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APPENDICES

Appendix A Fourier Transform Infrared Spectroscopy

The polymers (PSF and PVDF) and sulfonated polymers (SPSF and SPVDF) functional groups were determined using the FT-IR spectrometer (Nicolet, Nexus 670). The samples were measured directly in the wave number range of 400-1600 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans using potassium bromide (KBr; dried at 100 °C for 24 h) as a background materials. The composite material composed of sample and KBr was compressed into pellets and inserted in the sample holder (Macksasitorn *et al.*, 2012).

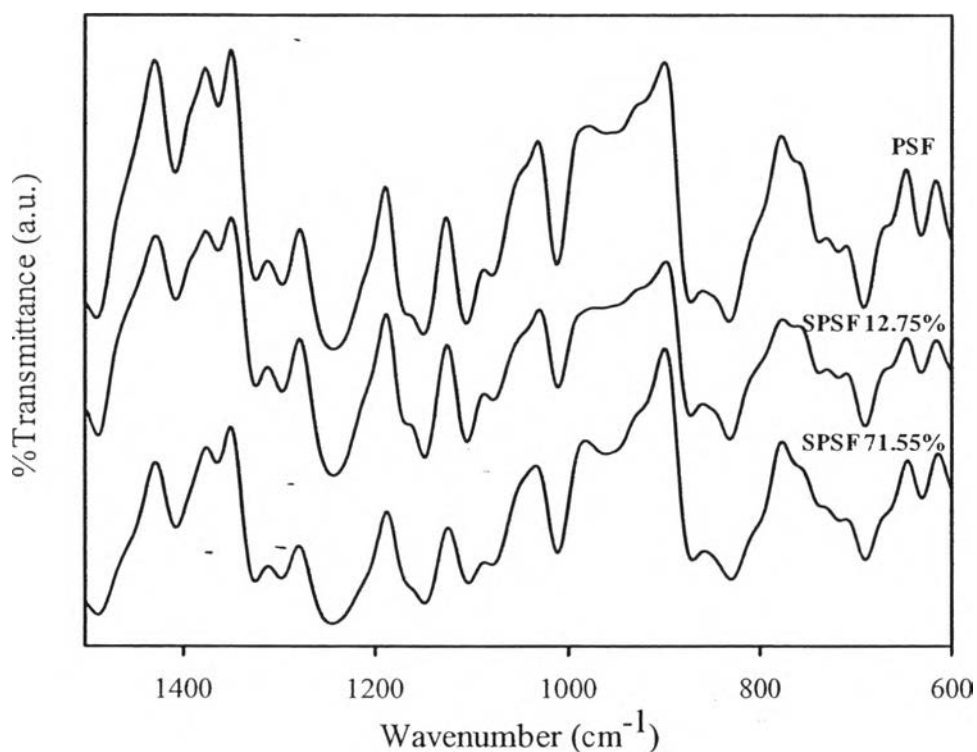


Figure A1 The FT-IR spectra of polysulfone (PSF) and sulfonated polysulfone (SPSF) at various degrees of sulfonation.

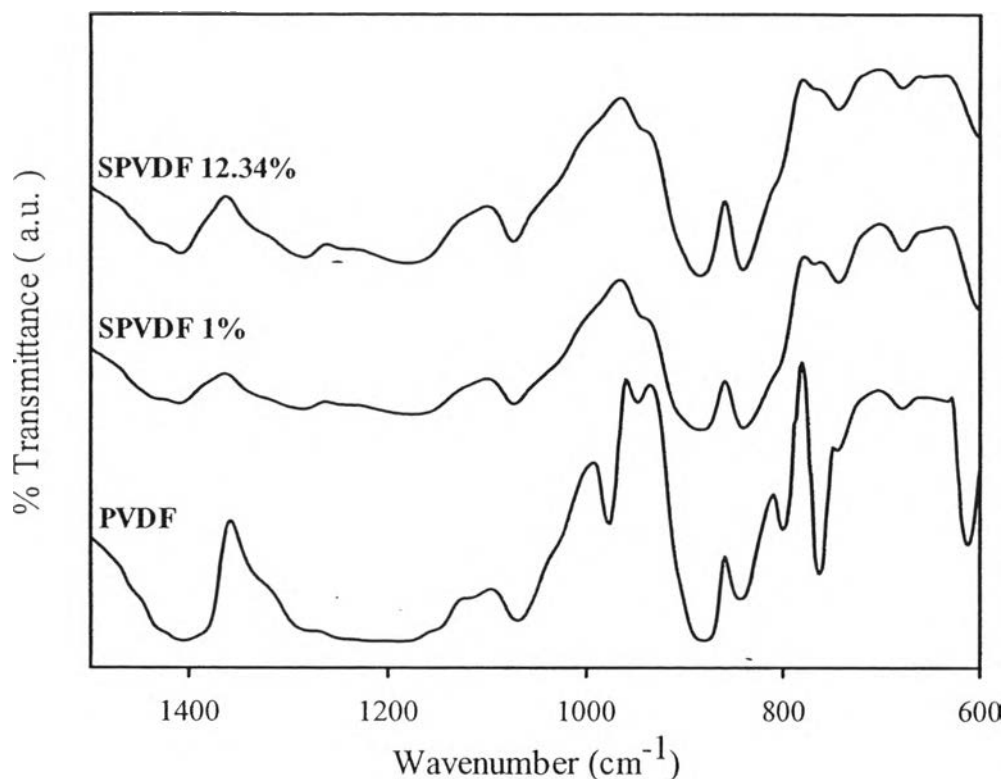


Figure A2 The FT-IR spectra of polyvinylidene fluoride (PVDF) and sulfonated polyvinylidene fluoride (SVDF) at various degrees of sulfonation.

Table A1 The FT-IR absorption spectra of PSF, SPSF, PVDF and SPVDF

Wavenumbers (cm ⁻¹)	Assignments	References
696	S=O stretching of sodium sulfonate groups	Xiao <i>et al.</i> , 2002
700	Symmetric S-O stretching	Devrim <i>et al.</i> , 2009
706	S-O stretching	Lakshmi <i>et al.</i> , 2005
709	S-O stretching	Zaidi <i>et al.</i> , 2003
1024	S=O stretching	Zaidi <i>et al.</i> , 2003
1026	S=O stretching	Lakshmi <i>et al.</i> , 2005
1080	Symmetric O=S=O stretching	Zaidi <i>et al.</i> , 2003

1104	Symmetric O=S=O stretching	Karlsson <i>et al.</i> , 2004
1164	Asymmetric O=S=O stretching	Lakshmi <i>et al.</i> 2005
1203	Asymmetric O=S=O stretching vibrations	Wang <i>et al.</i> , 2003
1245	Asymmetric O=S=O stretching	Karlsson <i>et al.</i> , 2004
1252	Asymmetric O=S=O stretching	Zaidi <i>et al.</i> , 2003
1482	Tri-substituted on-aromatic phenyl due to sulfonation in phenyl ring	Xing <i>et al.</i> , 2005
1490	C-C aromatic	Zaidi <i>et al.</i> , 2003
1501	Di-substituted on aromatic phenyl for non-sulfonated	Xing <i>et al.</i> , 2005
1029, 1086	Symmetric and asymmetric stretching vibration O=S=O due to sodium sulfonate group in polymer	Xing <i>et al.</i> , 2005
1030, 1098	Symmetric and asymmetric stretching of sulfonate	Wang <i>et al.</i> , 2003
1301, 1149	Asymmetric and symmetric O=S=O stretching of sulfone groups	Xiao <i>et al.</i> , 2002
1229, 1099, 1021	Asymmetric and symmetric O=S=O stretching vibrations of sulfonate groups	Wang <i>et al.</i> , 2006
1028, 1243, 1084	Asymmetric and symmetric O=S=O stretching of sulfonated groups	Xiao <i>et al.</i> , 2002
1492, 1470, 1414, 1402	1,3,4-trisubstituted aromatic C-C skeletal vibrations	Lakshmi <i>et al.</i> , 2005
3440, 1252, 1080, 1024	Sulfonic acid groups	Zaidi <i>et al.</i> , 2003
3450-3430	O-H vibration	Zaidi <i>et al.</i> , 2003

Appendix B Thermogravimetric Analysis

The thermal property of the polymers and sulfonated polymers was investigated using a Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA; Perkin Elmer, Pyris Diamond). The samples were inserted into an alumina pan at the weight of 4-10 mg and. The measurements were carried out under nitrogen flow with the temperature range of 25 °C to 700 °C at a heating rate of 10 °C. min⁻¹ (Zhang *et al.*, 2011).

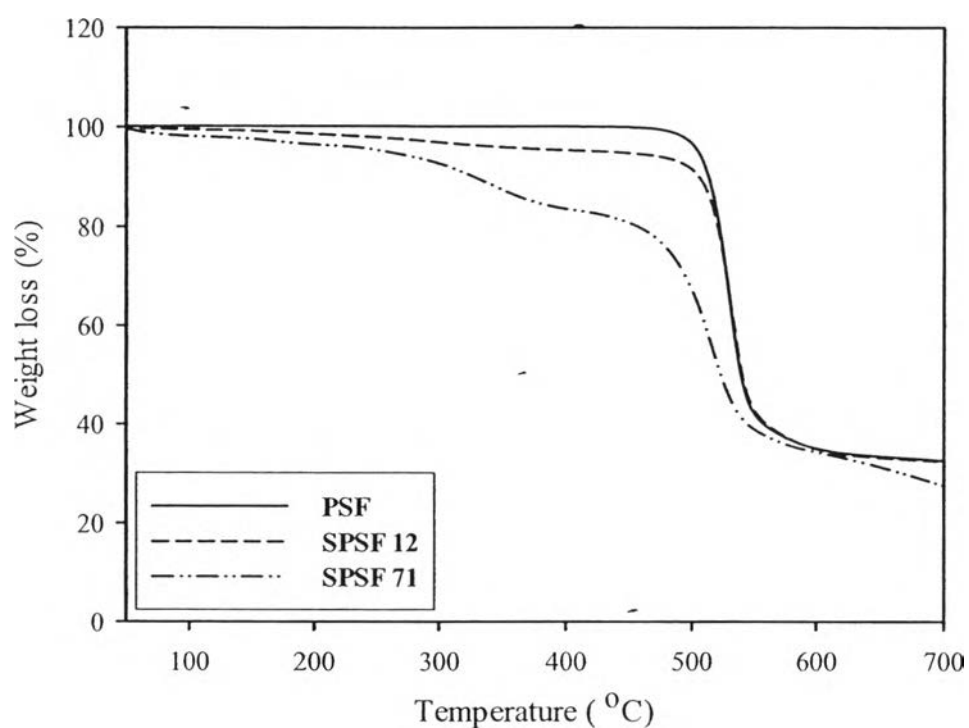


Figure B1 TGA thermograms of polysulfone (PSF) and sulfonated polysulfone (SPSF) at various degrees of sulfonation.

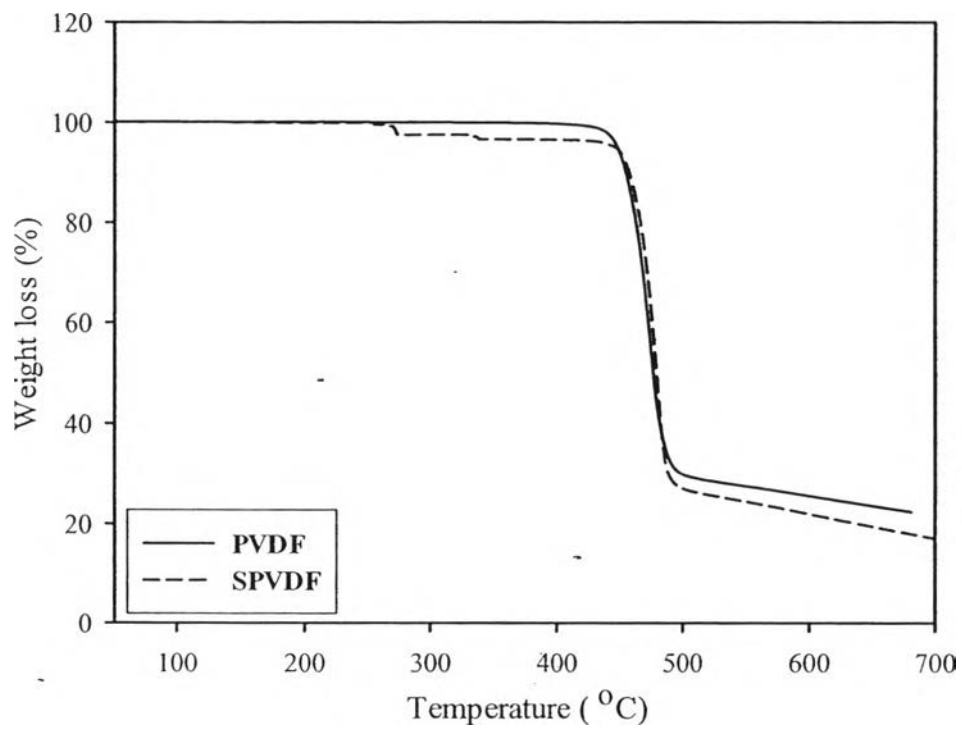


Figure B2 TGA thermograms of polyvinylidene fluoride (PVDF) and sulfonated polyvinylidene fluoride (SPVDF).

Appendix C Solubility and Precipitation of Polymer

The PSF or PVDF was weighed around 0.1 g and soaked in 10 ml of solvent at room temperature for 24 h to prepare polymer solutions for the sulfonation process.

Table C1 Solubility of PSF at various solvents of 25 °C

Solvent	Solubility
Water	Not-dissolve
NMP	Not -dissolve
DMSO	Not -dissolve
THF	Dissolve
DCM	Dissolve
DCE	Dissolve
Chloroform	Dissolve
Sulfuric acid	Dissolve

Table C2 Solubility of PVDF in various solvents and at different temperatures

Solvent	Temperature (°C)	Solubility
Water	25	Not-dissolved
NMP	25	Not-dissolved
	60	Dissolved
THF	25	Not-dissolved
DMSO	60	Not-dissolved
DMF	25	Not-dissolved
	60	Dissolved
DCM	25	Not-dissolved
DCE	25	Not-dissolved
Chloroform	25	Not-dissolved
Sulfuric acid	25	Not-dissolved
	60	Not-dissolved

Table C3 Precipitation of S-PSF with various precipitating agents

Precipitating agent	precipitation
Cooled water	Not-precipitated
Ice	Precipitated
Methanol	Precipitated
Ethanol	Precipitated

Table C4 Precipitation of S-PVDF with various precipitating agents

Precipitating agent	precipitation
Cooled water	Not-precipitated
Ice	Precipitated
Methanol	Precipitated
Ethanol	Precipitated

Appendix D Sulfonation Process and Degree of Sulfonation

Sulfonation process is method for attaching a sulfonic group to the polymer backbone. Degree of sulfonation (DS) is represented by the number of sulfonic acid group per repeating unit of polymer. The DS of sulfonated polymer was determined by titration the sulfonated polymer solution with 0.01 M NaOH using phenolphthalein as an indicator. The DS was calculated by the following Eq (D1):

$$DS(\%) = \frac{(V_{NaOH} \times M_{NaOH})/1000}{\text{Mole of polymer membrane}} \times 100 \quad (D1)$$

where V_{NaOH} refers to the volume of sodium hydroxide solution, C_{NaOH} refers to the concentration of sodium hydroxide solution.

Table D1 Sulfonation conditions and degree of sulfonation of PSF at 25 °C for 4 h

Weight of PSF (g)	Mole of H ₂ SO ₄	H ₂ SO ₄ /PSF Mole ratio	DCM volume (ml)	Volume fraction	Yield of SPSF (%)	DS (%)
1.2151	0.05	17	10	0.64	99.51	12.75
1.2014	0.10	35	10	0.64	99.50	14.12
1.1995	0.15	52	10	0.64	103.82	39.66
1.2030	0.20	70	10	0.64	102.03	33.09
1.2060	0.25	88	10	0.64	102.15	55.37

* S-PSF could not be cast to film.

DMC is dichloromethane.

Table D2 Sulfonation conditions of PSF at 25 °C for 4 h for upscale

Weight of PSF (g)	Mole of PSF	Volume of H ₂ SO ₄ (ml)	Mole of H ₂ SO ₄	H ₂ SO ₄ /PSF Mole ratio	DCM volume (ml)	Volume fraction	Yield (%)	DS (%)
2.0014	0.045	30	0.09	20	10	0.72	96.25	15.65
2.0104	0.045	30	0.18	40	10	0.72	85.36	19.90
2.0210	0.045	30	0.20	45	10	0.72	101.14	27.99
2.0034	0.045	30	0.25	55	10	0.72	105.53	44.66
2.0163	0.045	30	0.27	60	10	0.72	98.89	61.44
2.0410	0.045	30	0.36	80	10	0.72	115.74	71.55

Table D3 Sulfonation condition of PSF at 25 °C for 4 h for film casting

Weight of PSF (g)	Mole of PSF	Volume of H ₂ SO ₄ (ml)	Mole of H ₂ SO ₄	H ₂ SO ₄ /PSF Mole ratio	DCM volume (ml)	Volume fraction	Yield (%)	DS (%)
1.2151	0.0027	20	0.05	17	10	0.64	99.51	12.75
2.0014	0.045	30	0.09	20	10	0.72	96.25	15.65
2.0104	0.045	30	0.18	40	10	0.72	85.36	19.90
2.0163	0.045	30	0.27	60	10	0.72	98.89	61.44
2.0410	0.045	30	0.36	80	10	0.72	115.74	71.55

Table D4 Sulfonation conditions of PSF at 50 °C for 4 h

Weight of PSF (g)	Mole of PSF	Volume of H ₂ SO ₄ (ml)	Mole of H ₂ SO ₄	H ₂ SO ₄ /PSF Mole ratio	DCM volume (ml)	Volume fraction	Yield (%)	DS (%)
1.9933	0.045	30	0.09	20	10	0.72	109.25	52.64
2.0022	0.045	30	0.18	40	10	0.72	108.89	52.88
2.0058	0.045	30	0.27	60	10	0.72	110.05	51.10
2.0014	0.045	30	0.36	80	10	0.72	110.08	57.20

Table D5 Sulfonation conditions of PVDF at 25 °C for 4 h

Weight of PVDF (g)	Mole of PVDF	Volume of H ₂ SO ₄ (ml)	Mole of H ₂ SO ₄	H ₂ SO ₄ /PVDF Mole ratio	NMP volume (ml)	Volume fraction	Yield (%)	DS (%)
1.2273	0.0191	0.67	0.012	1	60	0.011	94.06	0.95
1.1949	0.0187	3.33	0.06	5	60	0.05	98.46	2.04
1.1985	0.0187	6.67	0.12	10	60	0.10	88.21	4.25
1.1813	0.0184	10	0.18	15	60	0.14	98.95	6.04
1.4207	0.0222	13.33	0.24	20	60	0.18	83.16	7.86
1.2171	0.0190	26.67	0.48	40	60	0.31	86.39	12.34

Table D6 Sulfonation conditions of PVDF at 50 °C for 4 h

Weight of PVDF (g)	Mole of PVDF	Volume of H₂SO₄ (ml)	Mole of H₂SO₄	H₂SO₄ /PVDF Mole ratio	NMP volume (ml)	Volume fraction	Yield (%)	DS (%)
1.2157	0.0190	13.33	0.24	20	60	0.18	84.18	15.01
1.2237	0.0191	26.67	0.48	40	60	0.31	92.58	16.08
1.2212	0.0191	40	0.72	60	60	0.40	100	16.64
1.2400	0.0193	53.33	0.96	80	60	0.47	94.19	13.34
1.2438	0.0194	66.67	1.2	100	60	0.52	79.36	12.23

Appendix E Water Uptake

The membranes were immersed into DI water for 24 h at room temperature. Superabundant water was absorbed from the membrane surface with a wipe paper and the membranes were weighed (noted as W_s). The membranes were dried at 100 °C for 24 h in an oven and weighed (noted as W_d). The percentage of water uptake was then calculated as following Eq. (E1):

$$\text{Water uptake} = \frac{(W_s - W_d)}{W_d} \times 100 \quad (\text{E1})$$

where W_d refers to the weight of dried polymer, and W_s is weight of swelled polymer.

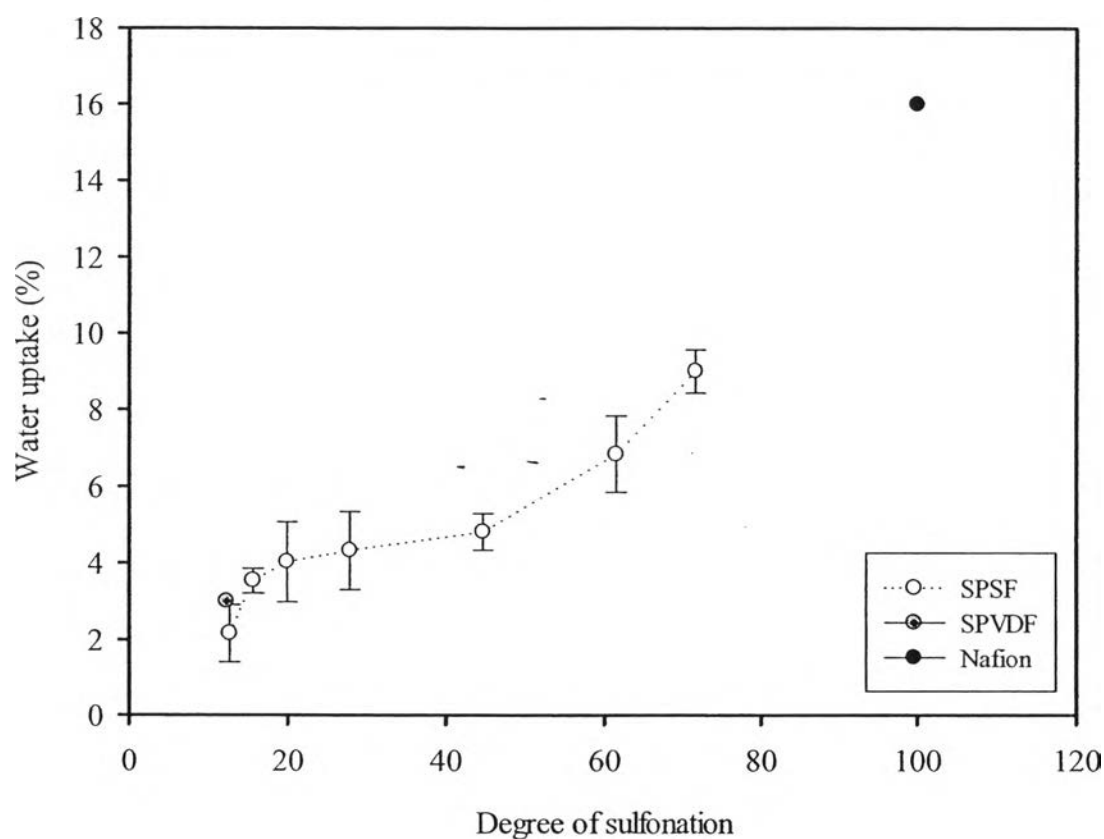


Figure E1 Water uptake of SPSF, SPVDF, and Nafion 117.

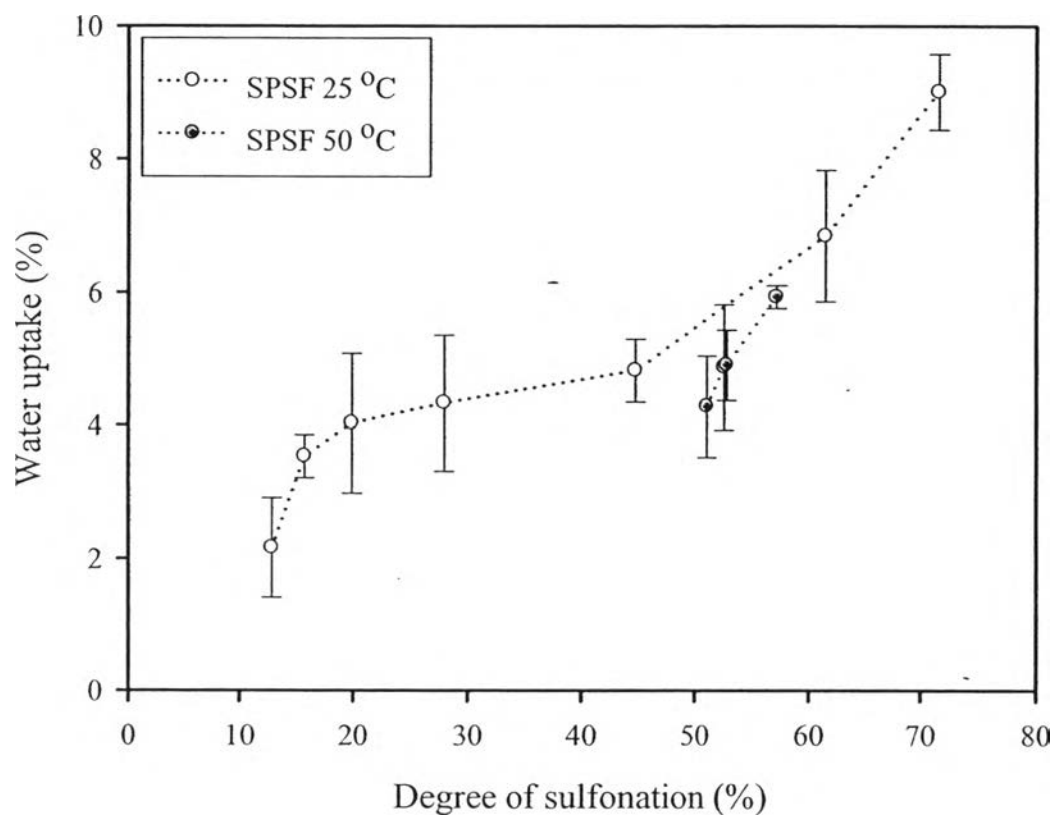


Figure E2 Water uptake of SPSF at various degrees of sulfonation at 25 °C and 50 °C.

Table E1 Water uptake of SPSF at various degrees of sulfonation at 25 °C

DS (%)	Dry (g)	Wet (g)	Water uptake (%)
12.75	0.093	0.096	2.91
	0.092	0.094	2.17
	0.092	0.093	1.41
	Water uptake average		2.16 ± 0.74
15.65	0.047	0.049	3.59
	0.047	0.049	3.19
	0.047	0.049	3.83
	Water uptake average		3.54 ± 0.32
19.90	0.114	0.119	4.93
	0.111	0.114	2.88
	0.112	0.117	4.28
	Water uptake average		4.03 ± 1.05
27.99	0.083	0.087	4.32
	0.084	0.087	3.32
	0.082	0.087	5.36
	Water uptake average		4.33 ± 1.02
44.66	0.087	0.092	5.04
	0.087	0.090	4.28
	0.085	0.090	5.15
	Water uptake average		4.82 ± 0.48
61.44	0.045	0.049	7.97
	0.044	0.047	6.11
	0.045	0.048	6.46
	Water uptake average		6.85 ± 0.99
71.55	0.104	0.114	8.93
	0.104	0.113	8.48
	0.103	0.113	9.61
	Water uptake average		9.01 ± 0.57

Table E2 Water uptake of SPSF at various degrees of sulfonation at 50 °C

DS (%)	Dry (g)	Wet (g)	Water uptake (%)
51.10	0.083	0.088	5.16
	0.083	0.087	3.84
	0.083	0.086	3.85
	Water uptake average		4.28 ± 0.76
52.64	0.053	0.056	5.88
	0.053	0.055	4.73
	0.052	0.055	4.01
	Water uptake average		4.87 ± 0.95
52.88	0.078	0.083	5.09
	0.079	0.083	5.32
	0.079	0.082	4.31
	Water uptake average		4.91 ± 0.53
57.20	0.052	0.055	5.95
	0.053	0.056	6.09
	0.052	0.055	5.75
	Water uptake average		5.93 ± 0.17

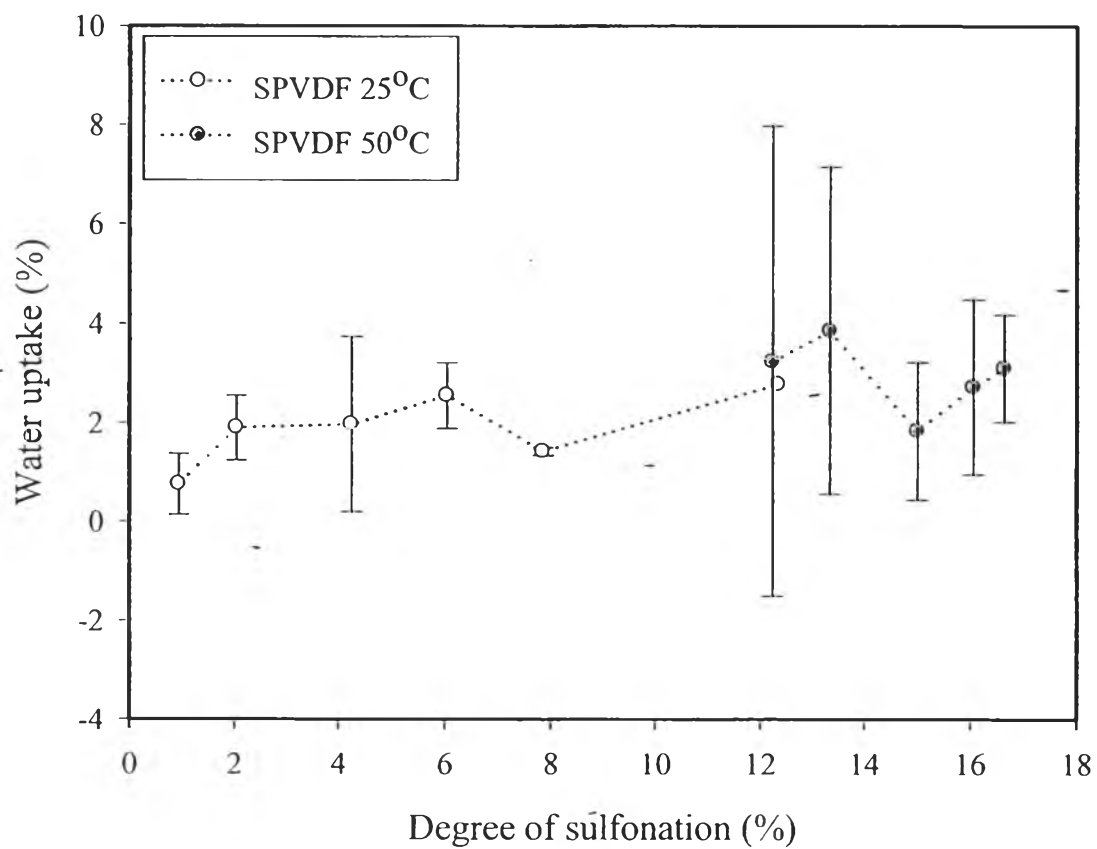


Figure E3 Water uptake of SPVDF at various degrees of sulfonation at 25 °C and 50 °C.

Table E3 Water uptake of SPVDF at various degrees of sulfonation at 25 °C

DS (%)	Dry (g)	Wet (g)	Water uptake (%)
0.95	0.078	0.079	0.90
	0.078	0.079	1.28
	0.01	0.077	0.079
	Water uptake average		1.29 ± 0.39
2.04	0.062	0.063	2.28
	0.062	0.062	1.14
	0.062	0.063	2.27
	Water uptake average		1.90 ± 0.66
4.25	0.040	0.041	2.46
	0.040	0.042	3.44
	0.041	0.041	0
	Water uptake average		1.97 ± 1.77
6.04	0.039	0.040	2.04
	0.039	0.041	3.31
	0.039	0.04	2.30
	Water uptake average		2.55 ± 0.67
7.86	0.066	0.067	1.51
	0.066	0.066	1.37
	0.065	0.066	1.38
	Water uptake average		2.65 ± 2.19
12.34	0.036	0.037	2.78
	0.036	0.037	2.78
	0.037	0.038	2.78
	Water uptake average		2.78 ± 0.42

Table E4 Water uptake of SPVDF at various degrees of sulfonation at 50 °C

DS(%)	Dry (g)	Wet (g)	Water uptake (%)
12.23	0.050	0.050	0.20
	0.049	0.050	0.81
	0.049	0.054	8.70
	Water uptake average		3.24 ± 4.74
13.34	0.073	0.074	0.96
	0.073	0.075	3.16
	0.073	0.078	7.44
	Water uptake average		3.85 ± 3.29
15.01	0.073	0.074	0.96
	0.073	0.073	1.10
	0.073	0.075	3.44
	Water uptake average		1.83 ± 1.39
16.06	0.075	0.076	0.80
	0.075	0.077	3.08
	0.075	0.078	4.28
	Water uptake average		2.72 ± 1.77
16.64	0.07	0.071	1.86
	0.07	0.073	3.86
	0.070	0.072	3.58
	Water uptake average		3.10 ± 1.08

Appendix F Ion Exchange Capacity

Ion exchange capacity is the method to determine number of milliequivalent of ions in 1 g of dry polymer (meq/g). The membranes were soaked in 0.1 M NaCl solution for 24 h to exchange H⁺ with Na⁺. H⁺ were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC was determined by following Eq (F1):

$$IEC (meq/g) = \frac{\text{Consumed NaOH (ml)} \times \text{molarity NaOH (M)}}{W_{dry} (mg)} \quad (F1)$$

where consumed ml (NaOH) is the consumed volume of NaOH solution. Molarity NaOH is molar of NaOH solution. Weight dried membrane is the weight of membrane in a dry state.

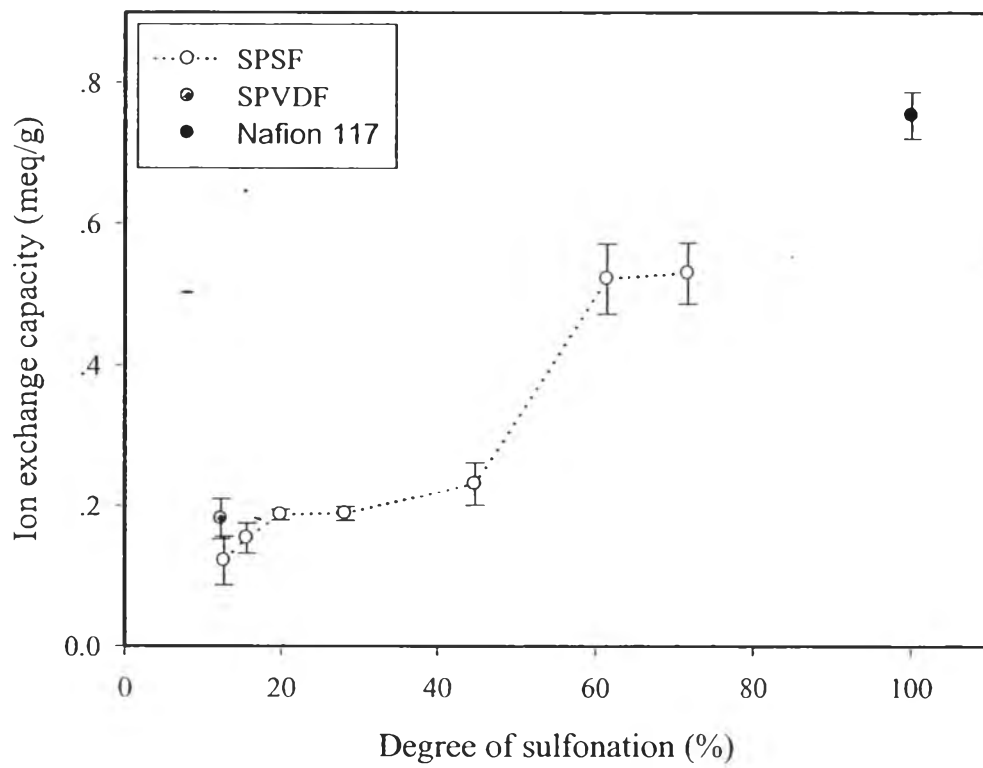


Figure F1 Ion exchange capacity of SPSF, SPVDF, and Nafion 117.

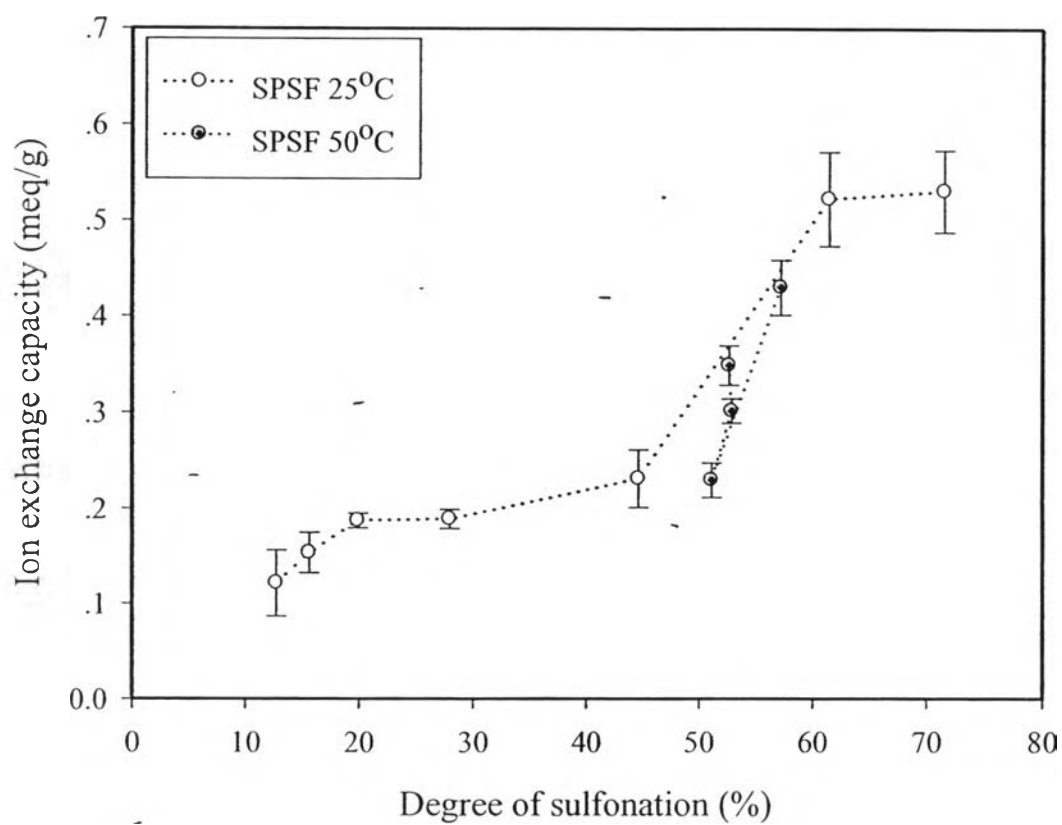


Figure F2 Ion exchange capacity of SPSF at various degrees of sulfonation at 25 °C and 50 °C.

Table F1 Ion exchange capacity of SPSF at various degrees of sulfonation

Sulfonation temperature (°C)	DS (%)	IEC			
		IEC 1 (meq/g)	IEC 2 (meq/g)	IEC 3 (meq/g)	IEC average (meq/g)
25	12.75	0.0868	0.1215	0.1562	0.1215 ± 0.03
	15.65	0.1289	0.1657	0.1657	0.1657 ± 0.02
	19.90	0.1872	0.1950	0.1794	0.1872 ± 0.01
	27.99	0.1889	0.1988	0.1789	0.1889 ± 0.01
	44.66	0.2379	0.2577	0.1982	0.2313 ± 0.03
	61.44	0.4850	0.5037	0.5783	0.5224 ± 0.05
	71.55	0.5055	0.5799	0.5055	0.5304 ± 0.04
50	52.64	0.3696	0.3490	0.3285	0.3490 ± 0.35
	52.88	0.2944	0.2944	0.3162	0.3017 ± 0.30
	51.10	0.2089	0.2403	0.2403	0.2298 ± 0.23
	57.20	0.4526	0.3978	0.4389	0.4298 ± 0.43

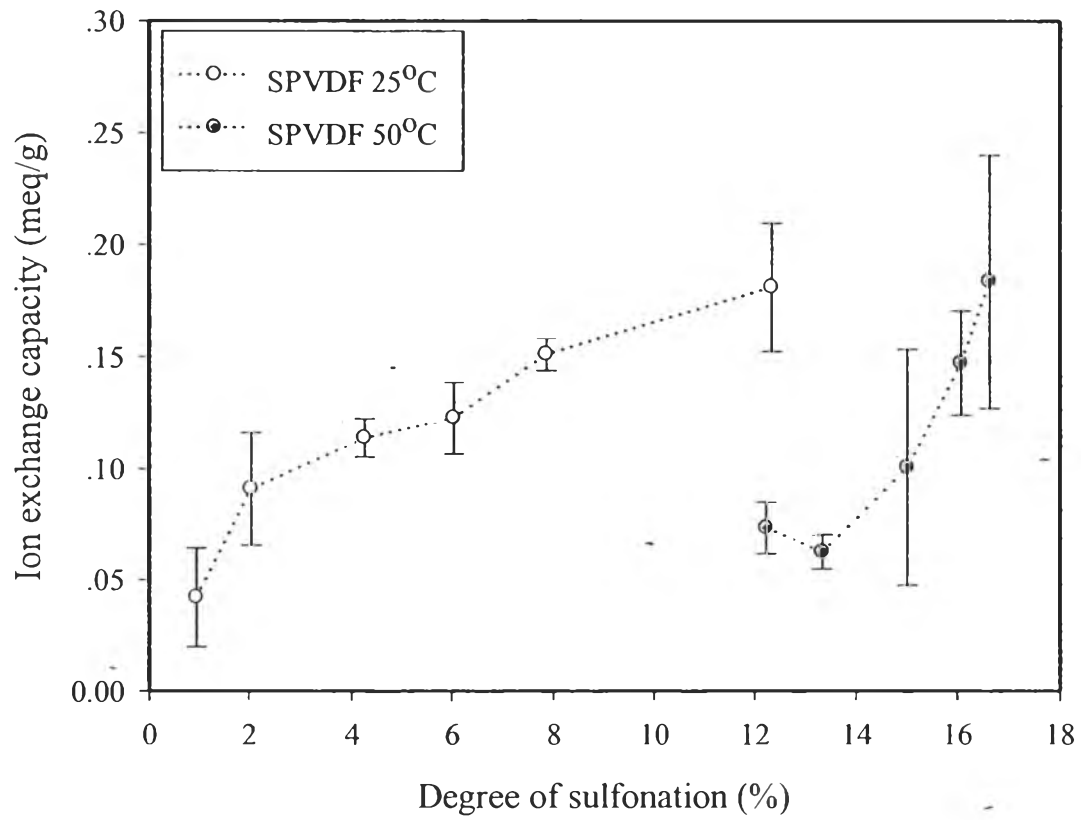


Figure F3 Ion exchange capacity of SPVDF at various degrees of sulfonation at 25 °C and 50 °C.

Table F2 Ion exchange capacity of of SPVDF at various degrees of sulfonation

Sulfonation temperature (°C)	DS (%)	IEC			
		IEC 1 (meq/g)	IEC 2 (meq/g)	IEC 3 (meq/g)	IEC average (meq/g)
25	0.95	0.0504	0.0588	0.0168	0.0420 ± 0.02
	2.04	0.1092	0.062	0.1014	0.0910 ± 0.02
	4.25	0.1040	0.1188	0.1188	0.1139 ± 0.01
	6.04	0.1263	0.1368	0.1052	0.1228 ± 0.02
	7.86	0.15547	0.1430	0.1554	0.1513 ± 0.01
	12.34	0.1872	0.2059	0.1498	0.1810 ± 0.03
50	12.23	0.0600	0.0800	0.0800	0.0733 ± 0.01
	13.34	0.0536	0.0670	0.0670	0.0626 ± 0.01
	15.01	0.1572	0.0917	0.0524	0.0917 ± 0.05
	16.08	0.1338	0.1740	0.1338	0.1473 ± 0.02
	16.64	0.1877	0.1251	0.2377	0.1836 ± 0.06

Appendix G Proton Conductivity Under Dry State

The impedance data was measured by using an impedance phase analyser HP 4194 at various frequencies from 100 Hz to 2 MHz and at room temperature. The membranes were cut to form $5 \times 5 \text{ cm}^2$ specimens for the measurement.

$$\sigma = \frac{d}{RS} \quad (\text{G1})$$

where d is the thickness (cm), S is the contact area of the sample ($\pi r^2 = \pi(3.8/2)^2 = 11.34 \text{ cm}^2$), and R can be derived from the low intercept of the high frequency semi-circle on a complex impedance plane with the $\text{Re}(Z)$ axis.

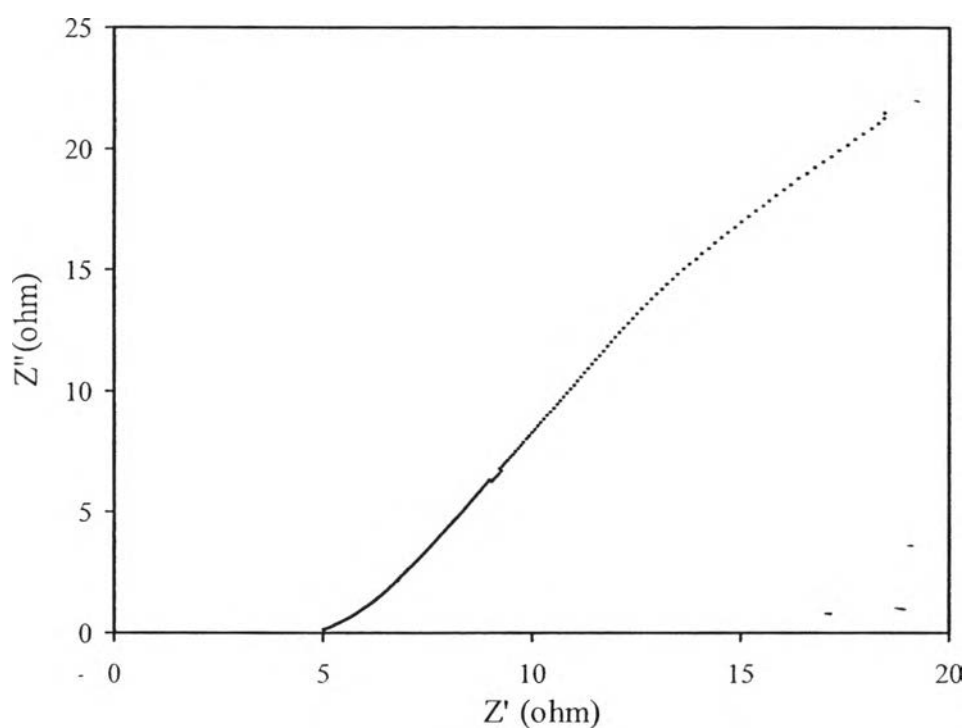


Figure G1 Nyquist plot of the Nafion 117 membrane.

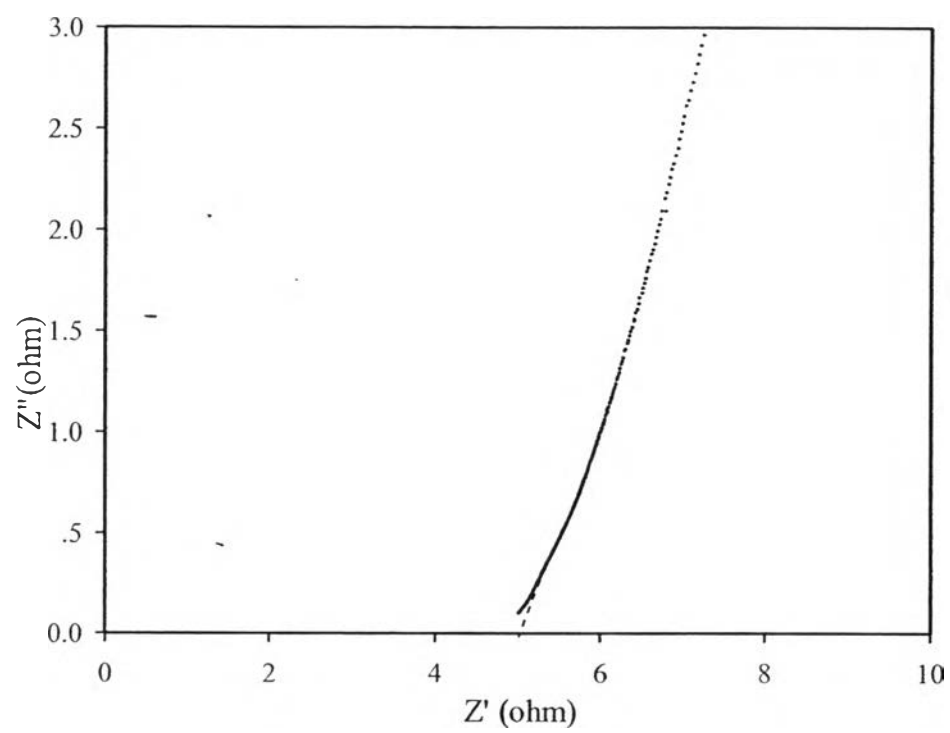


Figure G2 Enlarged Nyquist plot of the Nafion117 membrane.

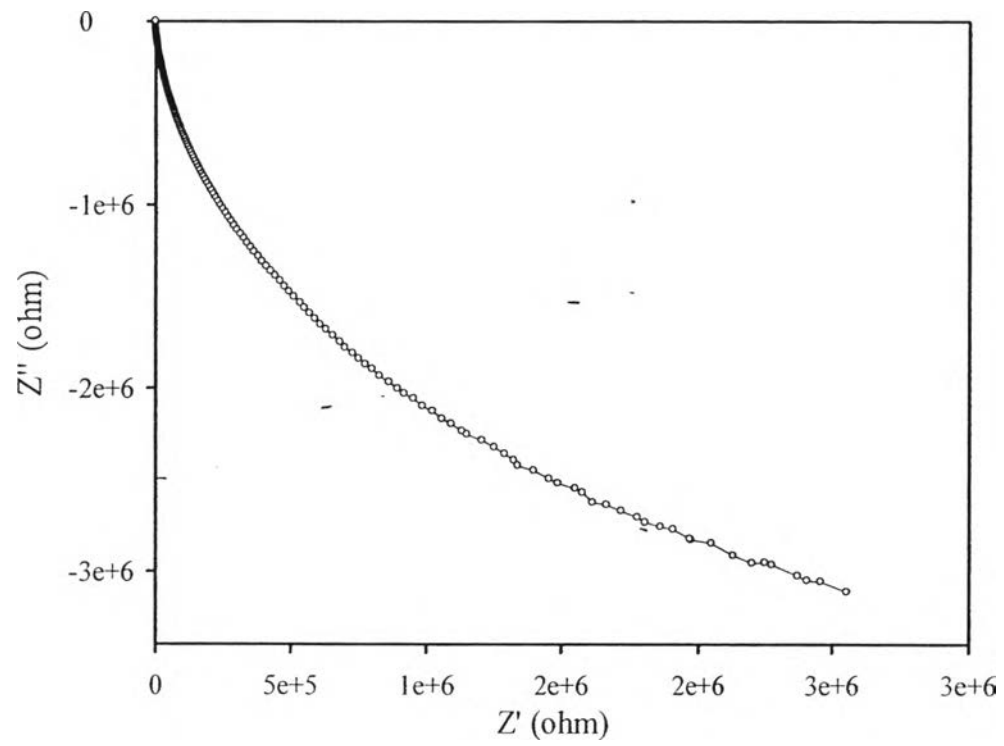


Figure G3 Nyquist plot of the SPSF DS 12.75% membrane.

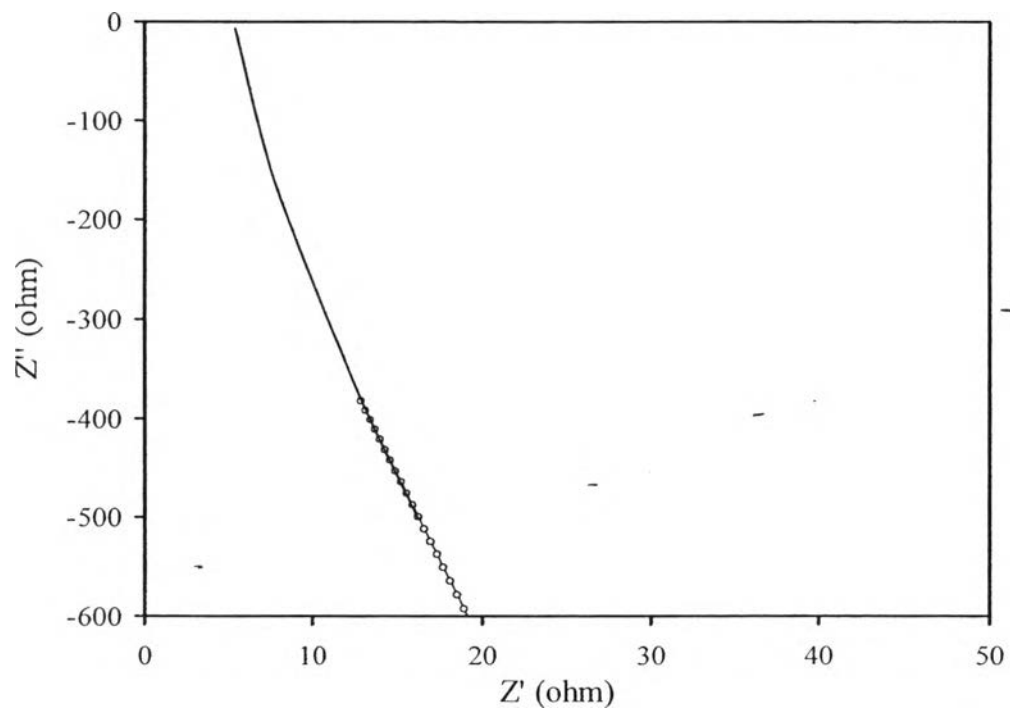


Figure G4 Enlarged Nyquist plot of the SPSF DS 12.75% membrane ($R = 6.1$ ohm).

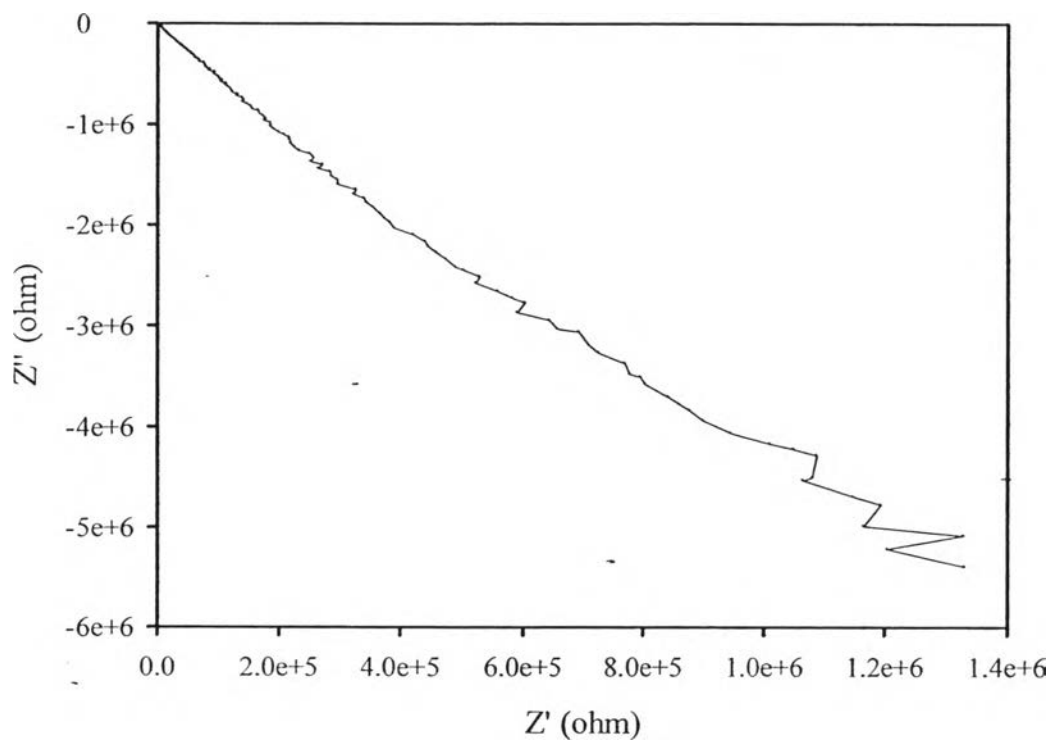


Figure G5 Nyquist plot of the SPSF DS 15.65% membrane.

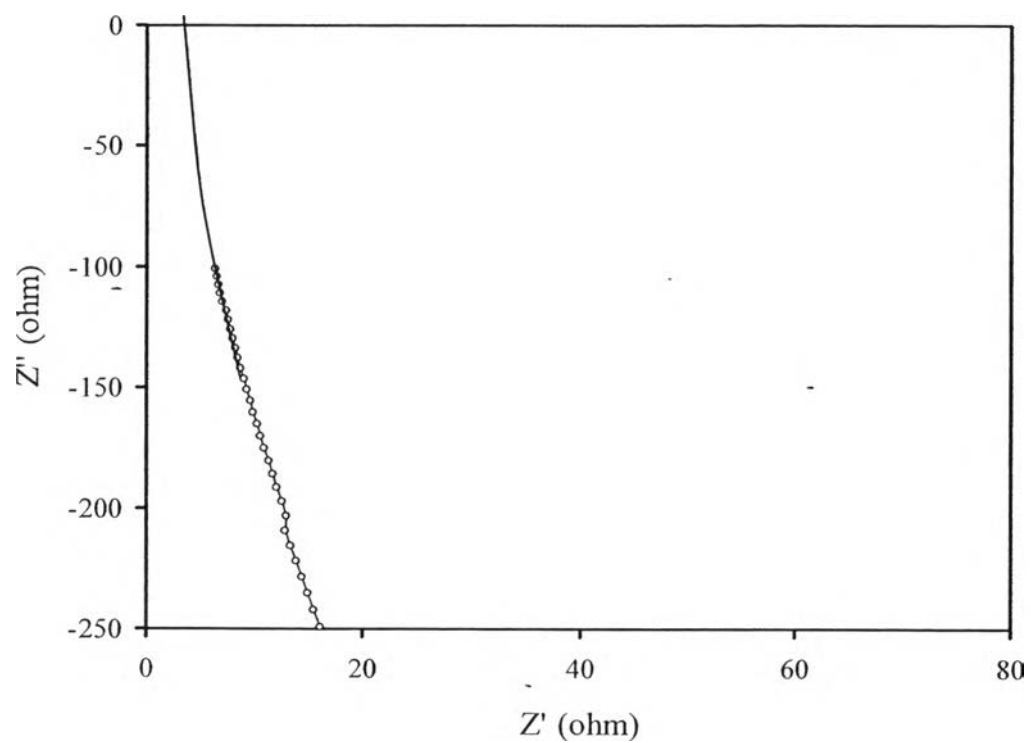


Figure G6 Enlarged Nyquist plot of the SPSF DS 15.65% membrane ($R = 5.74$ ohm).

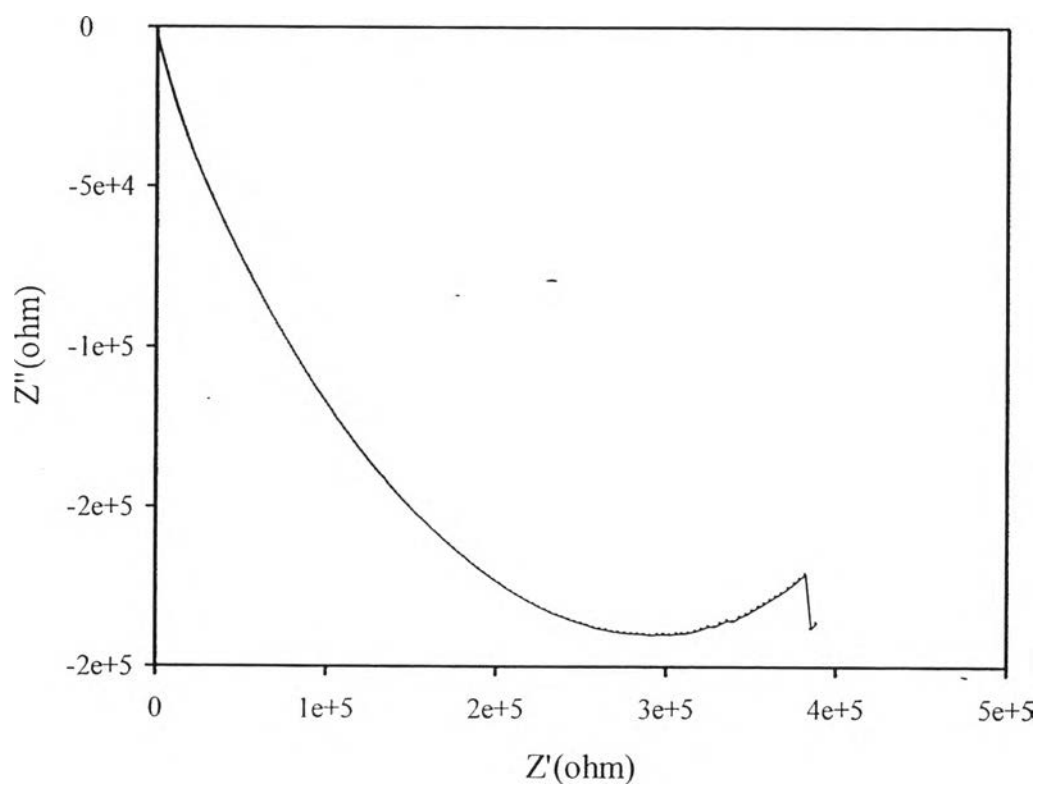


Figure G7 Nyquist plot of the SPSF DS 19.9% membrane.

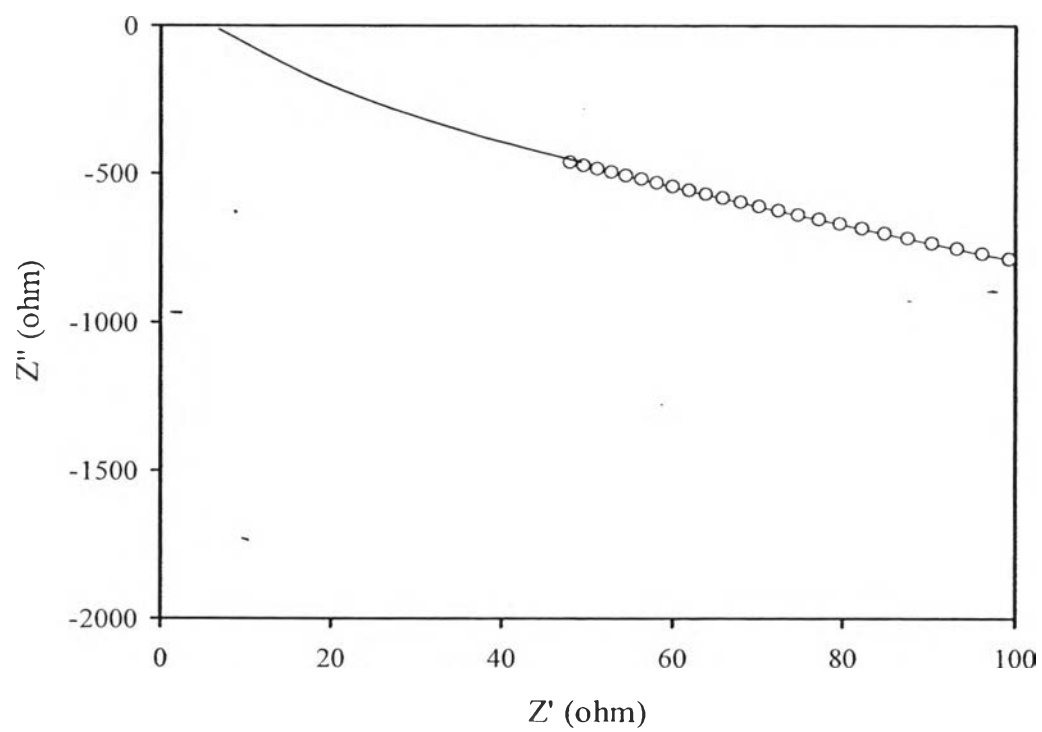


Figure G8 Enlarged Nyquist plot of the SPSF DS 19.9% membrane ($R = 6.43$ ohm).

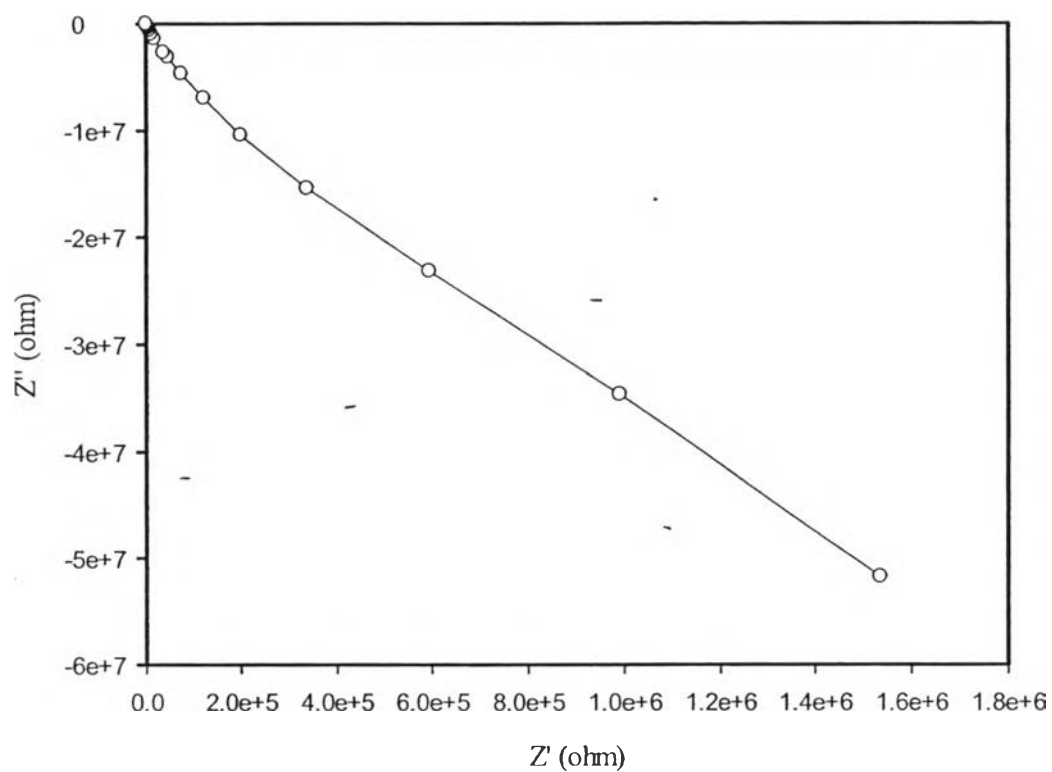


Figure G9 Nyquist plot of the SPSF DS 27.99% membrane.

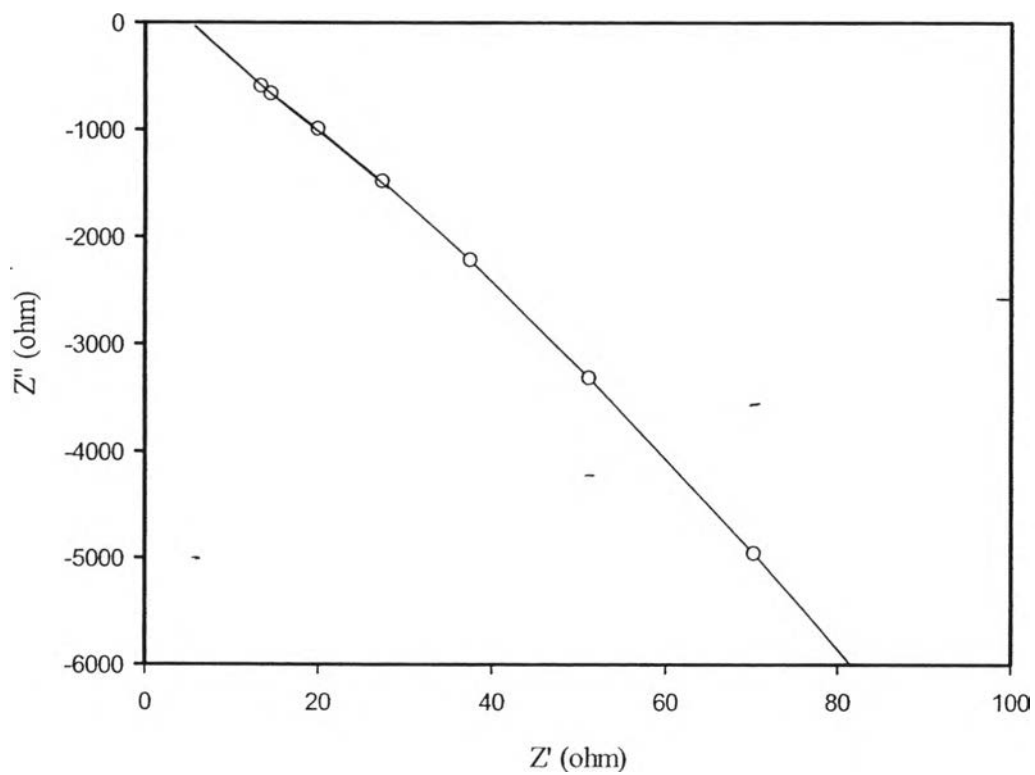


Figure G10 Enlarged Nyquist plot of the SPSF DS 27.99% membrane ($R = 6.52$ ohm).

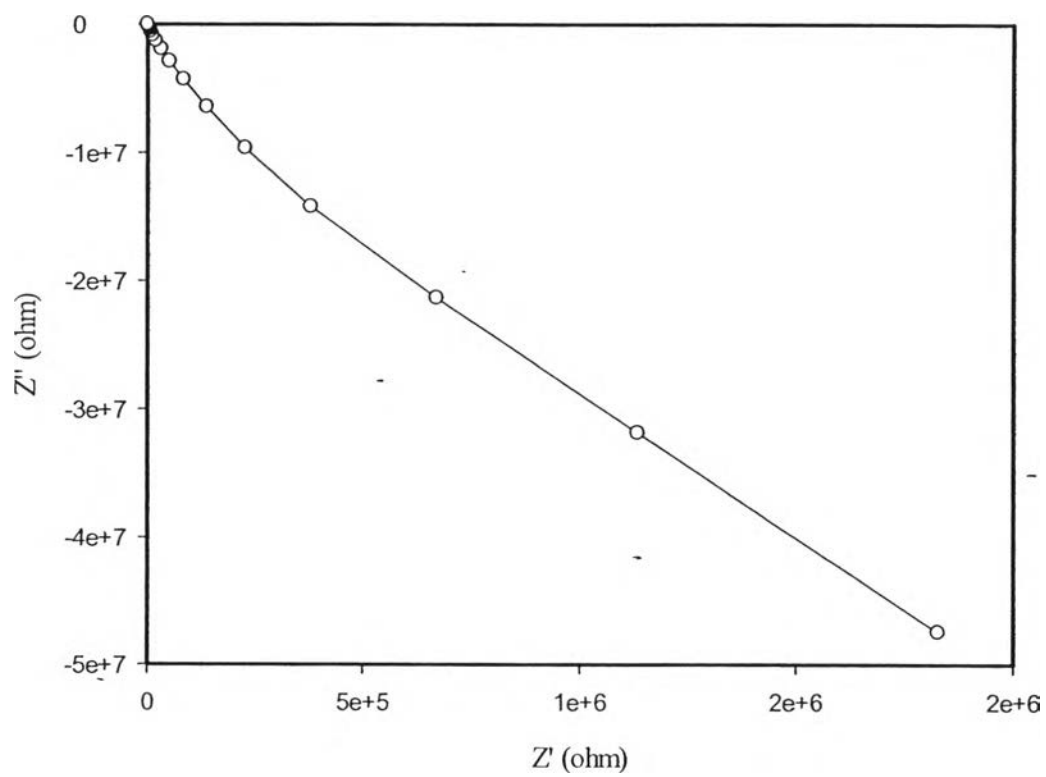


Figure G11 Nyquist plot of the SPSF DS 44.66% membrane.

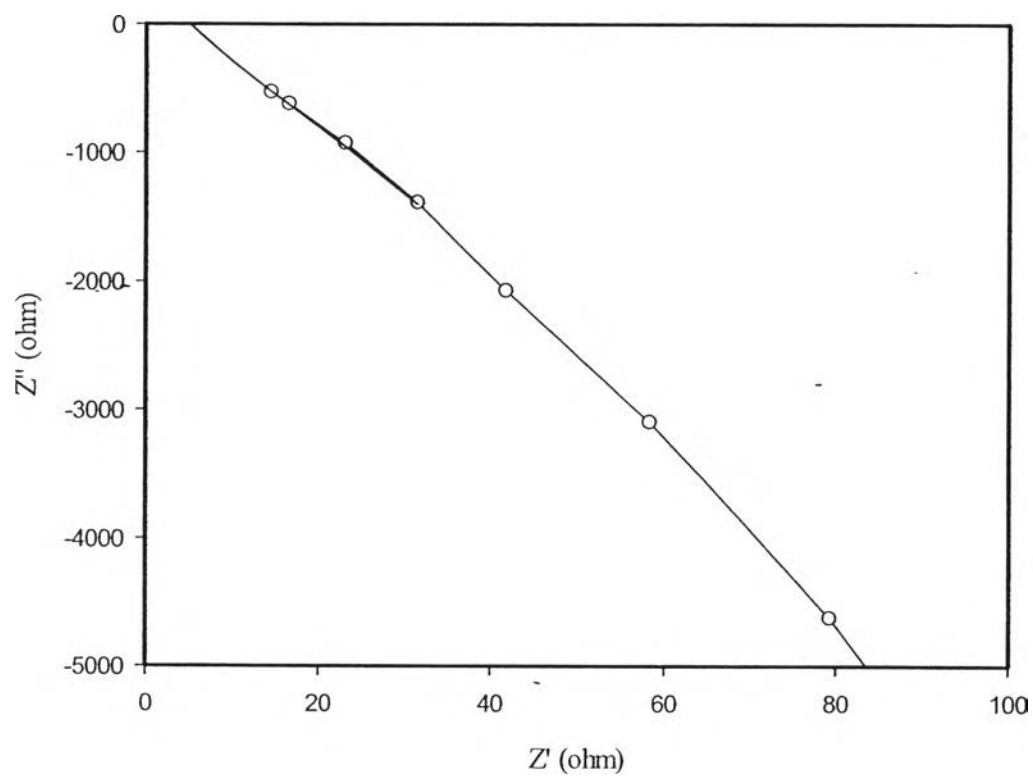


Figure G12 Enlarged Nyquist plot of the SPSF DS 44.66% membrane ($R = 5.21$ ohm).

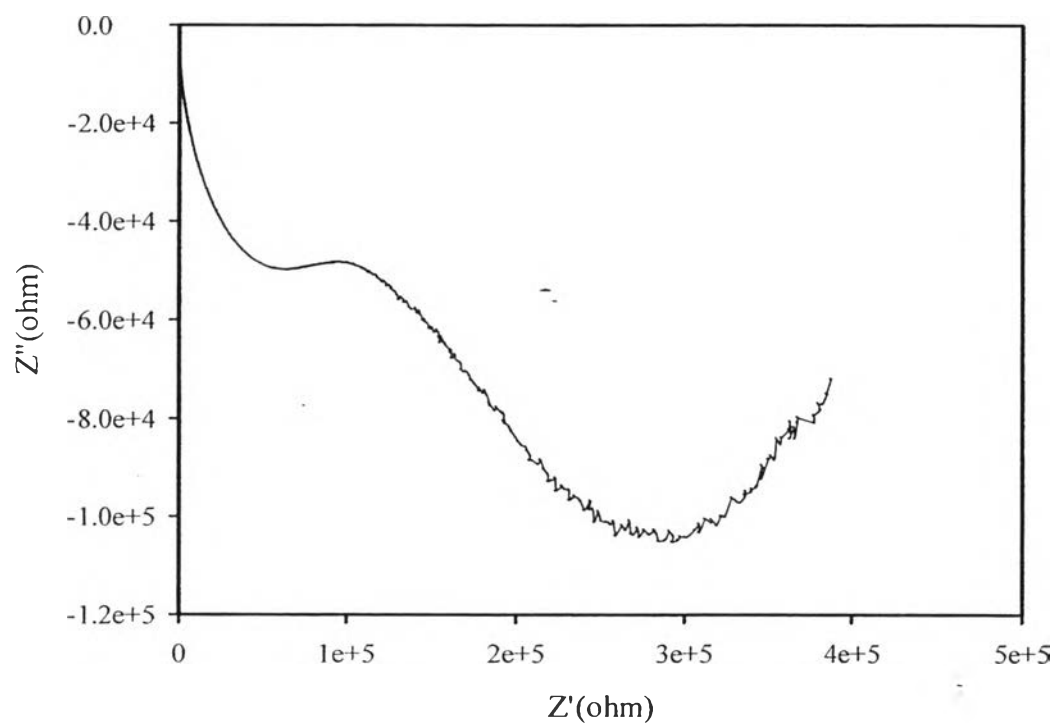


Figure G13 Nyquist plot of the SPSF DS 61.44 % membrane.

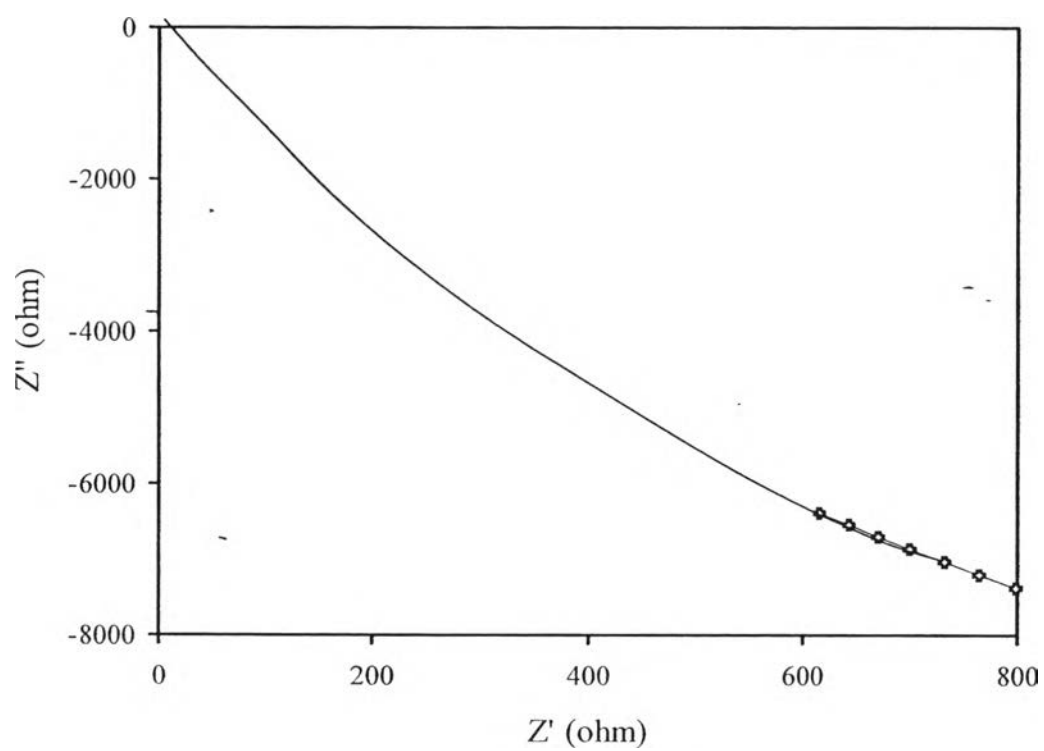


Figure G14 Enlarged Nyquist plot of the SPSF DS 61.44% membrane ($R = 5.56\text{ohm}$).

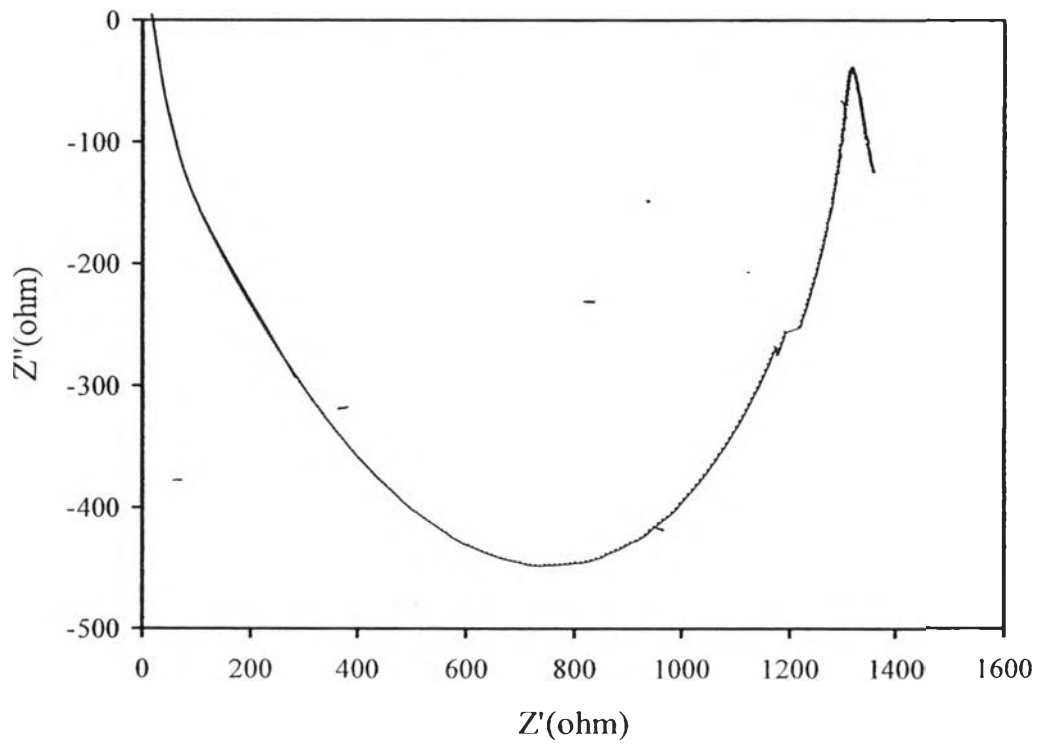


Figure G15 Nyquist plot of the SPSF DSDS 71.35% membrane.

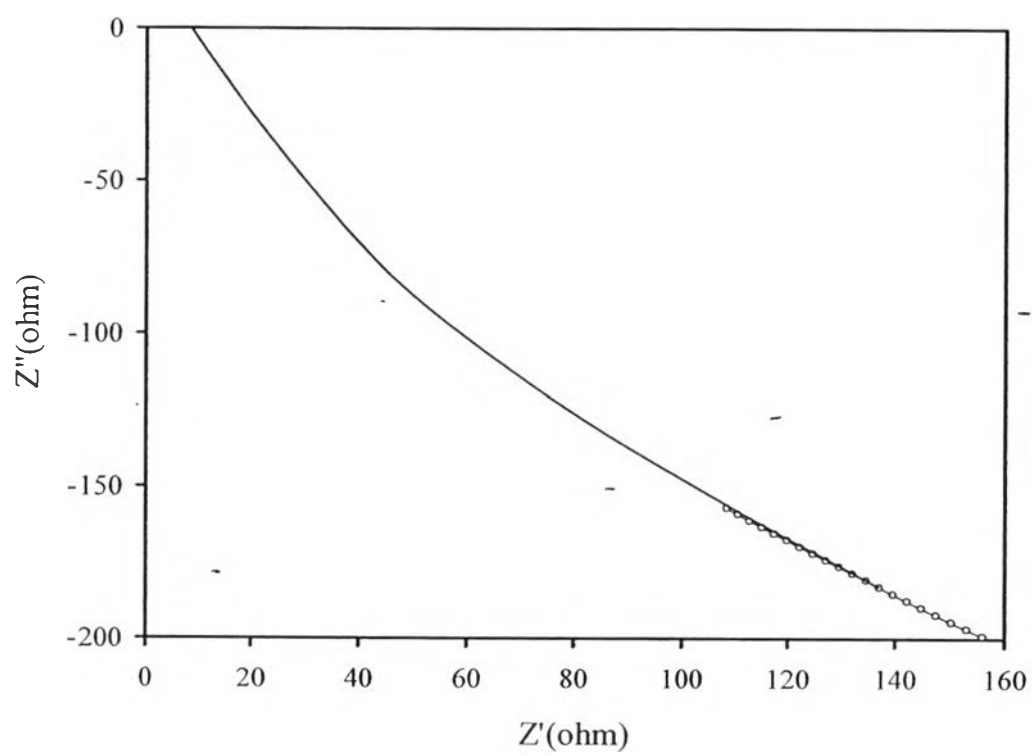


Figure G16 Enlarged Nyquist plot of the SPSF DS 71.35% membrane ($R = 4$ ohm).

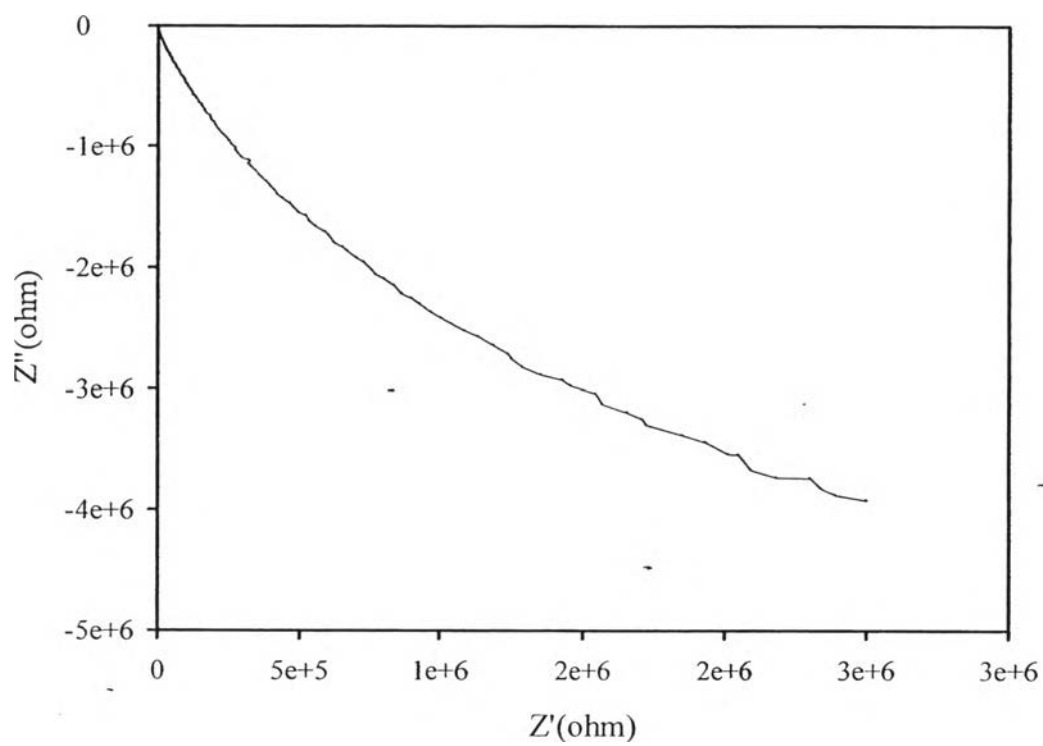


Figure G17 Nyquist plot of the SPVDF DS 12.34% membrane.

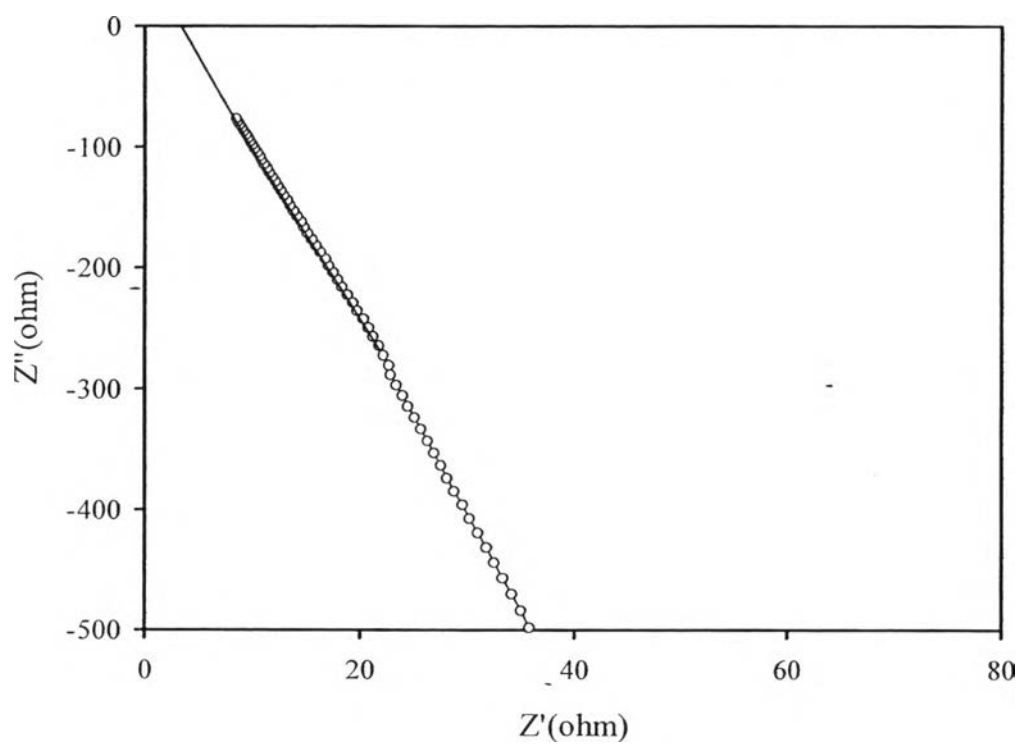


Figure G18 Enlarged Nyquist plot of the SPVDF DS 12.34% membrane ($R = 5$ ohm).

Table G1 Proton conductivity (S/cm) and water uptake under dry state at 27 °C

Polymer	Thickness (cm)	Contact area (cm²)	R (ohm)	Water uptake (%)	Proton conductivity (S/cm)
SPVDF DS 12.34%	0.0118	11.34	5.00	2.40	2.08E-04
SPSF DS 12.75%	0.0168	11.34	6.10	1.40	2.43E-04
SPSF DS 15.25%	0.0172	11.34	5.74	1.50	2.64E-04
SPSF DS 19.90%	0.0211	11.34	6.43	1.90	2.89E-04
SPSF DS 27.99%	0.0238	11.34	6.52	2.10	3.23E-04
SPSF DS 44.66%	0.0201	11.34	5.21	2.30	3.41E-04
SPSF DS61.44%	0.0281	11.34	5.56	2.30	4.46E-04
SPSF DS 71.35%	0.0246	11.34	4.00	2.40	5.42E-04
Nafion 117	0.0180	11.34	5.00	6.70	3.17E-04

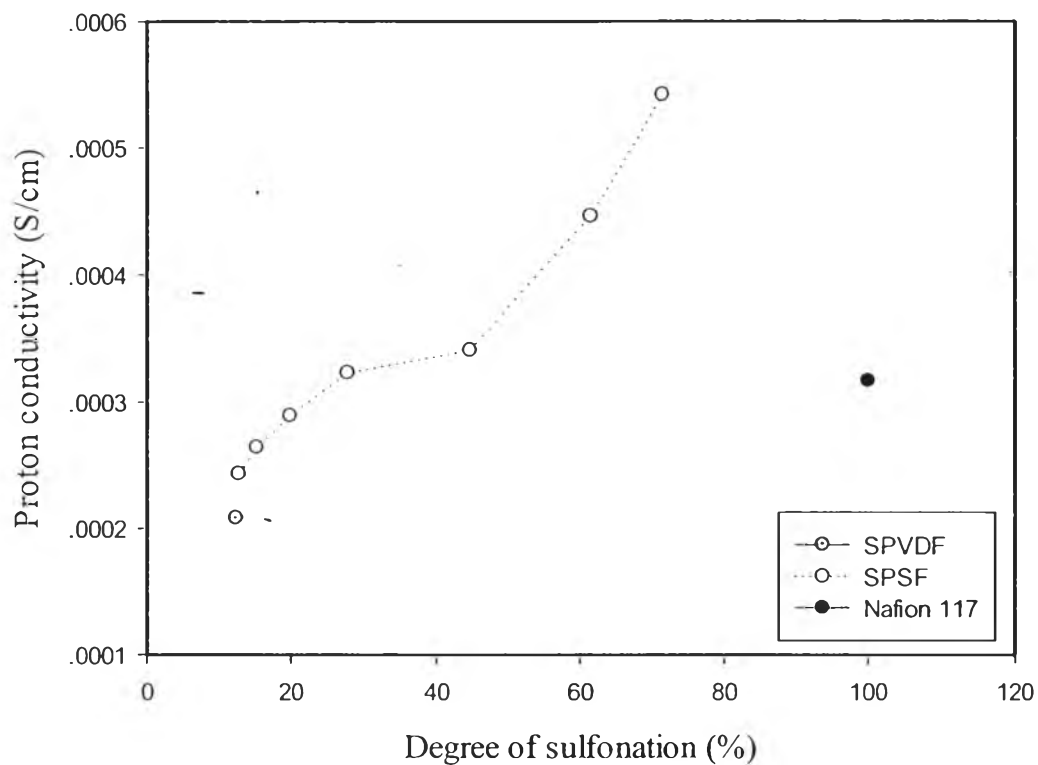


Figure G14 Proton conductivity with degree of sulfonation of SPVDF, SPSF and Nafion117 at dry state.

Appendix H Proton Conductivity under Wet State

The impedance data was measured by using an LCR meter (Agilent E4980A) at various frequencies from 100 Hz to 2 MHz and at room temperature. The membranes were cut to form $5 \times 5 \text{ cm}^2$ specimens for the measurement.

$$\sigma = \frac{d}{RS} \quad (\text{H1})$$

where d is the thickness, S is the contact area of the sample ($\pi r^2 = \pi(3.8/2)^2 = 11.34 \text{ cm}^2$), and R can be derived from the low intercept of the high frequency semi-circle on a complex impedance plane with the $\text{Re}(Z)$ axis.

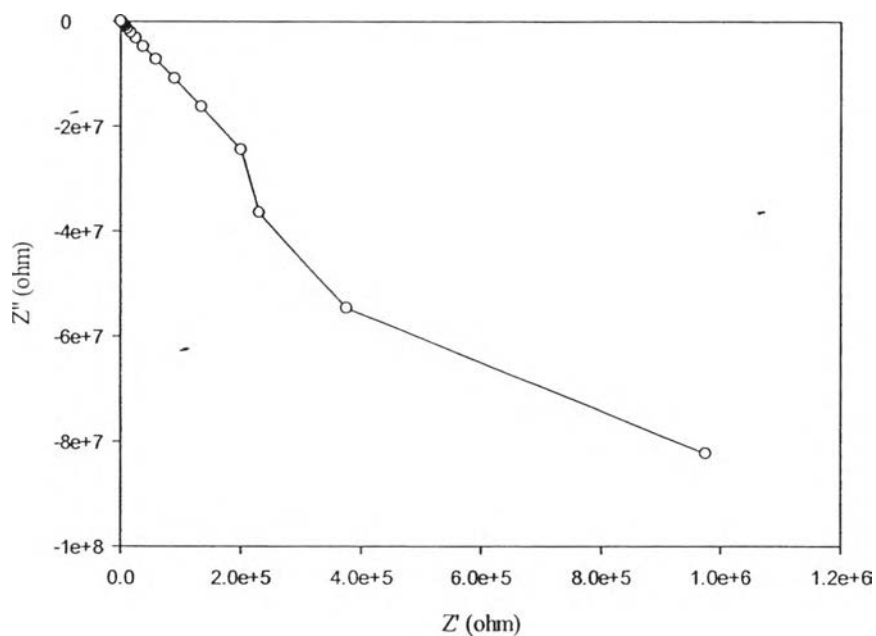


Figure H1 Proton conductivity of SPSF membrane with DS 12.75% was measured with an LCR meter (Agilent E4980A) under wet state at room temperature.

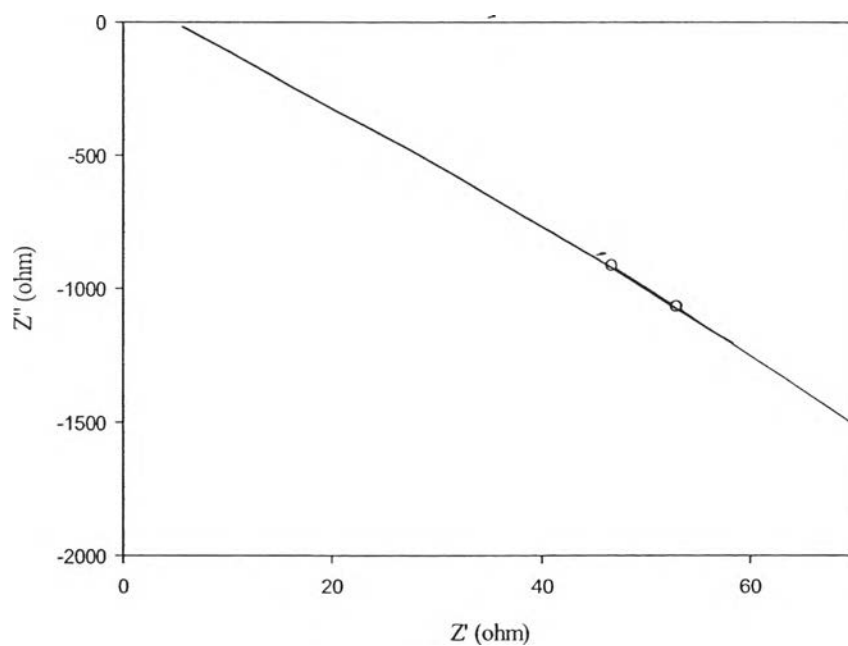
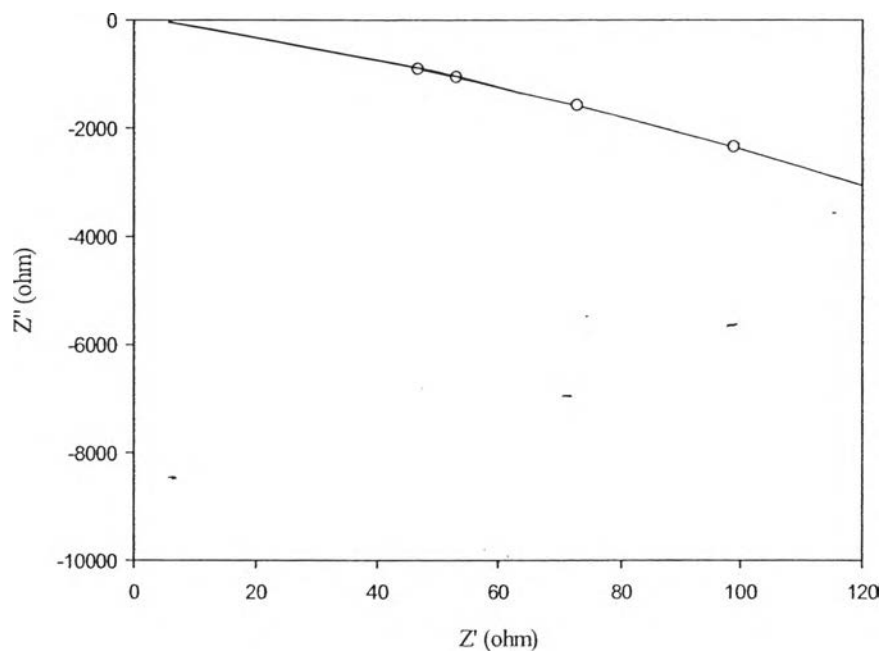


Figure H2 Blown up proton conductivity of SPSF membrane with DS 12.75% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

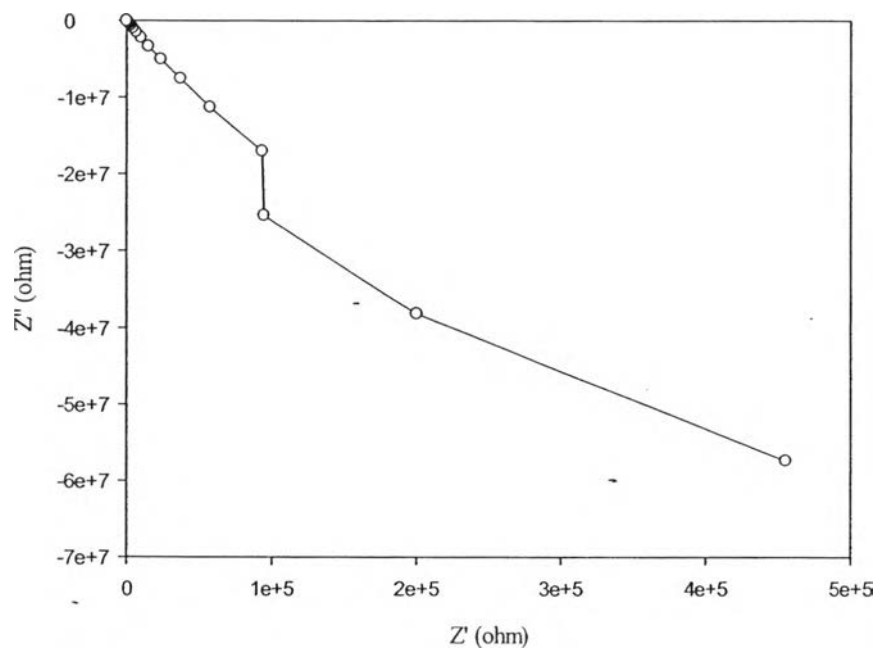


Figure H3 Proton conductivity of SPSF membrane with DS 15.65% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

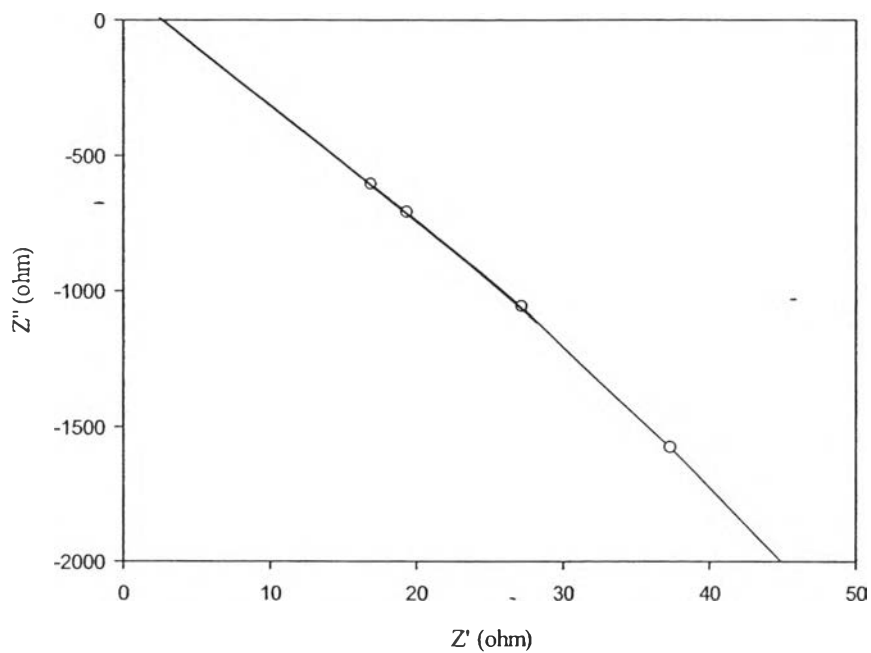


Figure H4 Blown up proton conductivity of SPSF membrane with DS 15.65% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

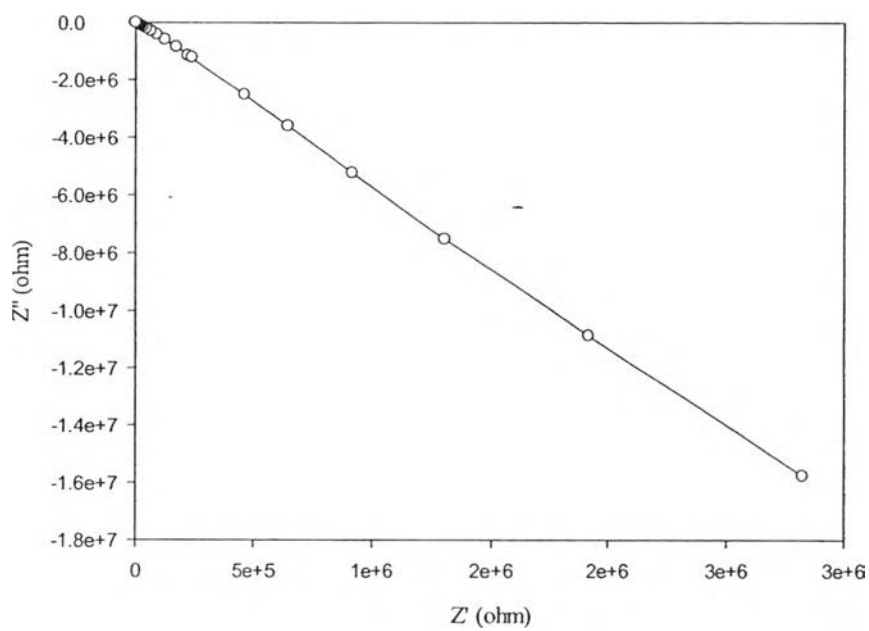


Figure H5 Proton conductivity of SPSF membrane with DS 19.9% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

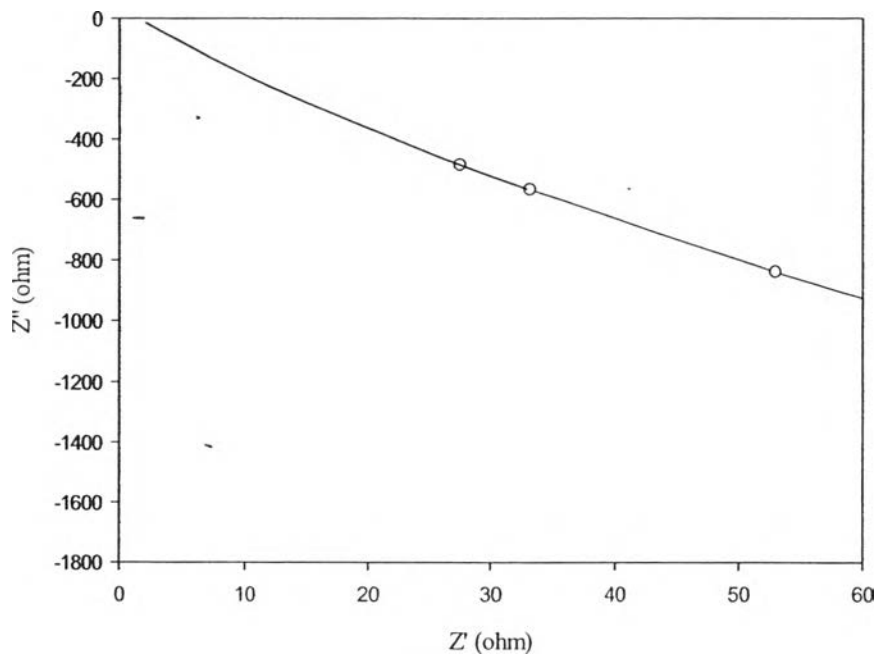


Figure H6 Blown up proton conductivity of SPSF membrane with DS 19.9% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

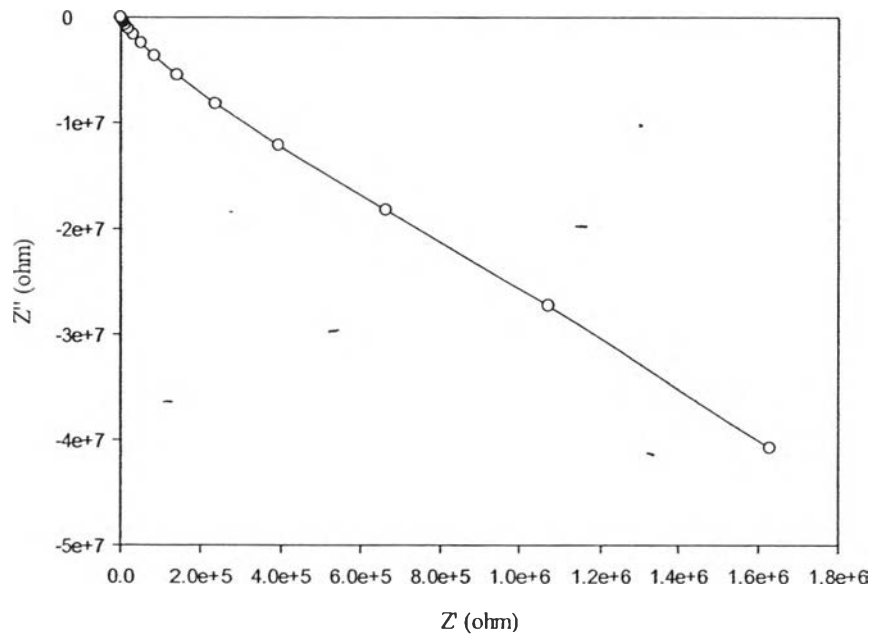


Figure H7 Proton conductivity of SPSF membrane with DS 27.99% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

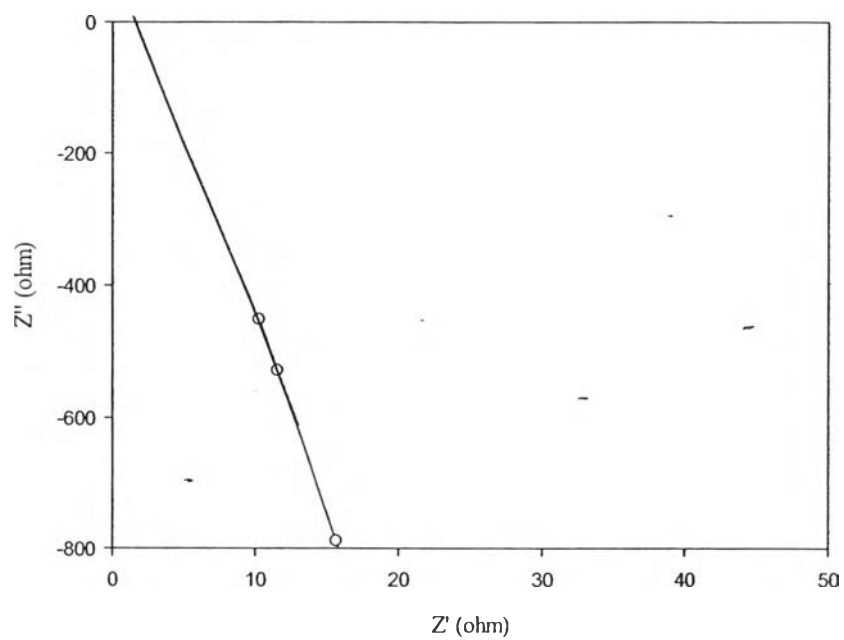


Figure H8 Blow up proton conductivity of SPSF membrane with DS 27.99% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

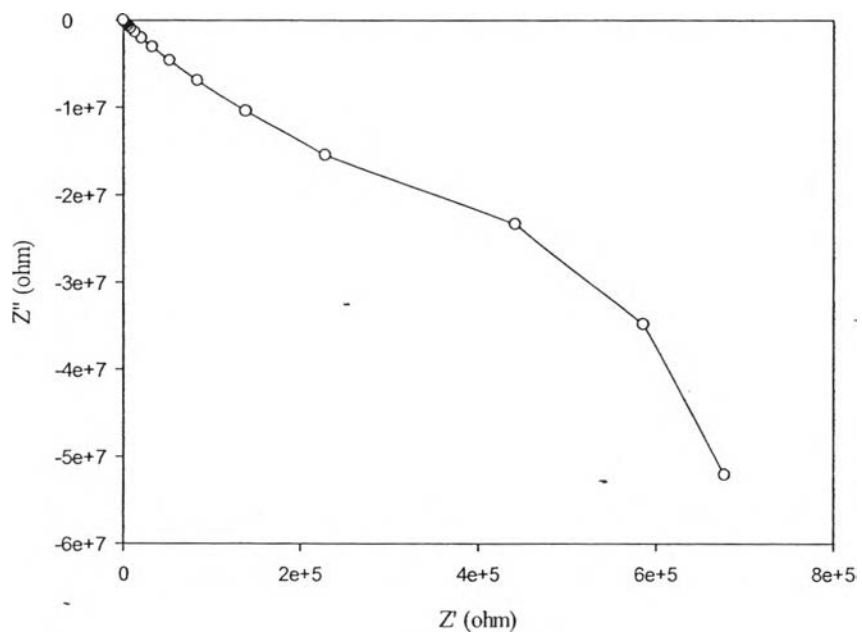


Figure H9 Proton conductivity of SPSF membrane with DS 44.66% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

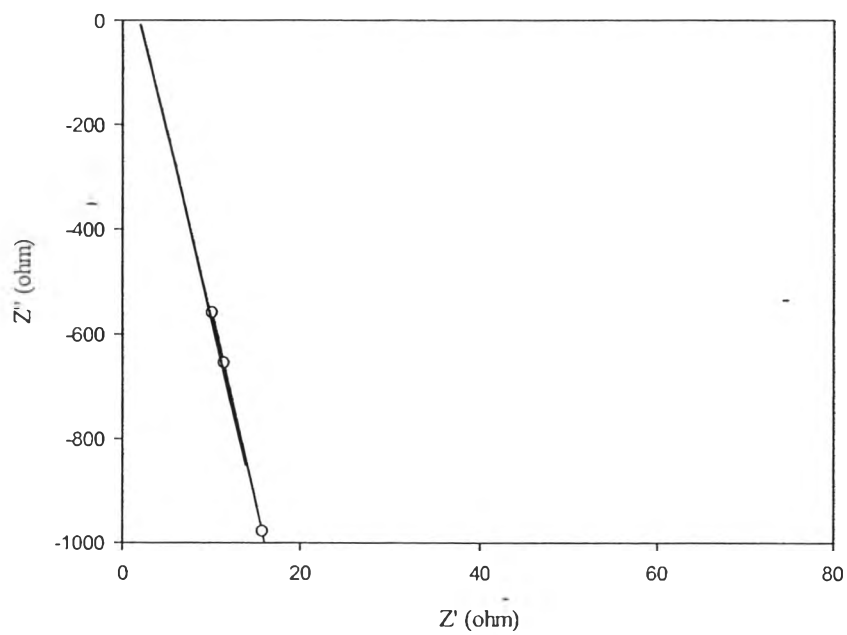


Figure H10 Blow up proton conductivity of SPSF membrane with DS 44.66% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

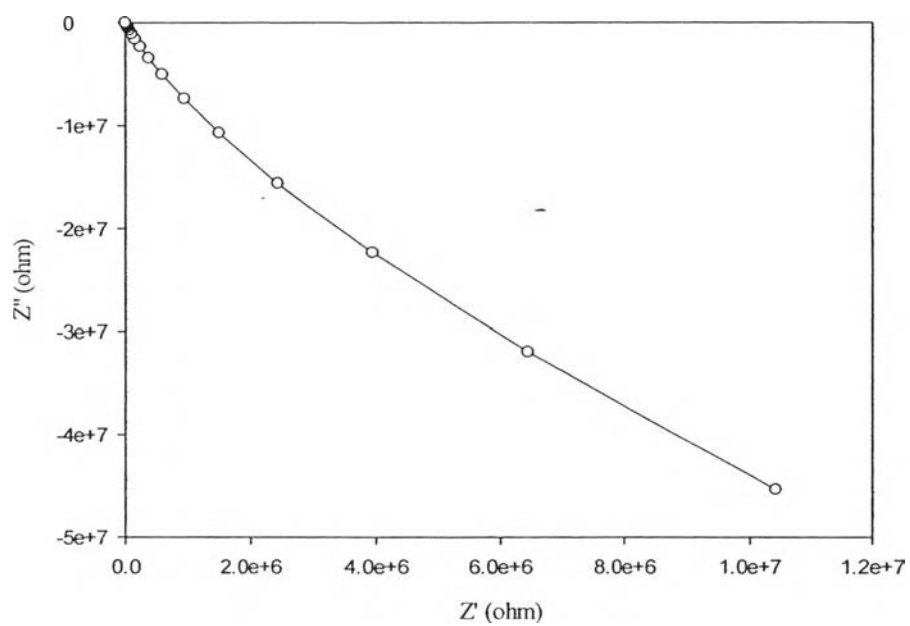


Figure H11 Proton conductivity of SPSF membrane with DS 61.44% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

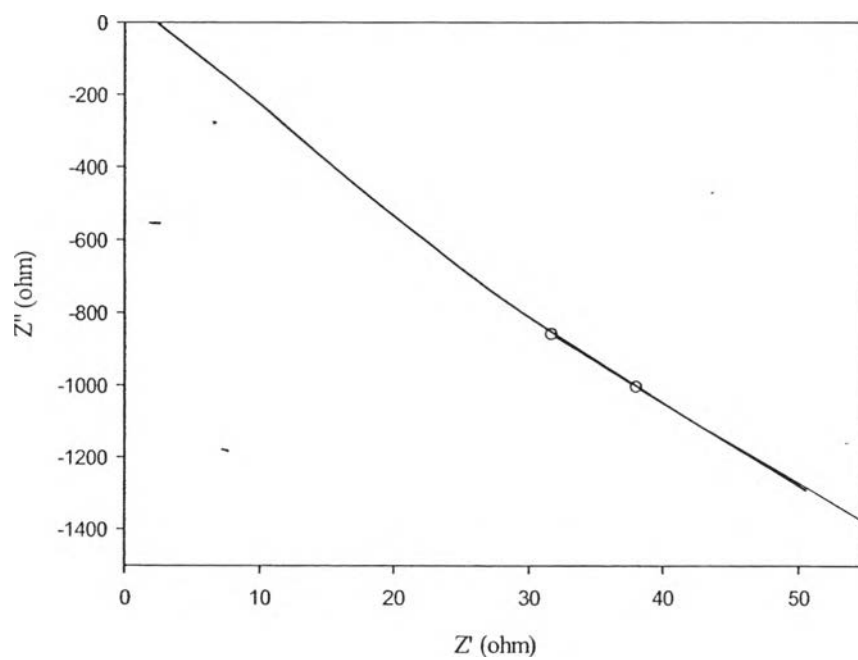


Figure H12 Blown up proton conductivity of SPSF membrane with DS 61.44% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

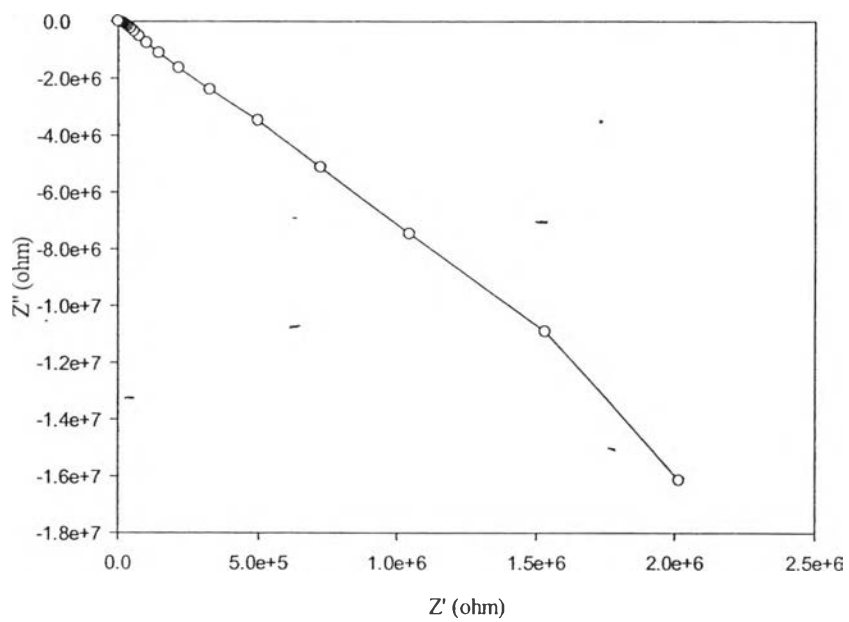


Figure H13 Proton conductivity of SPSF membrane with DS 71.55% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

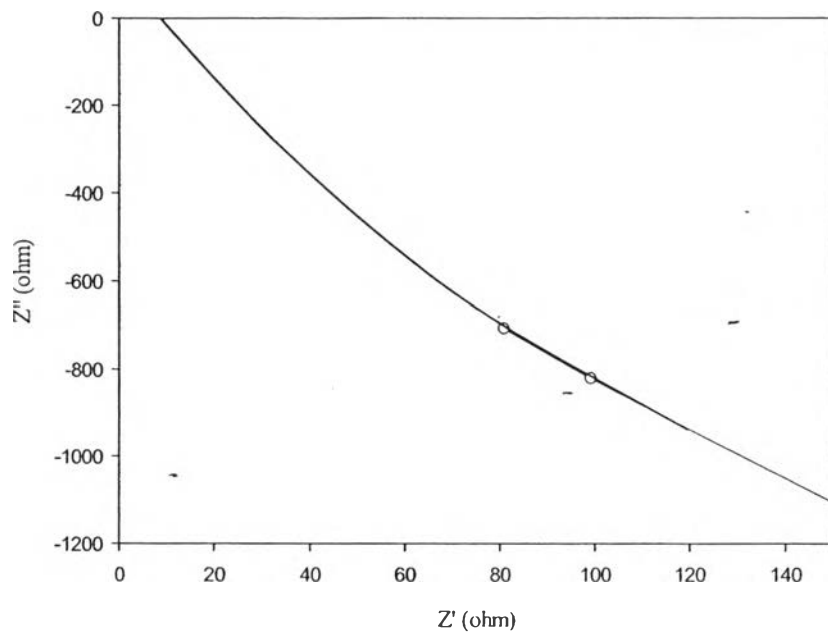


Figure H14 Blown up proton conductivity of SPSF membrane with DS 71.55% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

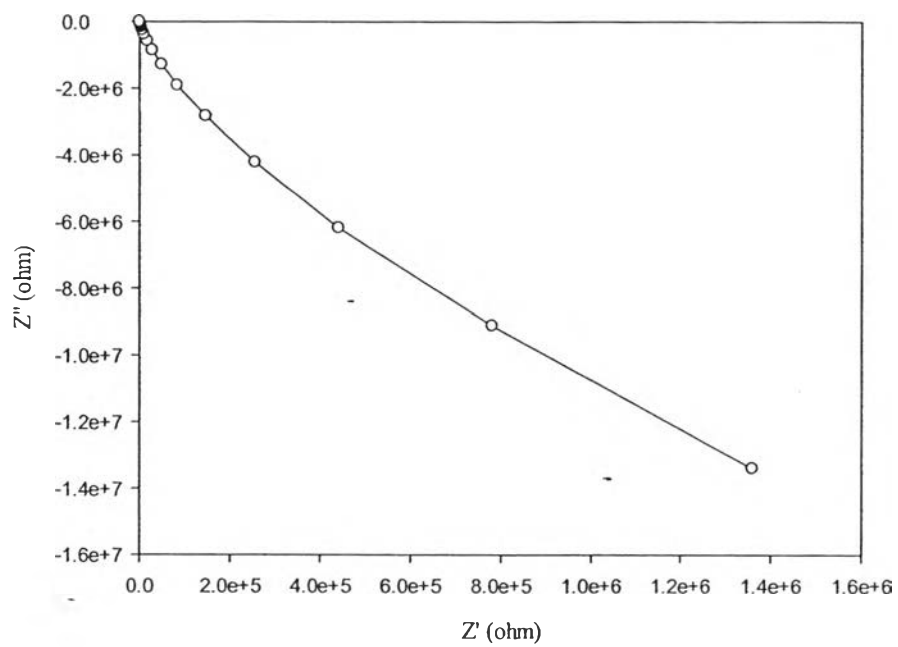


Figure H15 Proton conductivity of SPVDF membrane with DS 12.34% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

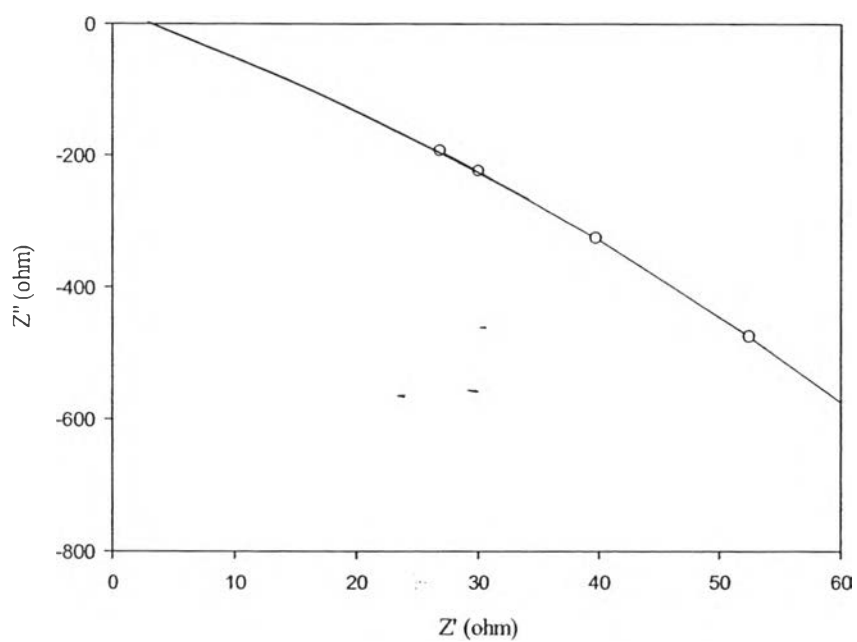
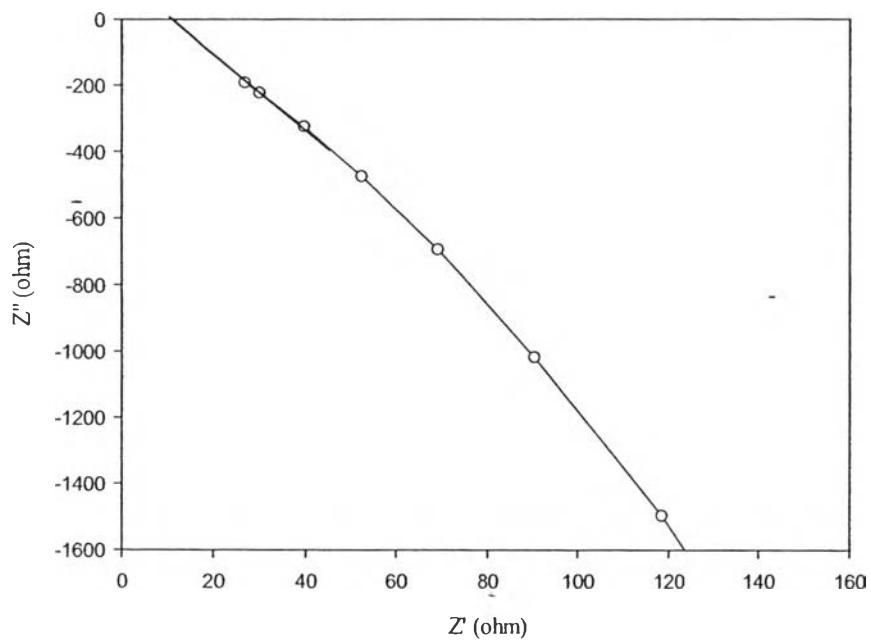


Figure H16 Blown up proton conductivity of SPVDF membrane with DS 12.34% was measured with LCR meter (Agilent E4980A) under wet state at room temperature.

Table H1 Proton conductivity (S/cm) and water uptake under wet state at room temperature

Polymer	Thickness (cm)	Contact area (cm ²)	R (ohm)	Water uptake (%)	Proton conductivity (S/cm)
SPVDF DS 12.34%	0.0118	11.34	4.98	2.78	2.09E-04
SPSF DS 12.75%	0.0168	11.34	3.22	2.16	4.60E-04
SPSF DS 15.25%	0.0172	11.34	2.86	3.54	5.30E-04
SPSF DS 19.9%	0.0211	11.34	2.50	4.03	7.44E-04
SPSF DS 27.99%	0.0238	11.34	2.74	4.33	7.66E-04
SPSF DS 44.66%	0.0201	11.34	2.26	4.82	7.84E-04
SPSF DS 61.44%	0.0281	11.34	2.69	6.85	9.21E-04
SPSF DS 71.55%	0.0246	11.34	2.22	9.01	9.77E-04
Nafion 117	0.0193	11.34	0.59	16.30	2.88E-04

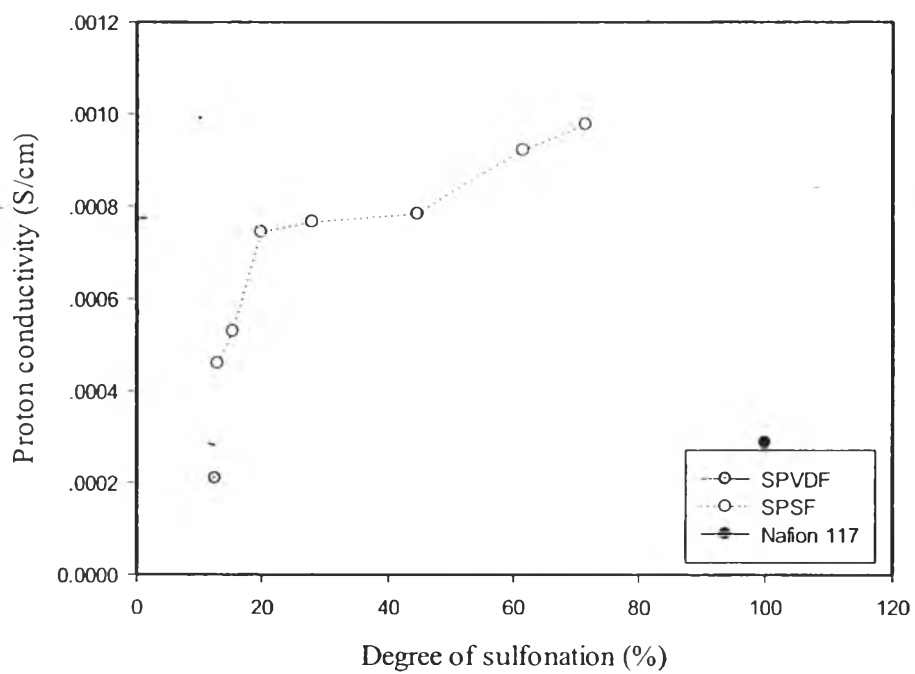


Figure H17 Proton conductivity with degree of sulfonation of SPVDF, SPSF and Nafion117 at wet state.

Appendix I Methanol Permeability

The methanol permeability shows the amount of methanol that permeates through the membrane. The permeation cell for the methanol permeability measurement consisted of chamber A and chamber B separated by a sulfonated polymer membrane. Chamber A was filled with a 250 ml 2.5 M methanol solution. Chamber B was filled with 250 ml DI water. The membrane was placed between the chamber A and chamber B. The methanol permeability was determined by the following Eq (11):

$$P \text{ (cm}^2\text{/s)} = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \quad (11)$$

where P = the methanol permeability, C_A = the methanol concentrations in the compartment A, C_B = the methanol concentrations in the compartment B, A = the area of a membrane, L = the thickness of a membrane, V_B = the volume of the solution in the compartment B, and k_B = the slope of the methanol concentration.

The methanol concentrations were determined by using gas chromatography (GC) with thermal conductivity detector (TCD); ethanol was used as the internal standard:

Calibration procedure

- The syringe was cleaned before sampling with DI water.
- Methanol solutions were prepared at various concentrations (0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 M). Methanol solution was pumped by a syringe about 0.05 ml and deposited in a bottle.
- Methanol permeability was calculated by TCD GC with a 1M 0.05ml ethanol solution as an internal standard.
- The calibration curve was established by plotting C_B with the peak ratio of MeOH/EtOH.

Measurement procedure

- The syringe was cleaned before sampling with DI water.
- Components A and B were pumped by a syringe about 0.05 ml and deposited in a bottle.
- Methanol permeability was calculated by TCD GC with 1M 0.05ml ethanol solution as an internal standard.
- The methanol concentration in component B (C_B) was determined by comparing the peak ratio of methanol/ethanol to calibration curve.

Table II Retention time composites

Sample	Retention time (min)
Water	2.65
Methanol	5.05
Ethanol	8.07

Table I2 Calibration concentration

Concentration (M)	Sampling (0.05ml)		Internal standard (0.05ml)	
	MeOH contained (ml)	Water contained (ml)	EtOH contained (ml)	Water contained (ml)
3.0000	0.0061	0.0439	0.0029	0.0471
2.5000	0.0051	0.0449	0.0029	0.0471
2.0000	0.0041	0.0459	0.0029	0.0471
1.5000	0.0030	0.0470	0.0029	0.0471
1.0000	0.0020	0.0480	0.0029	0.0471
0.5000	0.0010	0.0490	0.0029	0.0471
0.1000	0.0002	0.0498	0.0029	0.0471
0.0500	0.0001	0.0499	0.0029	0.0471
0.0010	0.0000	0.0500	0.0029	0.0471

Table I3 Calibration concentration of methanol

MeOH concentration (M)	Type of media	%Area	MeOH/EtOH
3.00	Water	90.21	2.19
	Methanol	6.72	
	Ethanol	3.07	
2.00	Water	92.05	1.73
	Methanol	5.89	
	Ethanol	2.06	
1.50	Water	92.94	1.25
	Methanol	3.92	
	Ethanol	3.13	
1.00	Water	95.34	0.79

	Methanol	2.05	
	Ethanol	2.6	
0.50	Water	95.81	0.51
	Methanol	1.42	
	Ethanol	2.77	
0.10	Water	97.01	*
	Methanol		
	Ethanol	2.9	
0.05	Water	97.83	*
	Methanol		
	Ethanol	2.17	
0.01	Water	97.67	*
	Methanol		
	Ethanol	2.33	

*Methanol did not permeate across the membrane.

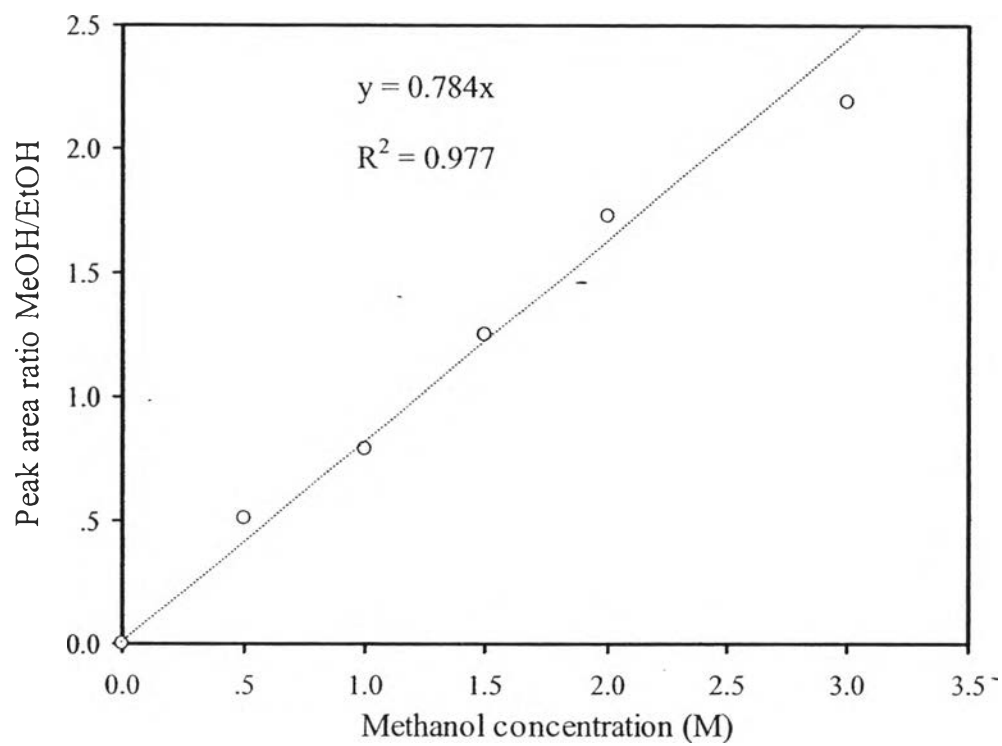


Figure 11 Calibration curve of methanol concentration versus the ratio of methanol and ethanol.

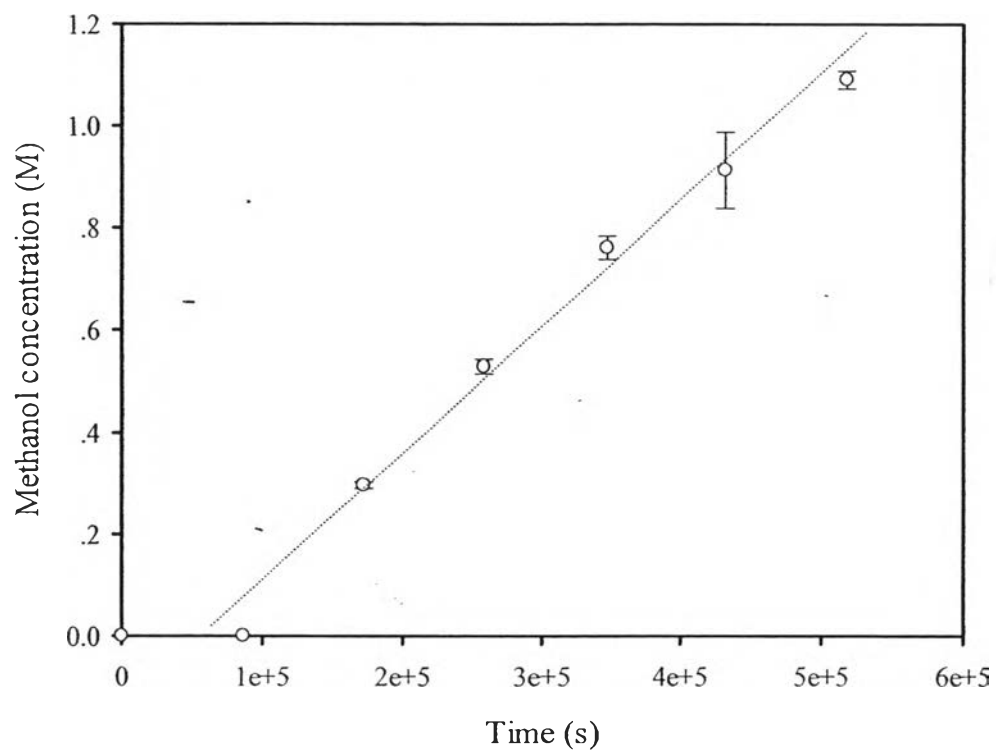


Figure I2 Methanol concentration in chamber B versus time at 70°C of Nafion 117.

$$y = 2E-06x - 0.003$$

- Delay time = Methanol did not permeate in this period of time.
- Delay time of Nafion 117 membrane was 259200 seconds.

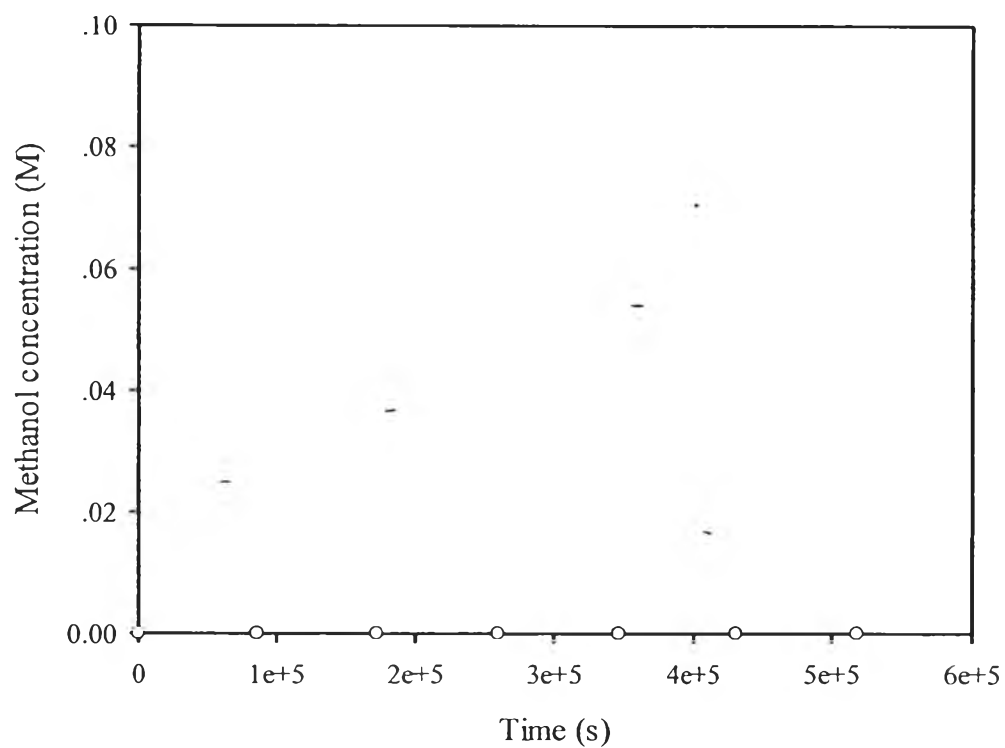


Figure I3 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 12.75%.

- Methanol solution did not permeate through SPSF of DS 12.75%.

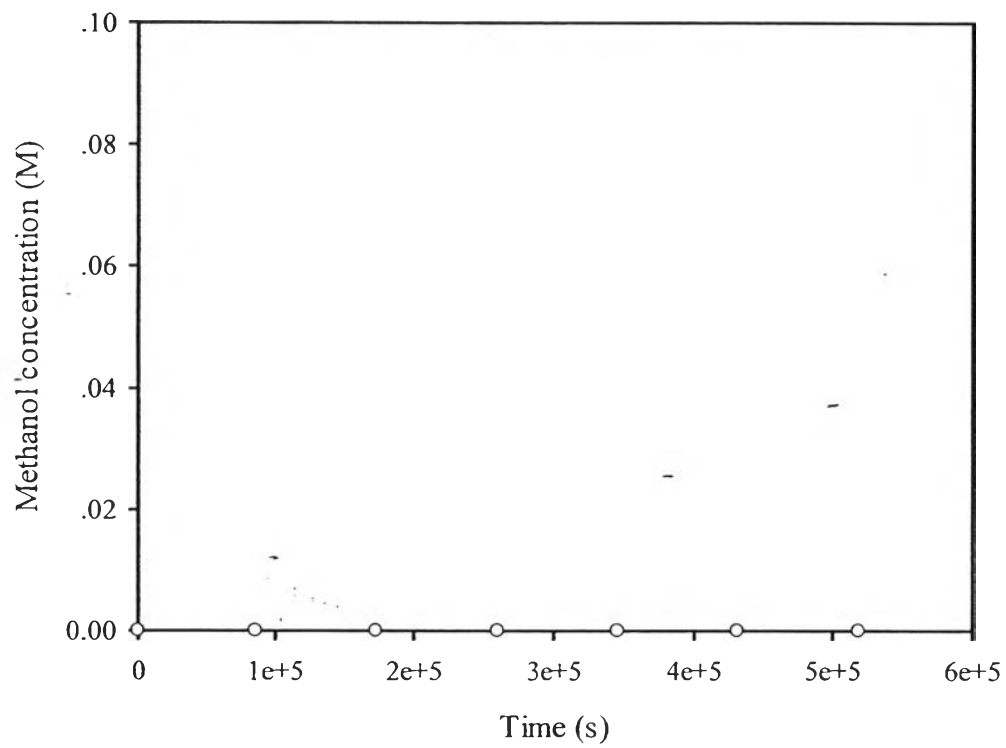


Figure I4 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 15.65%.

- Methanol solution did not permeate through SPSF of DS 15.65%.

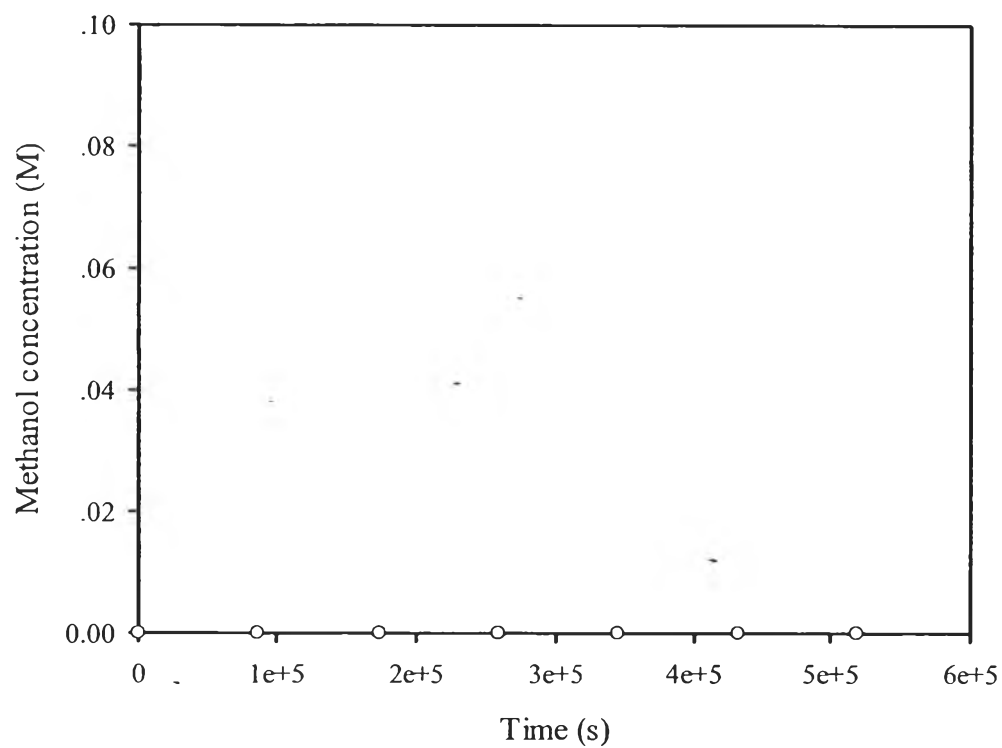


Figure I5 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 19.90%.

- Methanol solution did not permeate through SPSF of DS 19.90%.

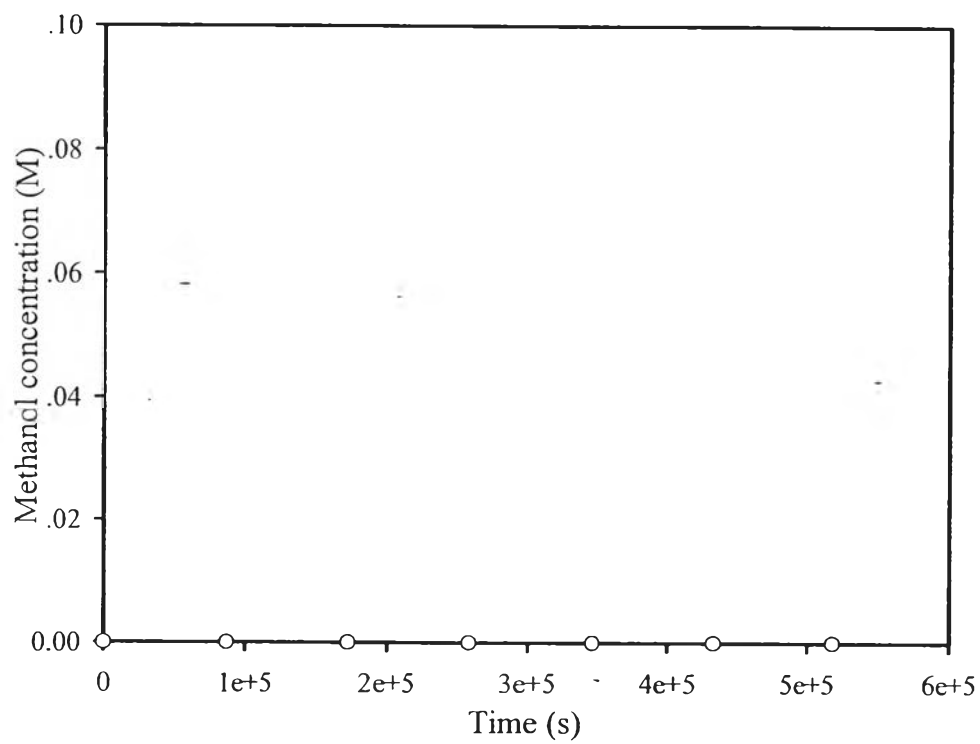


Figure I6 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 27.99%.

- Methanol solution did not permeate through SPSF of DS 27.99%.

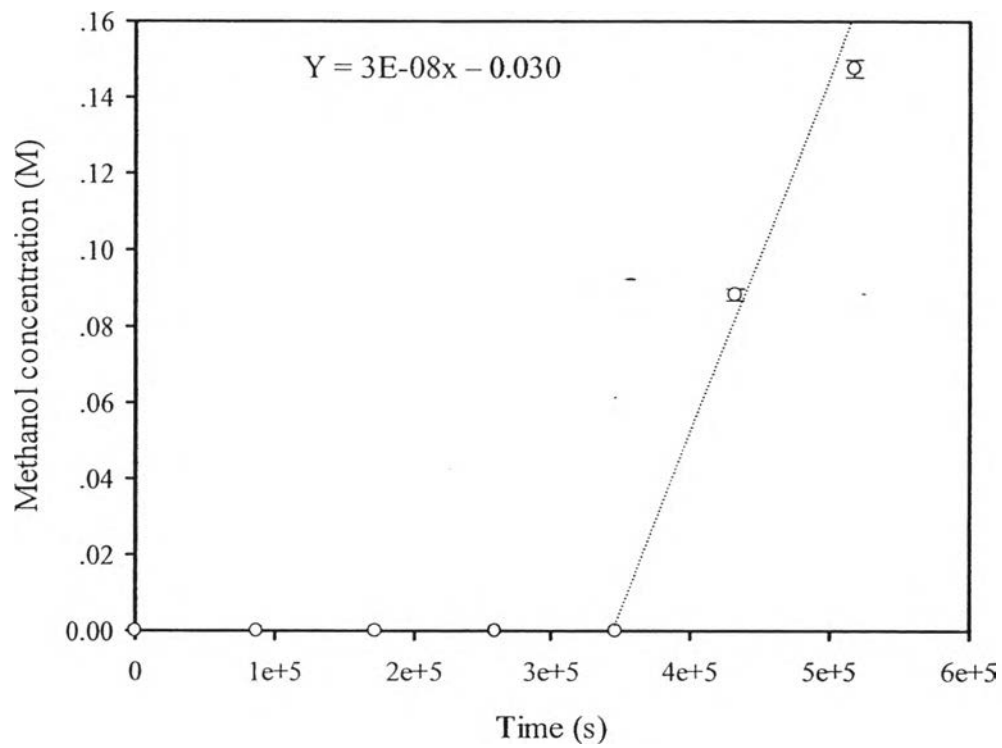


Figure I7 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 44.66%.

- Delay time of SPSF (DS 44.66%) membrane was 345600 seconds.

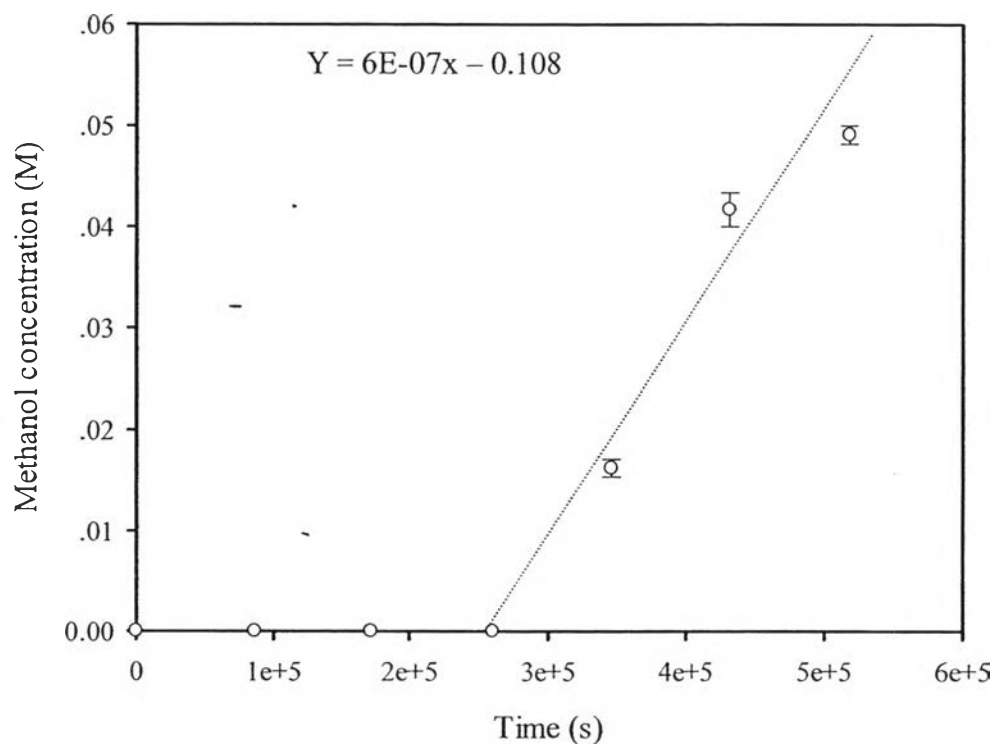


Figure I8 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 61.4%.

- Delay time of SPSF (DS 61.4%) membrane was 259200 seconds.

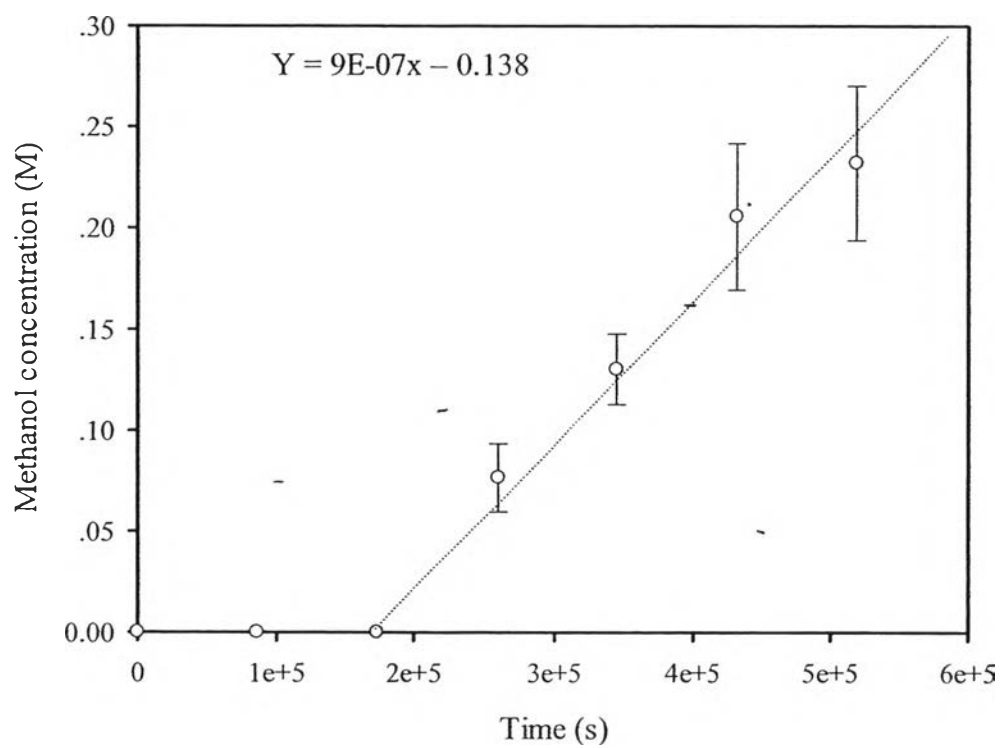


Figure I9 Methanol concentration in chamber B versus time at 70 °C of SPSF at DS 71.5%.

- Delay time of SPSF (DS 71.5%) membrane was 259200 seconds

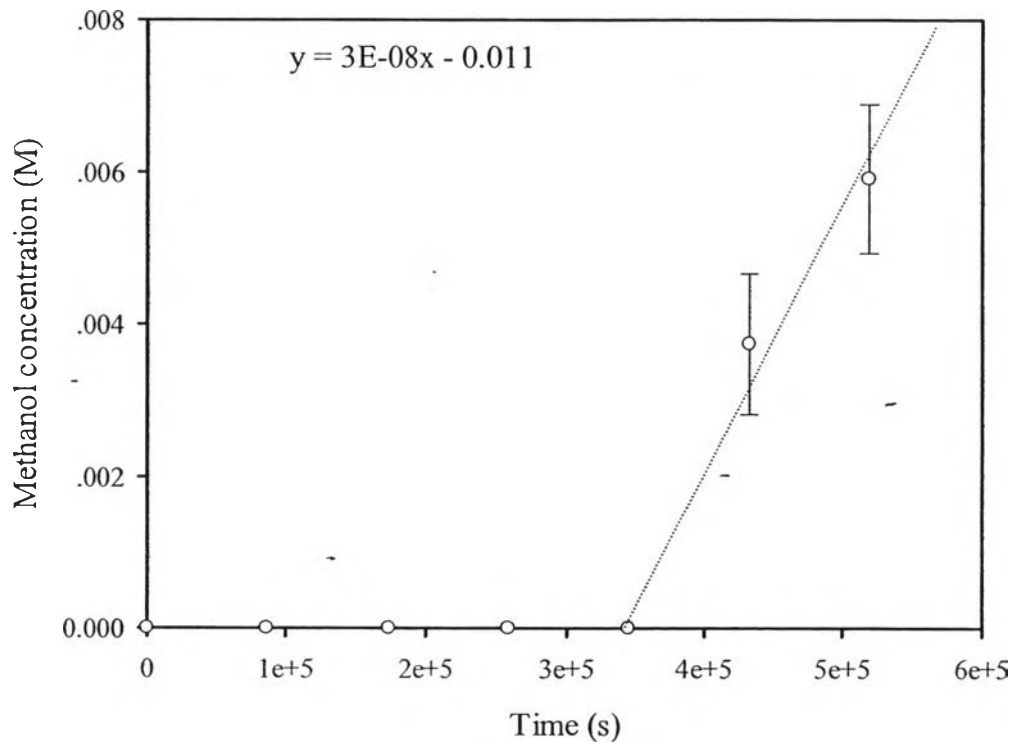


Figure 110 Methanol concentration in chamber B versus time at 70 °C of SPVDF at DS 12.34%.

- Delay time of SPVDF (DS 12.34%) membrane was 432000 seconds

Table I4 Methanol concentration in chamber B at 70 °C of SPSF (DS 12.75%) and SPSF (DS 15.65%) at various times

Time (s)	Methanol concentration (mol/l) in compartment A (C_A) and compartment B (C_B) at 70 °C			
	SPSF 12.75%		SPSF 15.65%	
	C_A (M)	C_A (M)	C_B (M)	C_B (M)
0	2.039	0	2.013	0
86400	2.092	0	2.005	0
172800	2.060	0	1.996	0
259200	2.008	0	1.998	0
345600	1.990	0	2.003	0
432000	1.971	0	1.960	0
518400	1.986	0	2.013	0

Table I5 Methanol concentration in chamber B at 70 °C of SPSF (DS 19.90%) and SPSF (DS 27.99%) at various times

Time (s)	Methanol concentration (mol/l) in compartment A (C_A) and compartment B (C_B) at 70 °C			
	SPSF 19.90%		SPSF 27.99%	
	$C_A(M)$	$C_A(M)$	$C_B (M)$	$C_B(M)$
0	2.013	0	2.013	0
86400	2.023	0	2.023	0
172800	1.996	0	1.996	0
259200	1.976	0	1.976	0
345600	1.974	0	1.974	0
432000	1.921	0	1.921	0
518400	1.837	0	1.837	0

Table I6 Methanol concentration in chamber B at 70 °C of SPSF (DS 44.66%) and SPSF (DS 61.44%) at various times

Time (s)	Methanol concentration (mol/l) in compartment A (C_A) and compartment B (C_B) at 70 °C			
	SPSF 44.66%		SPSF 61.44%	
	C_A (M)	C_A (M)	C_B (M)	C_B (M)
0	2.013	0	2.013	0
86400	2.023	0	2.023	0
172800	1.996	0	1.996	0
259200	1.976	0	1.976	0.063
345600	1.974	0	1.974	0.053
432000	1.921	0.088	1.921	0.207
518400	1.837	0.148	1.837	0.192

Table I7 Methanol concentration in chamber B at 70 °C of SPSF (DS 71.5%) and Nafion 117 at various times

Time (s)	Methanol concentration (mol/l) in compartment A (C_A) and compartment B (C_B) at 70 °C			
	SPSF 71.5%		Nafion 117	
	C_A (M)	C_B (M)	C_A (M)	C_B (M)
0	2.163	0	2.028	0.000
86400	1.793	0	2.014	0.000
172800	1.918	0	1.985	0.297
259200	2.146	0.098	1.182	0.529
345600	1.408	0.166	1.176	0.761
432000	1.850	0.262	1.064	0.913
518400	1.390	0.296	1.033	1.025

Table I8 Methanol concentration in chamber B at 70 °C of SPVDF (DS 12.34%) at various times

Time (s)	Methanol concentration (mol/l) in compartment A (C_A) and compartment B (C_B) at 70 °C of SPVDF 12.34%	
	C_A (M)	C_B (M)
0	2.121	0
86400	2.140	0
172800	2.125	0
259200	2.046	0
345600	2.016	0
432000	2.038	0.004
518400	2.012	0.006

Table I9 Methanol permeability (cm^2/s) of sulfonated membranes

Sample	Methanol permeability (cm^2/s)	Permeated Temperature ($^{\circ}\text{C}$)	Membrane thickness (cm)
Nafion 117	3.08E-05	70	0.0178
SPVDF 12.34%	5.23E-10	70	0.0152
SPSF 12.75%	0	70	0.0249
SPSF 15.65%	0	70	0.0181
SPSF 19.90%	0	70	0.0271
SPSF 27.95%	0	70	0.0293
SPSF 44.66%	3.75E-09	70	0.0302
SPSF 61.44%	4.53E-08	70	0.0178
SPSF 71.35%	9.59E-08	70	0.0169

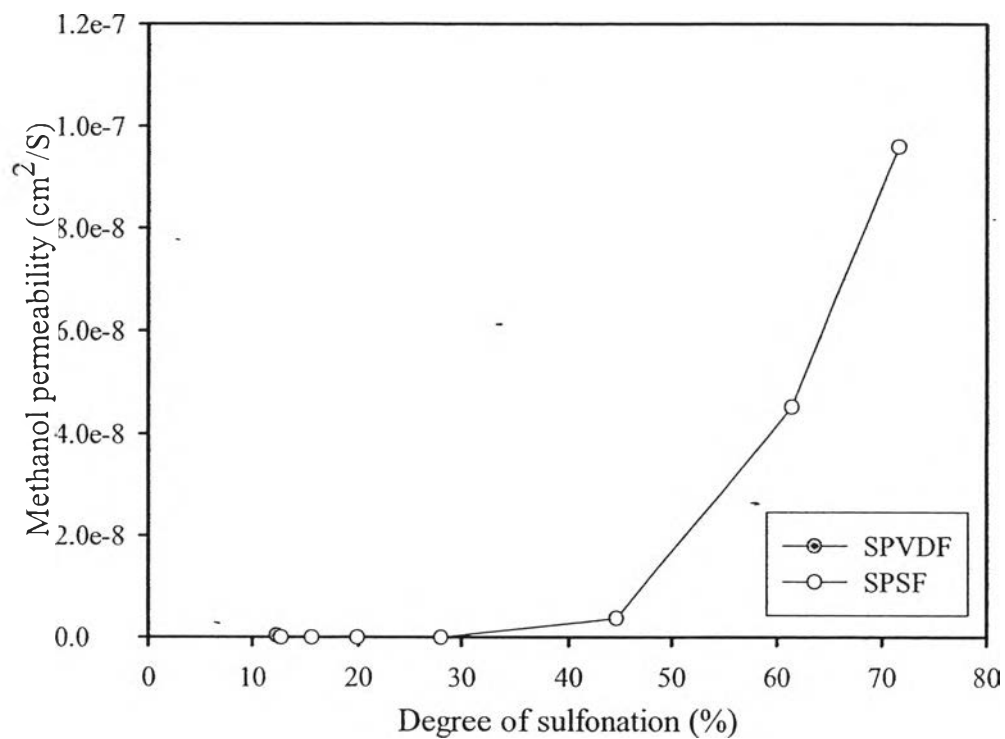


Figure I11 Methanol permeability at 70 °C of S-PSF and S-PVDF.

Appendix J Mechanical Properties

The mechanical properties: tensile strength, yield strain, and young's modulus, were recorded using a universal testing machine (Lloyd, model SMT2-500N) at room temperature with $25 \text{ mm}\cdot\text{min}^{-1}$ speed. The membranes (thickness less than 1.0 mm) were cut into $1 \text{ cm} \times 5 \text{ cm}$. The measurements were taken at least 5 times.

Table J1 Mechanical property of PSF

Sample	Breadth (mm)	Area (mm ²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
PSF	0.37	3.72	38.6	7.3	906
PSF	0.36	3.58	41.7	7.7	993
PSF	0.39	3.92	40.5	8.6	874
PSF	0.48	4.76	37.8	8.5	813
PSF	0.34	3.36	41.1	6.6	1018

Table J2 Mechanical property of SPSF 12.74%

Sample	Breadth (mm)	Area (mm ²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF12	0.28	2.82	35.5	5.4	1095
SPSF12	0.27	2.67	40.5	5.9	1157
SPSF12	0.31	3.13	38.3	6.6	957
SPSF12	0.18	1.81	48.6	7.0	1306
SPSF12	0.18	1.78	47.1	6.7	1294

Table J3 Mechanical property of SPSF 15.65%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF15	0.31	3.07	28.2	5.6	900
SPSF15	0.21	2.12	33.7	4.9	1277
SPSF15	0.25	2.53	33.6	5.2	1130
SPSF15	0.28	2.80	30.8	5.5	980
SPSF15	0.32	3.15	26.7	5.0	866

Table J4 Mechanical property of SPSF 19.90%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF19	0.31	3.10	30.5	5.4	952
SPSF19	0.31	3.14	33.3	5.8	960
SPSF19	0.25	2.47	29.5	4.4	1153
SPSF19	0.33	3.27	31.9	5.5	1072
SPSF19	0.29	2.94	33.0	5.4	1034

Table J5 Mechanical property of SPSF 27.99%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF19	0.22	2.22	29.66	5.1	999
SPSF19	0.25	2.47	29.66	4.7	885
SPSF19	0.31	3.05	30.91	5.9	1074
SPSF19	0.15	1.54	28.80	5.4	973
SPSF19	0.22	2.24	28.72	5.3	1044

Table J6 Mechanical property of SPSF 44.66%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF61	0.3	2.97	30.7	5.0	997
SPSF61	0.33	3.31	29.6	5.8	988
SPSF61	0.36	3.63	28.7	5.2	971
SPSF61	0.31	3.08	28.6	5.2	900
-SPSF61	0.31	3.05	29.0	5.1	1079

Table J7 Mechanical property of SPSF 61.44%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF61	0.33	3.32	30.7	6.4	844
SPSF61	0.32	3.23	30.0	5.8	847
SPSF61	0.30	3.04	30.1	5.5	984
SPSF61	0.28	2.76	28.2	4.2	995
SPSF61	0.14	1.37	25.9	4.4	1264

Table J8 Mechanical property of SPSF 71.55%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPSF71	0.48	4.77	21.8	5.5	662
SPSF71	0.39	3.91	24.7	5.9	691
SPSF71	0.28	2.83	32.2	5.8	933
SPSF71	0.31	3.11	35.2	6.5	930
SPSF71	0.22	2.16	28.2	6.9	1003

Table J9 Mechanical property of PVDF

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
PVDF	0.20	1.97	25.0	30.0	338
PVDF	0.23	2.33	25.2	32.4	324
PVDF	0.15	1.50	26.9	29.4	353
PVDF	0.17	1.70	26.4	30.3	397
PVDF	0.16	1.62	24.7	29.2	335

Table J10 Mechanical property of SPVDF 12.34%

Sample	Breadth (mm)	Area (mm²)	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
SPVDF	0.10	0.95	36.1	17.1	1005
SPVDF	0.10	1.00	32.5	17.5	869
SPVDF	0.11	1.09	32.3	17.6	840
SPVDF	0.14	1.35	36.7	17.4	983
SPVDF	0.11	1.06	29.9	13.2	725

Table J11 Mechanical properties of membranes

Sample	Tensile strength (MPa)	Yield strain (%)	Young's modulus (MPa)
PSF	39.9 ± 1.7	7.7 ± 0.9	921 ± 85
SPSF 12.74%	42.0 ± 5.7	6.3 ± 0.7	1162 ± 145
SPSF 15.65%	30.6 ± 3.2	5.2 ± 0.3	1030 ± 171
SPSF 19.90%	31.6 ± 1.6	5.3 ± 0.5	1034 ± 83
SPSF 27.99%	29.55 ± 0.9	5.3 ± 0.5	992 ± 73
SPSF 44.66%	29.32 ± 0.8	5.3 ± 0.3	987 ± 64
SPSF 61.44%	29.0 ± 2.0	5.3 ± 0.9	987 ± 171
SPSF 71.55%	28.4 ± 5.4	6.1 ± 0.6	844 ± 156
PVDF	25.7 ± 2.9	30.9 ± 1.9	349 ± 114
SPVDF 12.34%	33.5 ± 1.0	16.5 ± 1.3	884 ± 28
Nafion 117	11.0 ± 0.4	24.1 ± 1.9	185 ± 10

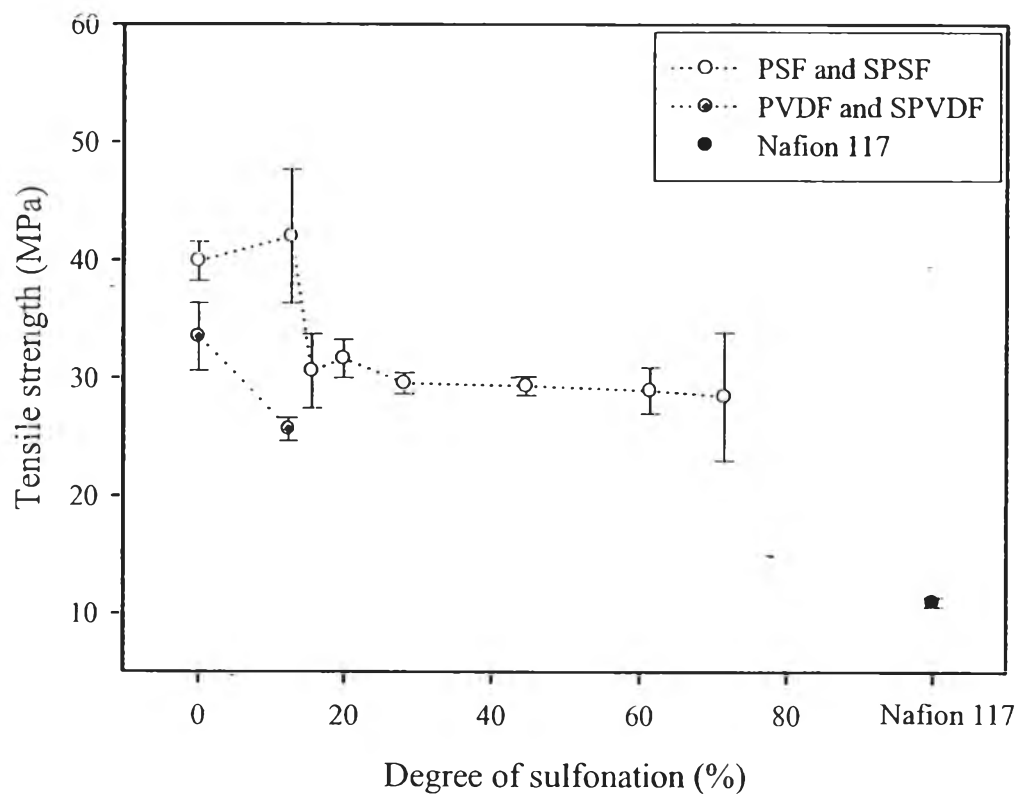


Figure J1 Tensile strength at various degrees of sulfonation of SPSF and SPVDF.

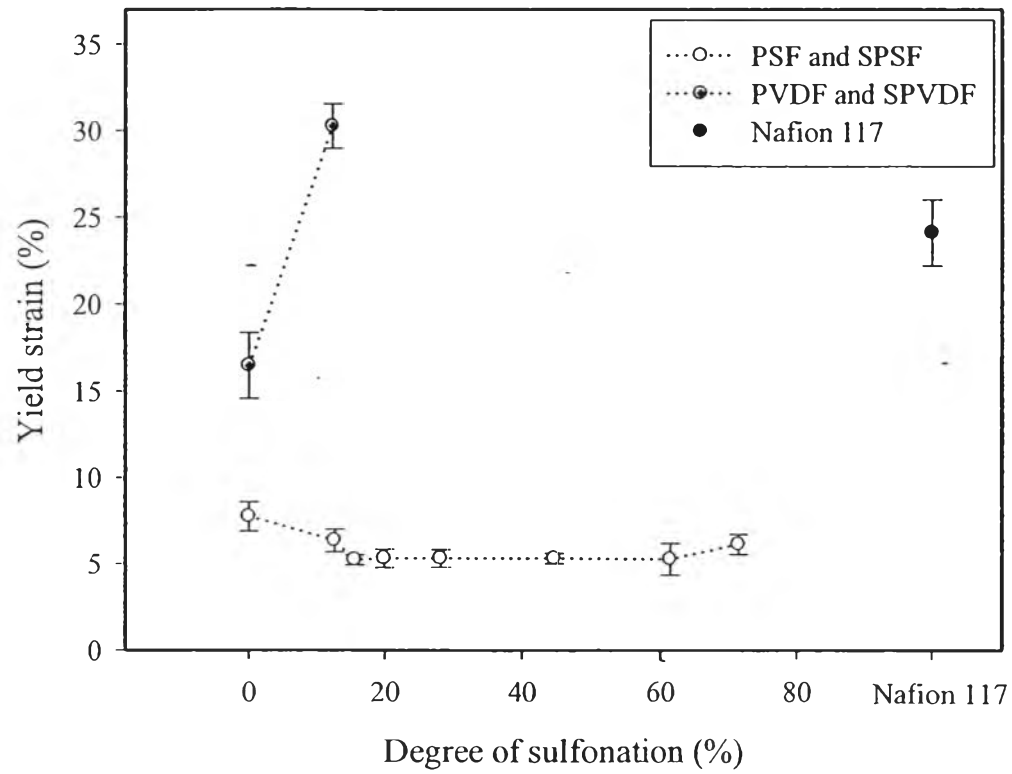


Figure J2 Yield strain at various degrees of sulfonation of SPSF and SPVDF.

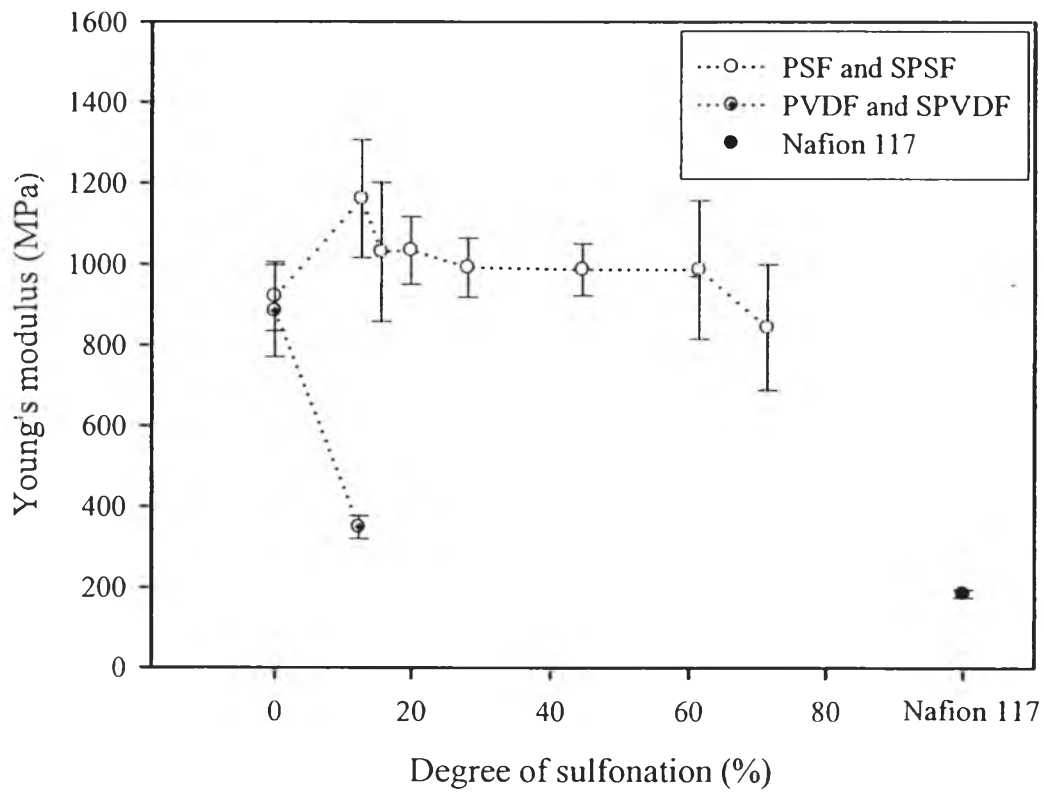


Figure J3 Young's modulus at various degrees of sulfonation of SPSF and SPVDF.

Appendix K X-ray Diffraction

The crystalline structure of polymer and sulfonated polymer was examined by a wide angle X-ray diffraction (Bruker AXS, D8 Advance). The CuK-alpha radiation source was operated at 40 kv/30 mA. The interference peak was eliminated by a K-beta filter. Divergence slit and scattering slit of 0.5° together with 0.3 mm of receiving slit were used. Each sample was mounted on a sample holder and a measurement was continuously run. The experiment was recorded by monitoring the diffraction pattern appearing in the 2θ range from 5 to 90, with a scan speed of $1^\circ/\text{min}$, and a scan step of 0.02° .

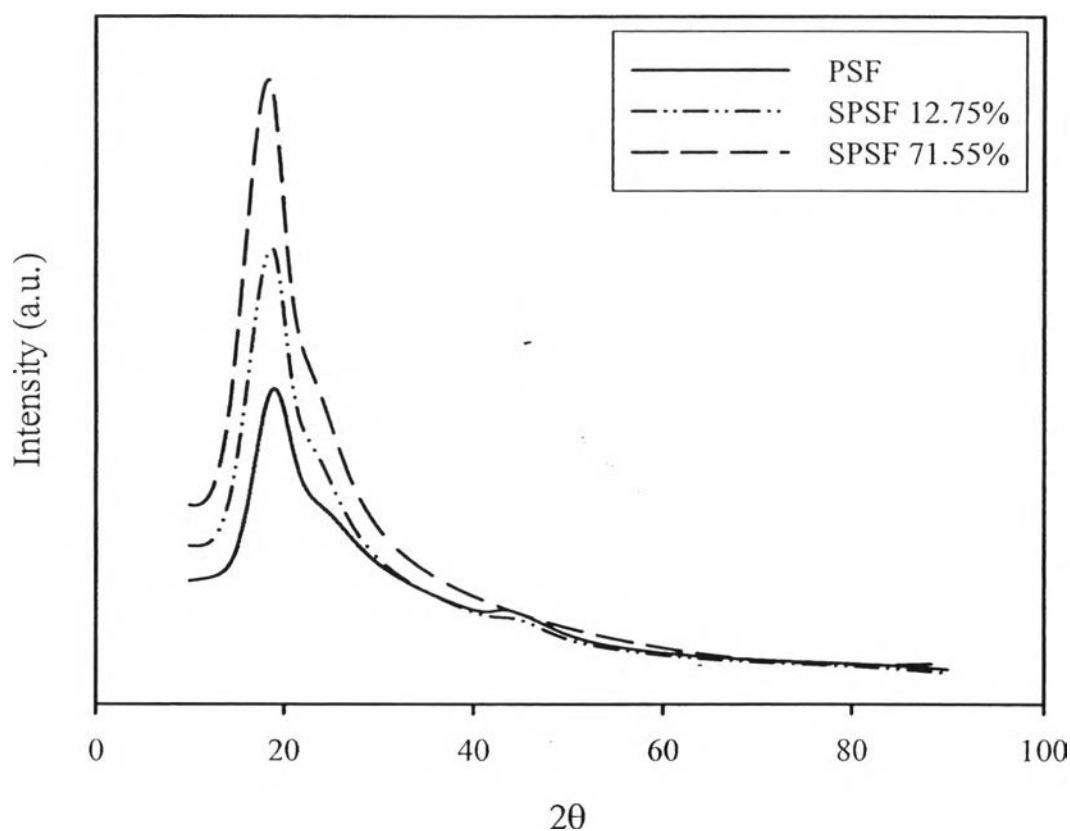


Figure K1 XRD pattern of PSF and SPSF at various degrees of sulfonation.

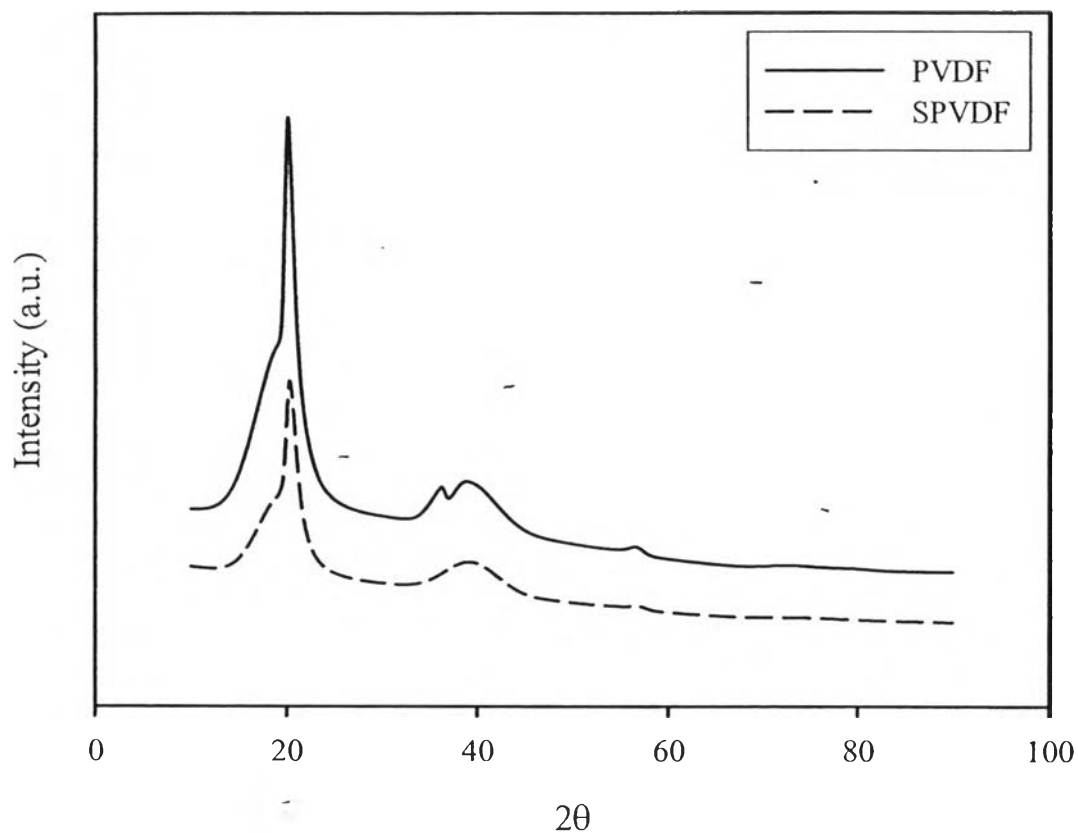


Figure K2 XRD pattern of PVDF and SPVDF at various degrees of sulfonation.

Figures K1 and K2 show a broad amorphous scattering of XRD pattern for both of polymers after sulfonation. The increase in DS provides more amorphous of the PSF and PVDF structure because more sulfonic acid pendant groups on the polymer backbone affecting the chain conformation and facilitating orientation of the amorphous structures [Reyna-Valencia et al., 2005; Zaidi, 2003].

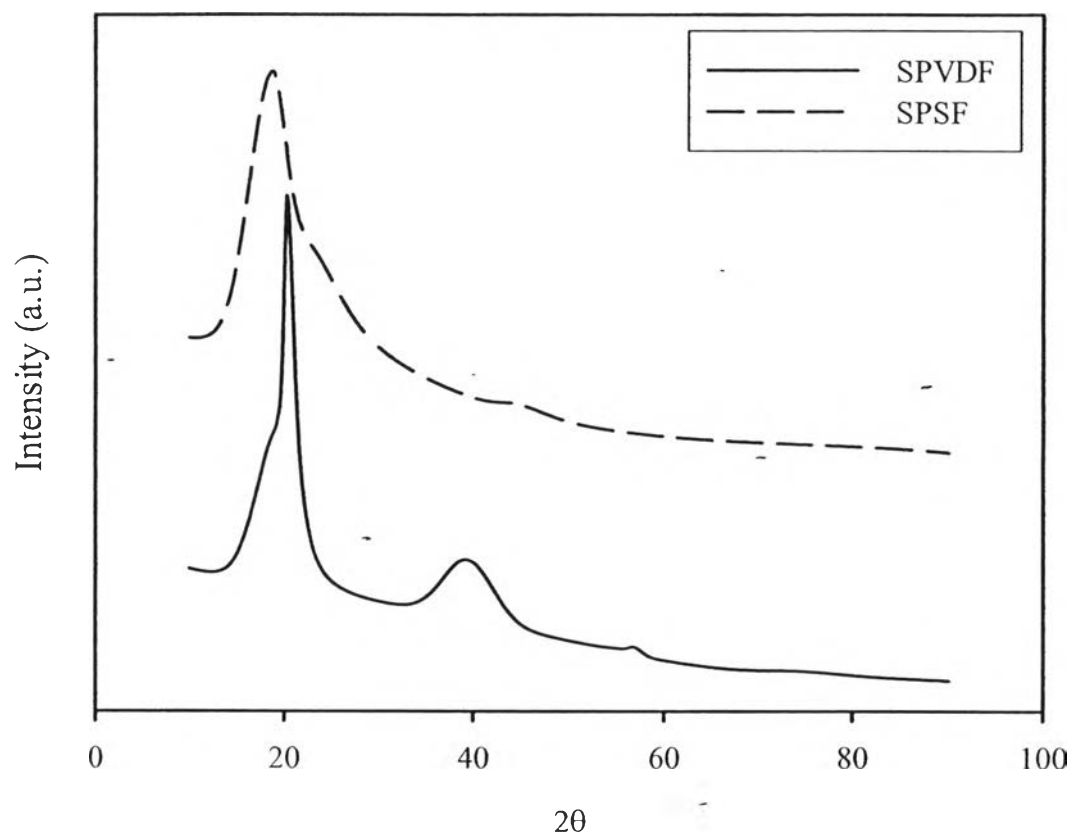


Figure K3 XRD pattern of SPSF and SPVDF.

Figure K3 shows that the XRD pattern of SPSF is broader than SPVDF because the SPSF has a benzene ring in the polymer backbone resulting in a lower chain packing.

Appendix L Nuclear Magnetic Resonance (NMR)

The structures of sulfonated PSF and PVDF were determined by a NMR spectrometer (Bruker Biospin Avance 500 MHz NMR spectrometer) using deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent at room temperature.

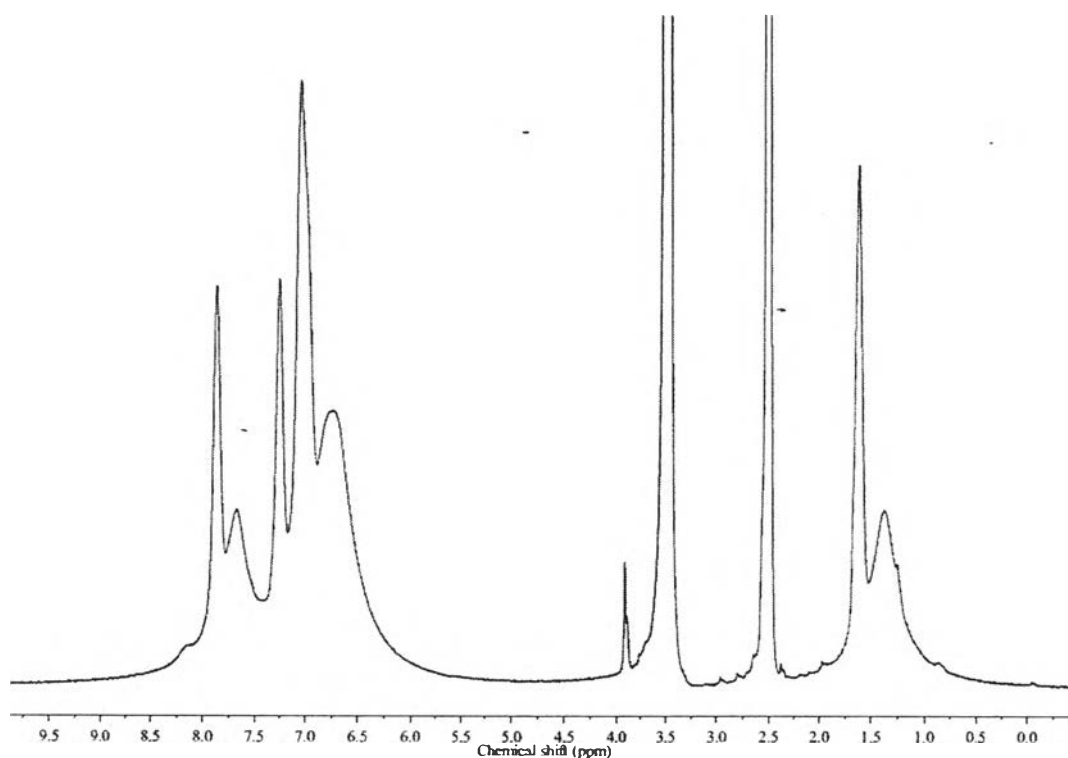


Figure L1 NMR spectrum of poly sulfonated polysulfone.

The proton resonance at 7.25 ppm is assigned to the proton adjacent to the new pendent sulfonic acid on the PSF structure [Deurim *et al.*, 2009].

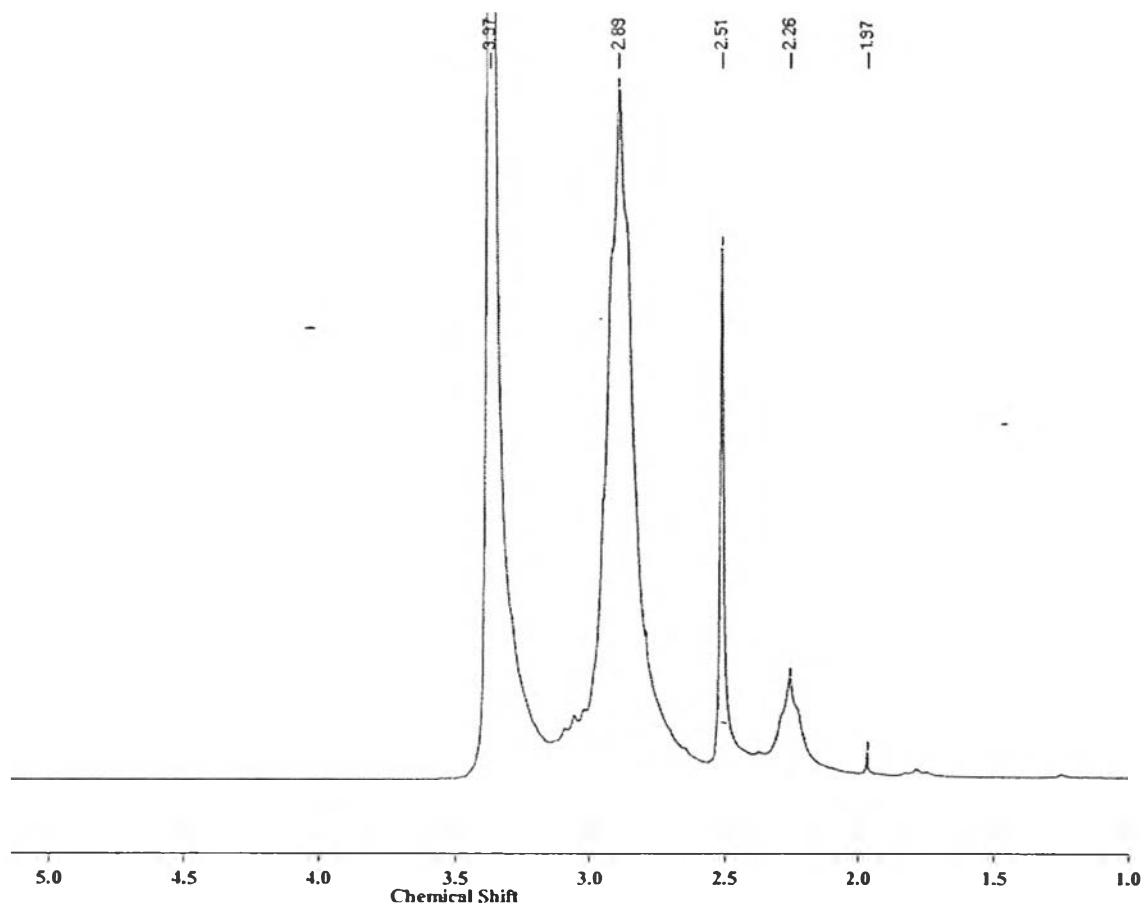


Figure L2 NMR spectrum of sulfonated polyvinylidene fluoride.

Sulfonated PVDF shows the proton resonance at 2.00 ppm for identify the sulfonic acid on the PVDF backbone.

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Proceedings:

1. 1. Pianmanakij, M.; Sirivat, A.; and Siemanond, K. (2014, April 22) Improving PEM with sulfonated polysulfone and polyvinylidene fluoride membranes for Direct Methanol Fuel cells. Proceedings of the 5th Research Symposium on Petrochemical and Materials Technology and the 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Ballroom, Queen Sirikit National Convention Center, Bangkok, Thailand.

Presentation:

2. 1. Pianmanakij, M.; Sirivat, A.; and Siemanond, K. (2014, April 22) Improving PEM with sulfonated polysulfone and polyvinylidene fluoride membranes for Direct Methanol Fuel cells. Paper presented at the 5th Research Symposium on Petrochemical and Materials Technology and the 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Ballroom, Queen Sirikit National Convention Center, Bangkok, Thailand.