2- Delivered status report on solubility, rheology and conductivity of modified polymers (Radel A 100, Radel R 5000 and SPTES) with and without main nano-particle, sulfonated octaphenyl POSS.

PROJECT Q-3

Milestones:

- 1] Analytical characterization of all polymer / synthesized nano – particle blend formulations and assessment of solubility, mixing, dispersion and morphological features completed.
- 2] Initial proton conductivity assessment of lab scale thin films produced from modified polymer blends completed.
- 3] Identification of potentially suitable solution casting methodologies capable of producing 1.0+ mil single layer and / or 10 – 20 micron thick (individual layer) compositions of multi – layer membranes from the candidate modified polymer blends completed.

Deliverables:

- 1] Complete status report on the analytical and conductivity analysis of the candidate modified polymer blends.
- 2] Complete status report on
 - (a) laboratory casting methods studied for single and multilayered films;
 - (b) drying , curing, annealing and release of various caliper single and multilayered films
 - (c) preliminary testing of thermal and mechanical stability, conductivity, film integrity, and water management of laboratory cast films.

Q-3 Deliverables

- 1-Delivered physical and electrical properties of sulfonated polymers and blends with nano-particles. See tables 9, 10, 11 &12 in MMI report
- 2- Delivered laboratory casting and pilot casting methods for the production of single layer and multilayer composite proton exchange membranes.
- 3- Delivered laboratory and pilot casting parameters for drying various calipers of sulfonated polymer.
- 4-Delivered tensile and DMA study of single layer sulfonated Radel R 5000, nano filled sulfonated Radel R 5000 and three layer, composite of neat outer layers of S-Radel R and middle layer of filled/S-Radel R 5000
- 5-Delivered Conductivity and Fuel Cell data indicating enhance performance (see figure 2; O2Task 4)

PROJECT Q-4

Milestones:

- 1] Completed profile of modified polymer blend candidates to characterize temperature, dimensional stability, physical, mechanical and chemical properties. This will form the basis for future polymer and additive research.
- 2] Development of basic laboratory procedures for solution casting / drying / curing / annealing of the selected modified polymer blends to form both single and multi – layer polymer membranes.
- 3] Development of a design of experiments plan for future pilot scale research and development of roll – to – roll membrane process parameters.

Deliverables:

- 1] Complete status report on polymer blend candidate properties characterization
- 2] Complete status report on baseline laboratory procedures for casting single and multi-layered films and a design of experiments for prototyping single and multi - layered films

Q-4 Deliverables

- 1-Delivered Dynamic Mechanical Analysis of 1) sulfonated Radel R 2) blend of sulfonated POSS and S-Radel R 3) single layers of 1 and 2 and 4) multilayered composite of sulfonated Radel R (outer layers) and 20% sulfonated POSS / 80% sulfonated Radel R 5000.
- 2- Delivered data on baseline procedures for casting single and multilayered films and experiments for prototyping. See O2 Tasks 4,5,6,7 &8.

Accomplishments versus Objectives

The completion of the research work tasks outlined above and the specified deliverables has resulted in the achievement of Objectives 1 and 2 of this project. Specifically we have as proposed 1) identified an engineering polymer with excellent chemical and physical characteristics 2) sulfonated the selected polymer at various levels to produce a carrier polymer with very high storage modulus, good tensile strength, good conductivity, binding power and compatibility with the nano filler 3) synthesized a stable, hydrophilic nano-particle with higher IEC than the polymer for enhance water management 4) developed a composite architecture that produces a membrane with improved conductivity at 90°C and 25% relative humidity and 5) identified multiple readily available processes to manufacture the composite membrane in a roll to roll format. The technical accomplishments have resulted in two major automotive companies (GM & Hyundai) requesting multilayer samples for evaluation.

Summary

The original hypothesis was to prepare a conductive polymer from an existing engineering polymer and enhance its performance by the addition of a hydrophilic nano-particle. It was also hypothesized that multilayer constructions would enhance membrane performance in the areas of membrane integrity, water management and conductivity. It was also hypothesized that the manufacturing of this membrane architecture in a cost effective, roll to roll format was viable based on the casting experiences at Chemsultants International Inc.

The hypotheses were based on the selected knowledge of polymers and nano-particles at Michigan Molecular Institute and Chemsultants International Inc., the analytical and equipment capabilities of both organizations and the considerable coating equipment and casting capabilities at Chemsultants International Inc.

Intellectual Property / Patents

1-US Patent Filing: US60/923,297. Improved Fuel Cell Proton Exchange Membranes. Bob Nowak, Claire Hartmann-Thompson, Lowell Thomas, Dale Meier, Ken Bruza. Filed April 13, 2007.

2- Provisional patent application (60 / 967,547) filed by Chemsultants International Inc on 9/4/07: Multilayered Composite Proton Exchange Membrane and a Process for Manufacturing the Same. Pasco R. Santurri, Joseph Mause, Denise Katona, Berry Decker

Publication:

1-Proton Conducting Polyhedral Oligosilsesquioxane Nanoadditives for Sulfonate Polyphenylsulfone Hydrogen Fuel Cell Proton Exchange Membranes, accepted by the Journal of Applied Polymer Science for publication.