REFERENCES

Ahmad, M.I., Zaidi, S.M.J., and Rahman, S.U. (2006) Proton conductivity and characterization of novel composite membranes for medium-temperature fuel cells. Desalination, 193, 387–397.

Carey, F.A. (2000). Reactions of aenes. Electrophilic aromatic substitution. Organic Chemistry. Massachusetts, United State of America, McGraw-Hill: 443-486.

Chen, D., Hickner, M.A., Wang, S., Pan, J., Xiao, M., and Meng, Y. (2012) Directly fluorinated polyaromatic composite membranes for vanadium redox flow batteries. Journal of Membrane Science, 415-16(0), 139-144.

Chen, D., Kim, S., Sprenkle, V., and Hickner, M.A. (2013) Composite blend polymer membranes with increased proton selectivity and lifetime for vanadium redox flow batteries. Journal of Power Sources, 231(0), 301-306.

Chen, D., Wang, S., Xiao, M., Han, D., and Meng, Y. (2010) Sulfonated poly (fluorenyl ether ketone) membrane with embedded silica rich layer and enhanced proton selectivity for vanadium redox flow battery. Journal of Power Sources, 195, 7701-7708.

Chen, D., Wang, S., Xiao, M., Han, D., and Meng, Y. (2011) Synthesis of sulfonated poly(fluorenyl ether thioether ketone)s with bulky-block structure and its application in vanadium redox flow battery. Polymer, 52(23), 5312-5319.

Chen, D., Wang, S., Xiao, M., and Meng, Y. (2010) Preparation and properties of sulfonated poly(fluorenyl ether ketone) membrane for vanadium redox flow battery application. Journal of Power Sources, 195(7), 2089-2095.

Chen, D., Wang, S., Xiao, M., and Meng, Y. (2010) Synthesis and characterization of novel sulfonated poly(arylene thioether) ionomers for vanadium redox flow battery applications. Energy & Environmental Science, 3(5), 622-628.

Chieng, S.C., Kazacos, M., and Skyllas-Kazacos, M. (1992) Preparation and evaluation of composite membrane for vanadium redox battery applications. Journal of Power Sources, 39(1), 11-19.

Dupuis, A.C. (2011) Proton exchange membranes for fuel cells operated at medium temperatures: Materials and experimental techniques. Progress in Materials Science, 56(3), 289-327.

Dupont. "Dupont Nafion PFSA Membranes." 2009. 26 March 2014.

Fujimoto, C., Kim, S., Stains, R., Wei, X.L., Li, L.Y., and Yang, Z.G. (2012) Vanadium redox flow battery efficiency and durability studies of sulfonated Diels Alder poly(phenylene)s. Electrochemistry Communications, 20, 48-51.

Fujimoto, C.H., Hickner, M.A., Cornelius, C.J., and Loy, D.A. (2005) Ionomeric Poly(phenylene) Prepared by Diels−Alder Polymerization: Synthesis and physical properties of a novel polyelectrolyte. Macromolecules, 38(12), 5010-5016.

Grot, W. (2011) Fuel cells and batteries. Fluorinated Ionomers. (pp. 157-182) Elsevier.

Jia, C., Liu, J., and Yan, C. (2010) A significantly improved membrane for vanadium redox flow battery. Journal of Power Sources, 195(13), 4380-4383.

Jin, X., Bishop, M.T., Ellis, T.S., and Karasz, F.E. (1985) A Sulphonated Poly(aryl Ether Ketone). British Polymer Journal, 17(1), 4-10.

Kim, S., Yan, J.L., Schwenzer, B., Zhang, J.L., Li, L.Y., Liu, J., Yang, Z.G., and Hickner, M.A. (2010) Cycling performance and efficiency of sulfonated poly(sulfone) membranes in vanadium redox flow batteries. Electrochemistry Communications, 12(11), 1650-1653.

Laxmeshwar, S.S., Viveka, S., Kumar, D.J.M., Dinesha, Bhajanthri, R.F., and Nagaraja, G.K. (2012) Preparation and characterization of modified cellulose fiber-reinforced polyvinyl alcohol/polypyrrolidone hybrid film composites. Journal of Macromolecular Science Part a-Pure and Applied Chemistry, 49(8), 639-647.

Li, Z., Xi, J., Zhou, H., Liu, L., Wu, Z., Qiu, X., and Chen, L. (2013) Preparation and characterization of sulfonated poly(ether ether ketone)/poly(vinylidene fluoride) blend membrane for vanadium redox flow battery application. Journal of Power Sources, 237, 132-140.

Luo, Q.T., Zhang, H.M., Chen, J., Qian, P., and Zhai, Y.F. (2008) Modification of Nafion membrane using interfacial polymerization for vanadium redox flow battery applications. Journal of Membrane Science, 311(1-2), 98-103.

Macksasitorn, S., Changkhamchom, S., Sirivat, A., and Siemanond, K. (2012) Sulfonated poly(ether ether ketone) and sulfonated poly(1,4-phenylene ether ether sulfone) membranes for vanadium redox flow batteries. High Performance Polymers, 24(7), 603-608.

Mai, Z., Zhang, H., Li, X., Bi, C., and Dai, H. (2011) Sulfonated poly(tetramethydiphenyl ether ether ketone) membranes for vanadium redox flow battery application. Journal of Power Sources, 196(1), 482-487.

Mai, Z., Zhang, H., Li, X., Xiao, S., and Zhang, H. (2011) Nafion/polyvinylidene fluoride blend membranes with improved ion selectivity for vanadium redox flow battery application. Journal of Power Sources, 196(13), 5737-5741.

Mai, Z., Zhang, H., Zhang, H., Xu, W., Wei, W., Na, H., and Li, X. (2013) Anion-conductive membranes with ultralow vanadium permeability and excellent performance in vanadium flow batteries. ChemSusChem, 6, 328 – 335.

Mohammadi, T. and Skyllas-Kazacos, M. (1995) Preparation of sulfonated composite membrane for vanadium redox flow battery applications. Journal of Membrane Science, 107(1-2), 35-45.

Parasuraman, A., Lim, T.M., Menictas, C., and Skyllas-Kazacos, M. (2013) Review of material research and development for vanadium redox flow battery applications. Electrochimica Acta, 101, 27-40.

Park, C.H., Lee, C.H., Guiver, M.D., and Lee, Y.M. (2011) Sulfonated hydrocarbon membranes for medium-temperature and low-humidity proton exchange membrane fuel cells (PEMFCs). Progress in Polymer Science, 36(11), 1443-1498.

Pauling, L. (1960) The sizes of ions and the structure of the ionic crystals. The Nature of the Chemical Bond. (pp. 505-562) Ithaca: Cornell University Press.

Rahman, F. and Skyllas-Kazacos, M. (2009) Vanadium redox battery: Positive half-cell electrolyte studies. Journal of Power Sources, 189(2), 1212-1219.

Rikukawa. M. and Sanui, K. (2000) Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers. Progress in Polymer Science, 25(10), 1463-1502.

Sancho, T., Soler, J., and Pina, M.P. (2007) Conductivity in zeolite-polymer composite membranes for PEMFCs. Journal of Power Sources, 169(1), 92-97.

Sang, S., Wu, Q., and Huang, K. (2007) Preparation of zirconium phosphate (ZrP)/Nafion1135 composite membrane and H+/VO2+ transfer property investigation. Journal of Membrane Science, 305(1-2), 118-124.

Smitha, B., Sridhar, S., and Khan, A.A. (2003) Synthesis and characterization of proton conducting polymer membranes for fuel cells. Journal of Membrane Science, 225(1-2), 63-76.

Sukkar, T. and Skyllas-Kazacos, M. (2003) Modification of membranes using polyelectrolytes to improve water transfer properties in the vanadium redox battery. Journal of Membrane Science, 222(1-2), 249-264.

Sukkar, T. and Skyllas-Kazacos, M. (2003) Water transfer behaviour across cation exchange membranes in the vanadium redox battery. Journal of Membrane Science, 222(1-2), 235-247.

Sukkar, T. and Skyllas-Kazacos, M. (2004) Membrane stability studies for vanadium redox cell applications. Journal of Applied Electrochemistry, 34(2), 137-145.

Teng, X., Zhao, Y., Xi, J., Wu, Z., Qiu, X., and Chen, L. (2009) Nafion/organically modified silicate hybrids membrane for vanadium redox flow battery. Journal of Power Sources, 189(2), 1240-1246.

Teng, X.G., Zhao, Y.T., Xi, J.Y., Wu, Z.H., Qiu, X.P., and Chen, L.Q. (2009) Nafion/organic silica modified TiO2 composite membrane for vanadium redox flow battery via in situ sol-gel reactions. Journal of Membrane Science, 341(1-2), 149-154.

Unveren, E.E., Erdogan, T., Çelebi, S.S., and Inan, T.Y. (2010) Role of post-sulfonation of poly(ether ether sulfone) in proton conductivity and chemical stability of its proton exchange membranes for fuel cell. International Journal of Hydrogen Energy, 35(8), 3736-3744.

Vynnycky, M. (2011) Analysis of a model for the operation of a vanadium redox battery. Energy, 36(4), 2242-2256.

Wang, Z., Li, X., Zhao, C., Ni, H., and Na, H. (2007) Sulfonated poly(ether ether sulfone) copolymers for proton exchange membrane fuel cells. Journal of Applied Polymer Science, 104(3), 1443-1450.

Weber, A., Mench, M., Meyers, J., Ross, P., Gostick, J., and Liu, Q. (2011) Redox flow batteries: a review. Journal of Applied Electrochemistry, 41(10), 1137-1164.

Whitehead, A.H. and Harrer, M. (2013) Investigation of a method to hinder charge imbalance in the vanadium redox flow battery. Journal of Power Sources, 230, 271-276.

Whittingham, M.S. (2008) Materials challenges facing electrical energy storage. MRS Bulletin, 33(04), 411-419.

Xi, J., Wu, Z., Qiu, X., and Chen, L. (2007) Nafion/SiO2 hybrid membrane for vanadium redox flow battery. Journal of Power Sources, 166(2), 531-536.

Xing, P., Robertson, G.P., Guiver, M.D., Mikhailenko, S.D., Wang, K., and Kaliaguine, S. (2004) Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. Journal of Membrane Science, 229(1–2), 95-106.

Yan, J.L., Huang, X.M., Moore, H.D., Wang, C.Y., and Hickner, M.A. (2012) Transport properties and fuel cell performance of sulfonated poly(imide) proton exchange membranes. International Journal of Hydrogen Energy, 37(7), 6153-6160.

Yee, R., Zhang, K., and Ladewig, B. (2013) The effects of sulfonated poly(ether ether ketone) ion exchange preparation conditions on membrane properties. Membranes, 3(3), 182-195.

Yuan, X.-Z., Song, C., Wang, H., and Zhang, J. (2010) EIS diagnosis for PEM fuel cell performance. Electrochemical Impedance Spectroscopy in PEM Fuel Cells. (pp. 193-262) London: Springer.

Zaidi, J. (2003) Polymer sulfonation - A versatile route to prepare proton-conducting membrane material for advanced technologies. The Arabian Journal for Science and Engineering, 28.

Zhai, F., Guo, X., Fang, J., and Xu, H. (2007) Synthesis and properties of novel sulfonated polyimide membranes for direct methanol fuel cell application. Journal of Membrane Science, 296(1-2), 102-109.

Zhang, Z., Desilets, F., Felice, V., Mecheri, B., Licoccia, S., and Tavares, A.C. (2011) On the proton conductivity of Nafion/Faujasite composite membranes for low temperature direct methanol fuel cells. Journal of Power Sources, 196(22), 9176-9187.

APPENDICES

Appendix A Fourier Transform Infrared Spectroscopy

The FT-IR spectra of pristine polymer as PEEK and PPEES and sulfonated polymer as S-PEEK and S-PPEES were obtained employing a spectrometer (Thermo Nicolet, Nexus 670) to examine the presence of sulfonic acid group (-SO_3H) in polymer samples. The spectrometer was operated in the absorption mode with a resolution of 4 cm^{-1} and wave numbers range of 4000-400 cm^{-1}. KBr was employed as the background material for thesample of sulfonated polymer , respectively

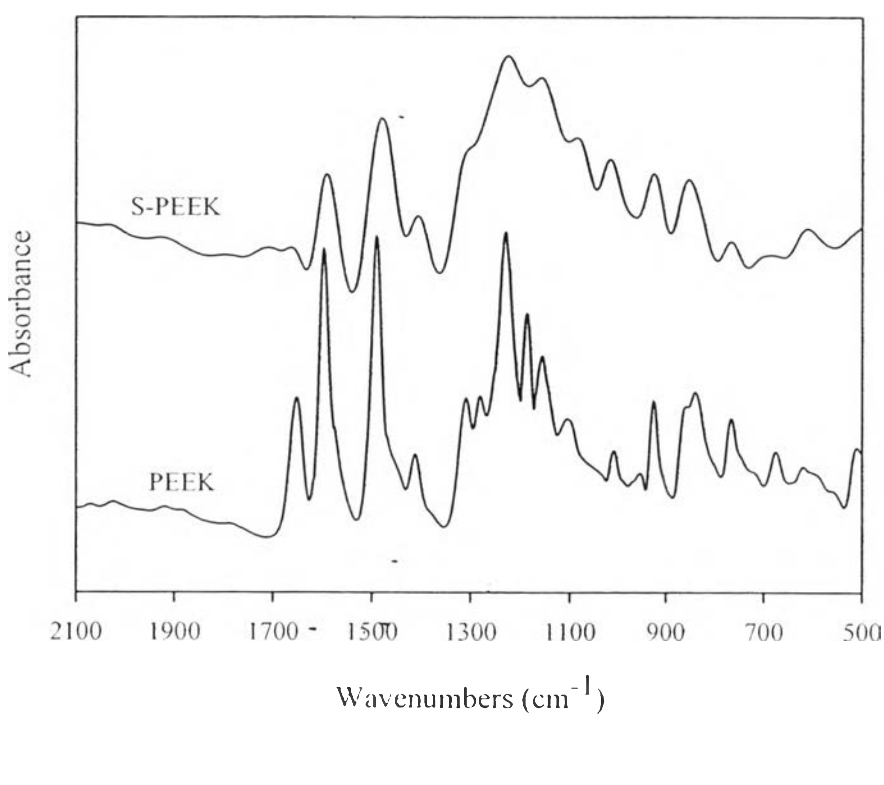

Figure A1 FTIR spectrum of sulfonated poly(ether ether ketone).

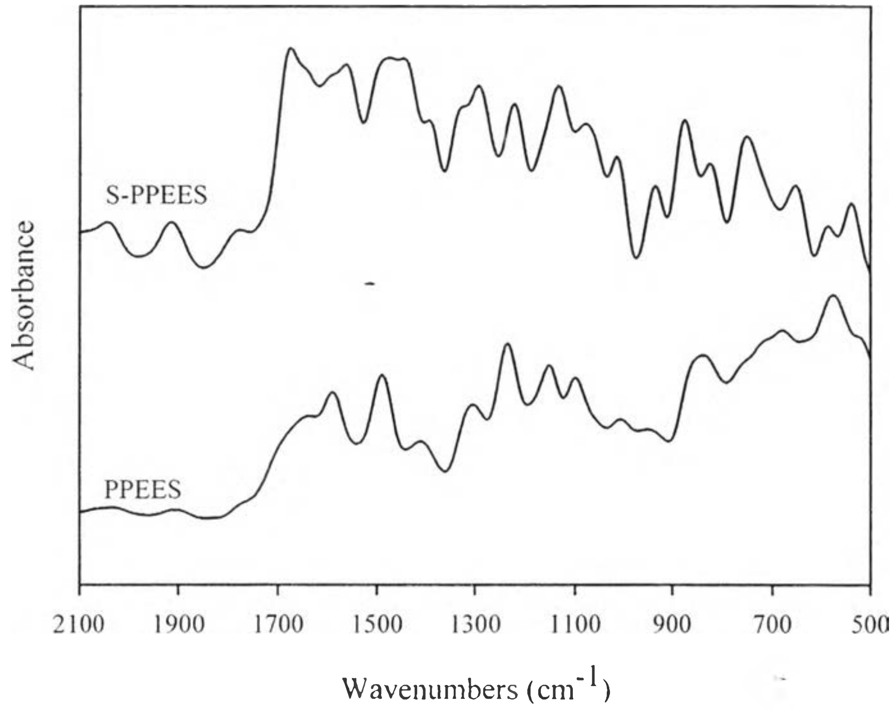

Figure A2 FTIR spectrum of sulfonated poly(phenylene ether ether ketone).

Table A1 The FT-IR absorption spectra of PEEK, S-PEEK, PPEES, and S-PPEES.

Wavenumbers (cm^{-1})	Assignments	References
709	Symmetric S-O stretching	(Zaidi, 2003)
1020	Symmetric S=O stretching	(Zaidi, 2003)
1360	Asymmetric S=O stretching	(Smitha *et al.*, 2003)
1080	Symmetric O=S=O stretching	(Xing *et al.*, 2004)
1255	Asymmetric O=S=O stretching	(Zaidi, 2003)
1222	C-O-C	(Macksasitorn *et al.*, 2012)
1489	C-C Aromatic	(Xing *et al.*, 2004)
1650	C=O stretching	(Macksasitorn *et al.*, 2012)
3460	O-H stretching	(Xing *et al.*, 2004)

Appendix B Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of pristine polymer and sulfonated polymer were conducted using a Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA). The measurements were carried out under nitrogen flow with a temperature range of 50-900 °C at a heating rate of 10 °C/min.

B1 Poly(ether ether ketone)

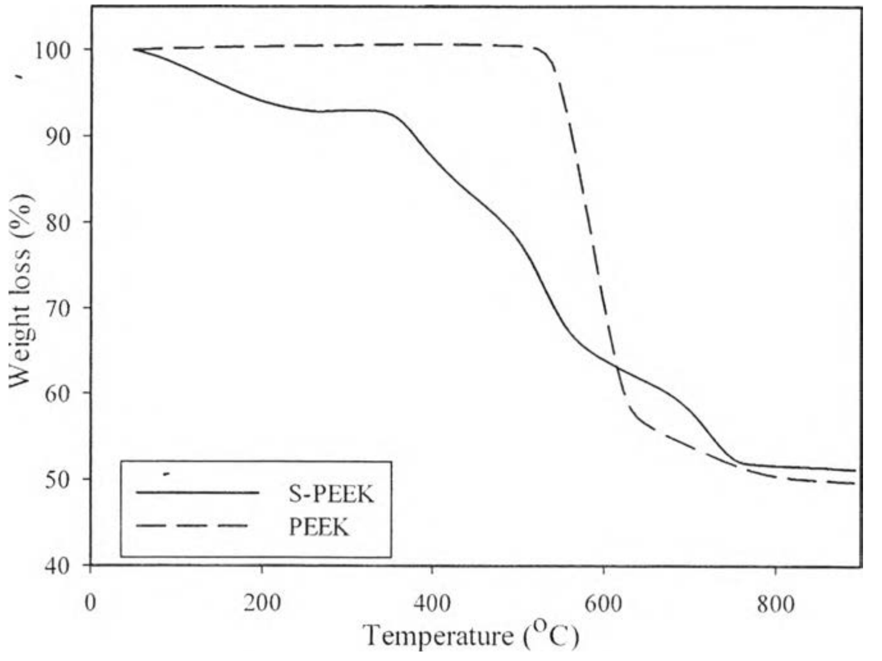

Figure B1 Thermogravimetric analysis and thermograms of PEEK and S-PEEK.

B2 Poly(phenylene ether ethersulfone)

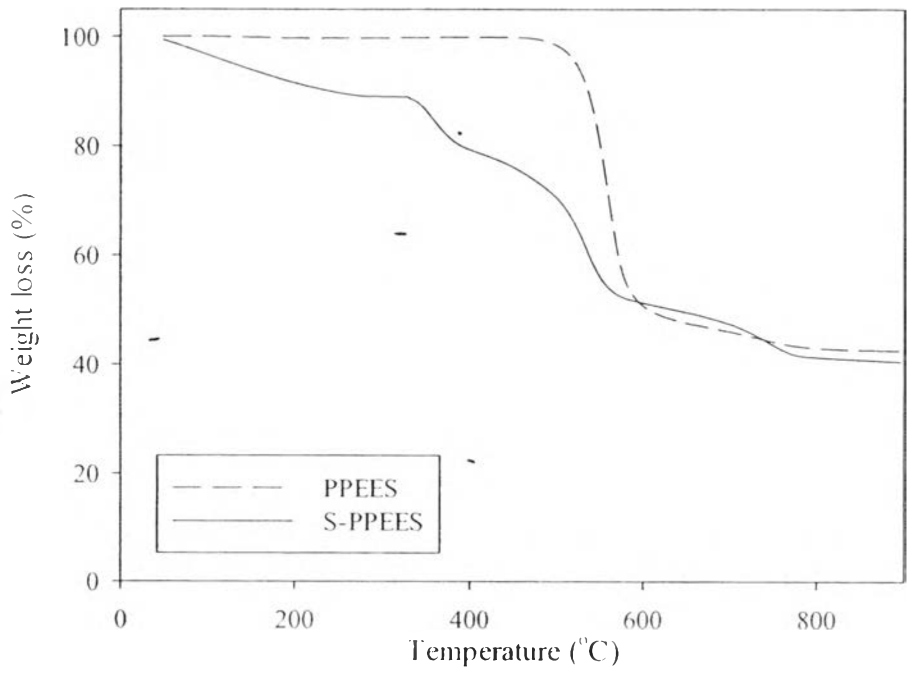

Figure B2 Thermogravimetric analysis and thermograms PPEES and S-PPEES.

Appendix C Sulfonation and Film Casting

C1 Sulfonation process

1.1 Excess molar ratio

Excess molar ratio is the simple ratio as between mole of sulfuric acid and mole of repeating unit of polymer.

1.1.1 Poly(ether ether ketone)

Molar mass of repeating unit (M_R)	=	288 g/mol
Mass of weighed polymer	=	M_S g
Mole of weighed polymer	=	$M_S/288$ mole
Concentration of sulfuric acid	=	18 M = 0.018 mole/cm^3
Volume of sulfuric acid	=	V cm^3
Mole of sulfuric acid	=	0.018V mole

So that, Excess molar ratio (R_{molar}) $= \frac{0.018V}{MS/288} = \frac{5.184V}{Ms}$

1.1.2 Poly(phenylene ether ether sulfone)

Molar mass of repeating unit (M_R)	=	324 g/mol
Mass of weighed polymer	=	M_S g
Mole of weighed polymer	=	$M_S/324$ mole
Concentration of sulfuric acid	=	18 M = 0.018 mole/cm^3
Volume of sulfuric acid	=	V cm^3
Mole of sulfuric acid	=	0.018V mole

So that, Excess molar ratio (R_{molar}) $= \frac{0.018V}{MS/324} = \frac{5.832V}{Ms}$

1.2 Volume fraction

Volume fraction refers the composition of sulfuric acid volume to whole solution under sulfonation reaction.

Mass of weighed polymer	=	M_S g
Volume of weighed polymer	=	$M_S / \rho = V_P$ cm^3
Volume of sulfuric acid	=	V cm^3

So that, Volume fraction $= \left(\frac{V}{V+V_P}\right) \times 100$ %

Table C1 Polymer density from gas pycnometer

Polymer	Company	V (g)	S_a (g)	S_b (g)	Density (g/cm^3)	Deviation (%)
PEEK power	Victrex	2.8100	0.5614	0.5613	1.1512	1.89
PPEES pellet	Aldrich	2.8099	1.4928	1.4925	1.3166	0.52

1.2.1 Poly(ether ether ketone)

For excess molar ratio = 200, M_S = 2.592 g, and V = 100 cm^3

Volume of weighed polymer = $\frac{2.592\ g}{1.1512\ g/cm^3}$ = 2.2516 cm^3

Volume of sulfuric acid = 100 cm^3

So that, Volume fraction = $\left(\frac{100}{100+2.2516}\right) \times 100$ = 97.80 %

1.2.2 Poly(phenylene ether ether sulfone)

For excess molar ratio = 100, M_S = 2.916 g, and V = 50 cm^3

Volume of weighed polymer = $\frac{2.916\ g}{1.3166\ g/cm^3}$ = 2.2148 cm^3

Volume of sulfuric acid = 50 cm^3

So that, Volume fraction = $\left(\frac{50}{50+2.2148}\right) \times 100$ = 95.76 %

Table C2 Relation between excess molar ratio and volume fraction for poly(ether ether ketone) sulfonation

Excess molar ratio	Polymer (g)	Sulfuric acid (cm^3)	Volume fraction (%)
50	10.368	100	91.74
100	5.184	100	95.69
150	3.456	100	97.09
200	2.592	100	97.80
300	1.728	100	98.52
400	1.296	100	98.89

Table C3 Relation between excess molar ratio and volume fraction for poly(phenylene ether ether sulfone) sulfonation

Excess molar ratio	Polymer (g)	Sulfuric acid (cm^3)	Volume fraction (%)
50	11.664	100	91.86
100	5.832	100	95.76
150	3.888	100	97.13
200	2.916	100	97.83
300	1.944	100	98.54
400	1.458	100	98.91

1.3 Sulfonation conditions

Table C4 Poly(ether ether ketone) sulfonation conditions

Temperature (°C)	PEEK (g)	H_2SO_4 (ml)	H_2SO_4 (mol ratio)	Volume fraction (%)	Time (h)	Sulfonated products (g)	Sulfonated products	Dried products	Membranes
80	2.602	100	200	97.80	1	1.460	Swelling rubber	Clear sheet	Water soluble
80	2.614	100	200	97.80	3	2.788	Swelling rubber	Clear sheet	Water soluble
80	2.611	100	200	97.80	5	2.106	Swelling rubber	Clear sheet	Water soluble
50	2.616	25	50	91.74	3	6.962	White rubber	White rubber	Homogeneous
50	2.611	50	100	95.69	3	2.801	White rubber	White rubber	Homogeneous
50	2.604	75	150	97.09	3	1.425	White rubber	White rubber	Homogeneous
50	2.606	100	200	97.80	3	2.512	White rubber	White rubber	Homogeneous
50	2.593	100	200	97.80	1	1.322	White rubber	White rubber	Homogeneous
50	2.593	100	200	97.80	5	2.608	White rubber	White rubber	Homogeneous
50	2.604	100	200	97.80	12	0.991	Swelling rubber	White rubber	Homogeneous

Table C5 Poly(phenylene ether ether sulfone) sulfonation conditions

Temperature (°C)	PPEES (g)	H_2SO_4 (ml)	H_2SO_4 (mol ratio)	Volume fraction (%)	Time (h)	Sulfonated products (g)	Sulfonated products	Dried products	Membranes
80	2.932	50	100	95.76	1	1.324	Swelling rubber	Clear sheet	Water soluble
80	2.934	50	100	95.76	3	2.427	Swelling rubber	Clear sheet	Water soluble
80	2.918	50	100	95.76	5	2.614	Swelling rubber	Clear sheet	Water soluble
50	2.937	50	100	95.76	1	1.104	Swelling rubber	Clear sheet	Homogeneous
50	2.924	50	100	95.76	3	1.181	Swelling rubber	Clear sheet	Homogeneous
50	2.942	50	100	95.76	5	2.543	Swelling rubber	Clear sheet	Homogeneous
25	2.919	25	50	91.86	24	3.127	White rubber	Clear sheet	Homogeneous
25	1.463	25	100	95.76	3	-	Cannot be dissolved in sulfuric acid		
25	1.461	25	100	95.76	6	1.324	White rubber	Clear sheet	Homogeneous
25	1.460	25	100	95.76	9	1.347	White rubber	Clear sheet	Homogeneous
25	1.465	25	100	95.76	12	1.437	White rubber	Clear sheet	Homogeneous
25	1.452	25	100	95.76	24	1.588	White rubber	Clear sheet	Homogeneous
25	1.951	50	150	97.13	24	1.711	White rubber	Clear sheet	Homogeneous
25	0.724	25	200	97.83	24	0.095	Swelling rubber	Black solid	Homogeneous
25	0.973	50	300	98.54	24	0.353	Swelling rubber	Black solid	Homogeneous
25	0.726	50	400	98.91	24	0.575	Swelling rubber	Black solid	Homogeneous

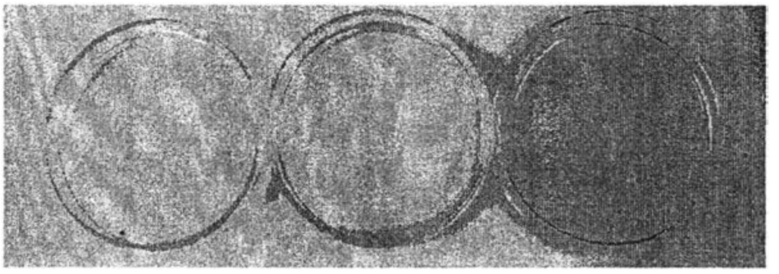

Figure C1 PEEK sulfonation at 80 °C at different sulfonation times of: 1 h (left); 3 h (middle); and 5 h (right).

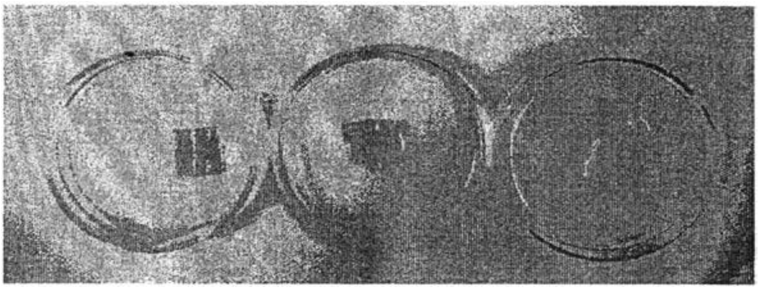

Figure C2 PEEK sulfonation at 50 °C at different sulfonation times of: 1 h (left); 3 h (middle); and 5 h (right).

Figures C1 and C2 show that the S-PEEK membranes swell easily with increasing sulfonation time. The water uptake increases with increasing degree of sulfonation because of a greater hydrophilicity. From Figure C1, the S-PEEK membranes were fully dissolved in water, S-PEEK membrane at sulfonation temperature of 80 °C is not suitable for V-RFB application which has water containing vanadium electrolyte.

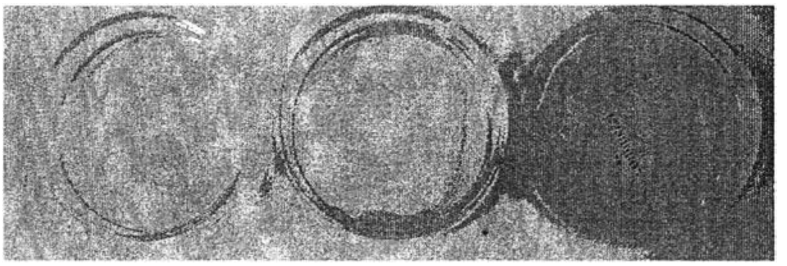

Figure C3 PPEES sulfonation at 80 °C at different sulfonation times of: 1 h (left); 3 h (middle); and 5 h (right).

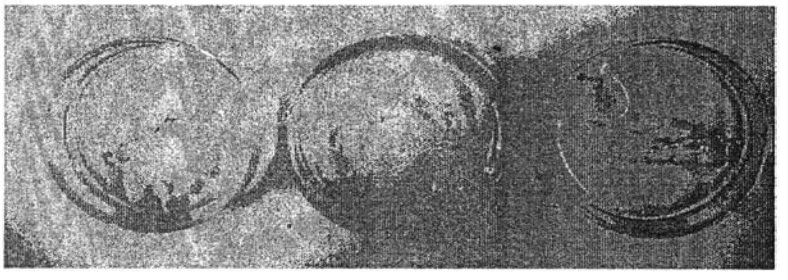

Figure C4 PPEES sulfonation at 50 °C at different sulfonation times of: 1 h (left); 3 h (middle); and 5 h (right).

Higher sulfonation time and temperature induce shape transformation as shown in Figures C3 and C4. In the worst case, the prepared membrane was fully dissolved in water, both sulfonation temperatures of 50 and 80 °C are not suitable for VRFB application which has water containing vanadium electrolyte.

C2 Degree of sulfonation

The polymer membranes were washed with deionization water and dried at 100 °C for 24 h. The degree of sulfonation of solution was determined by the titration with 0.01 M sodium hydroxide until pH neutral using phenolphthalein as an indicator. The degree of sulfonation (DS) is defined as the number of sulfonic acid groups divided by the number of repeating units in a polymer chain that was calculated by the following relation.

$$DS\ (\%) = \frac{(V_{NaOH} \times C_{NaOH})/1000}{\text{Mole of polymer membrane}} \times 100 \qquad (C1)$$

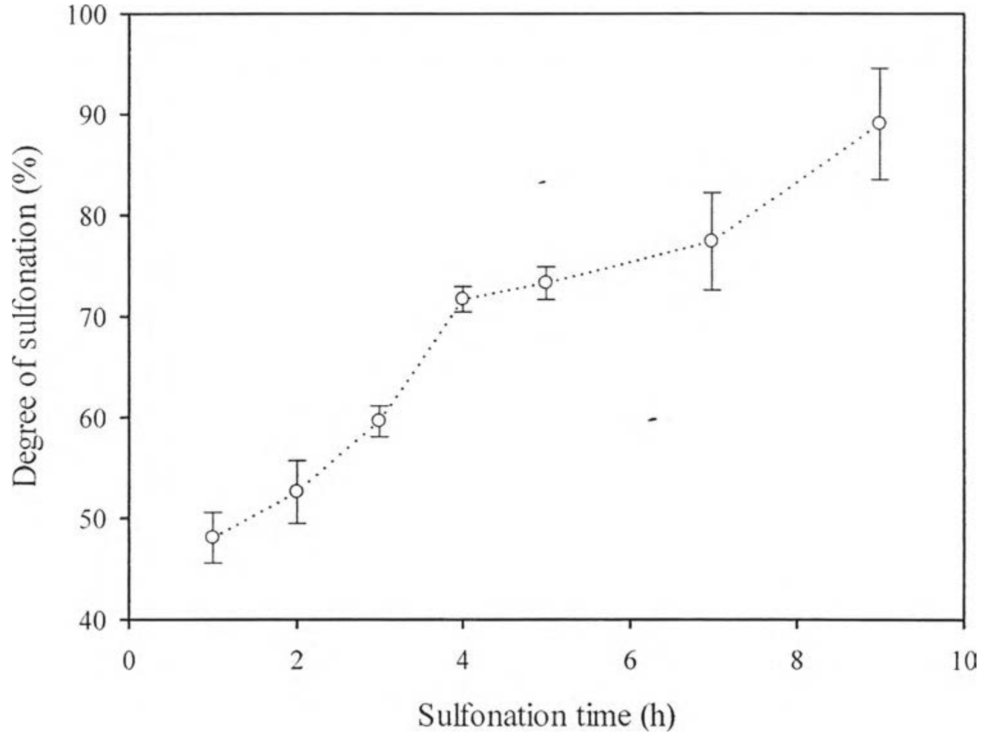

Figure C5 Effect of sulfonation time on the degree of sulfonation of PEEK at sulfonation temperature of 50 °C and acid/polymer mol ratio of 200.

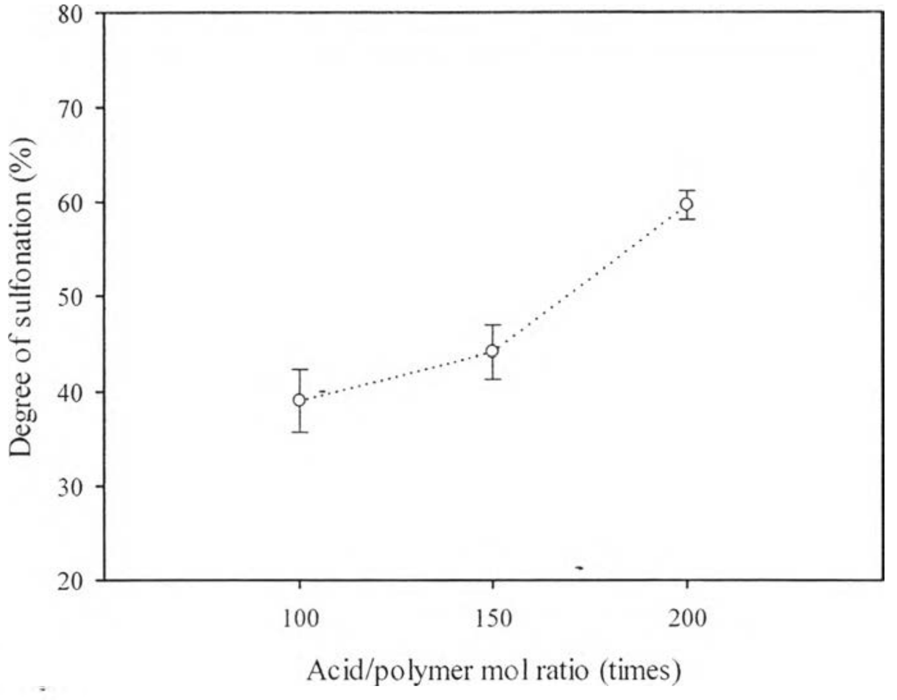

Figure C6 Effect of acid/polymer mol ratio on the degree of sulfonation of S-PEEK at sulfonation temperature of 50 °C and sulfonation time of 3 h.

Table C6 Degree of sulfonation of S-PEEK at sulfonation temperature of 50 °C

H_2SO_4 (mol ratio)	Time (h)	Degree of sulfonation (%)			
		DS1	DS2	DS3	Average
100	3	38.38	36.07	42.62	39.02 ± 3.33
150	3	47.08	43.85	41.48	44.14 ± 2.81
200	1	49.97	45.21	48.98	48.05 ± 2.51
200	2	49.01	54.043	54.69	52.58 ± 3.11
200	3	61.20	58.14	59.47	59.60 ± 1.53
200	4	71.86	70.38	72.89	71.71 ± 1.26
200	5	71.66	73.41	74.88	73.32 ± 1.62
200	7	72.68	77.34	82.28	77.43 ± 4.80
200	9	90.51	93.68	82.95	89.04 ± 5.51

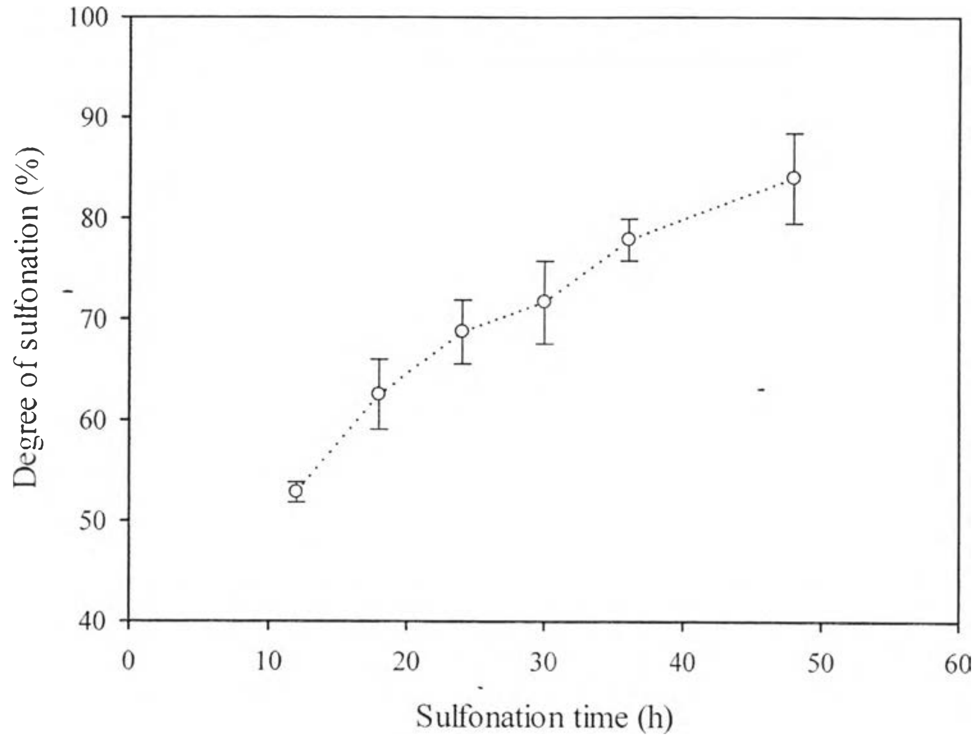

Figure C7 Effect of sulfonation time on the degree of sulfonation of S-PPEES at sulfonation temperature of 25 °C acid/polymer mol ratio of 100.

Table C7 Degree of sulfonation of S-PPEES at controlled temperature of 25 °C

H_2SO_4 (mol ratio)	Time (h)	Degree of sulfonation (%)			
		DS1	DS2	DS3	Average
100	9	-	-	-	A*
100	12	52.39	52.09	53.96	52.81 ± 1.00
100	18	58.86	62.99	65.73	62.53 ± 3.46
100	24	71.04	65.12	70.03	68.73 ± 3.17
100	30	68.47	70.29	76.31	71.69 ± 4.11
100	36	75.50	79.06	79.09	77.88 ± 2.07
100	48	88.77	79.85	83.40	83.99 ± 4.47
200	24	-	-	-	B*
300	24	-	-	-	B*
400	24	-	-	-	B*

Remarks
A*: The PPEES could not be dissolve in sulfuric acid with sulfonation time that was less than 9 h.
B*: The swelling sulfonated products contained contaminated acid and they could not be washed out easily.

Appendix D Proton Conductivity under Dry State

Proton conductivity of the membrane was determined by a Hewlett Packard 4194A impedance gain/phase analyzer under dry state at 25 °C. The 5 cm × 5 cm film was measured at 1 V potential using the alternating current in the frequency range of 100 Hz – 2 MHz. The graphs show the relationship between the real impedance (Zcosθ) and the imaginary impedance (-Zsinθ). The proton-conductivity (σ) was calculated using Eq. D1:

$$\sigma = \frac{d}{R \times A} \text{ (S/cm)} \tag{D1}$$

where σ is the proton conductivity (S/cm), d is the thickness of the membrane (cm), A is the surface area of membrane in contact with the electrodes (cm^2), and R refers to the measured resistance of the membrane (Ω) which was derived from the Re (Z) axis intersect of the high frequency on a complex impedance plane.

D1 Proton conductivity under dry state compared in present work

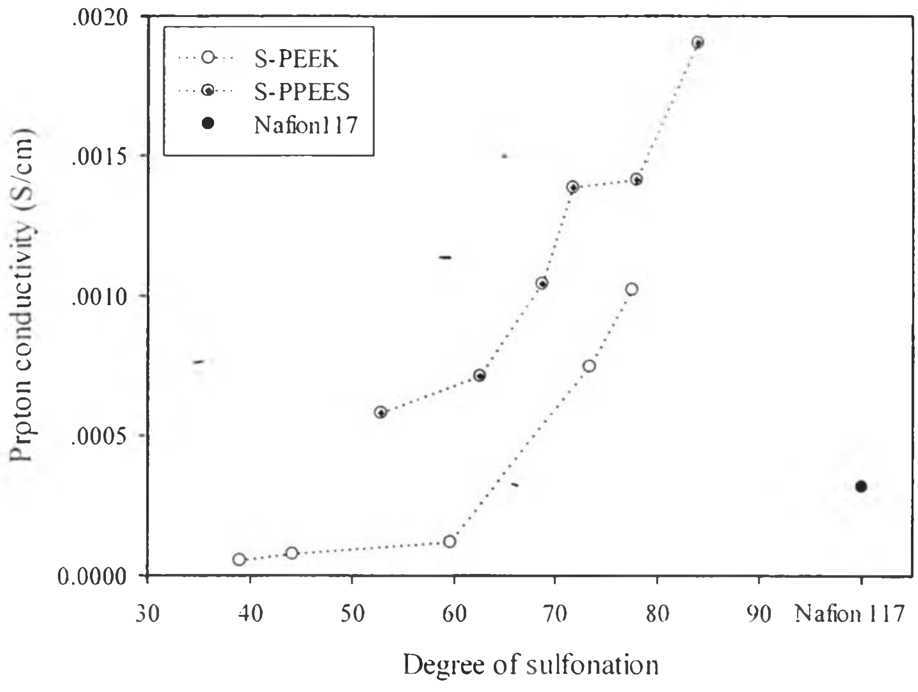

Figure D1 Effect of degree of sulfonation on the proton conductivity under dry state of S-PEEK, S-PPEES, and Nafion117.

D2 Proton conductivity under dry state of Nafion117

Table D1 Proton conductivity of Nafion117 under dry state at 25 °C

Sample	DS (%)	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Water uptake (%)	Proton conductivity ($S.cm^{-1}$)
Nafion117	-	0.0180	11.3411	5.00	6.70	3.174×10^{-4}

D3 Proton conductivity under dry state of sulfonated poly(ether ether ketone)

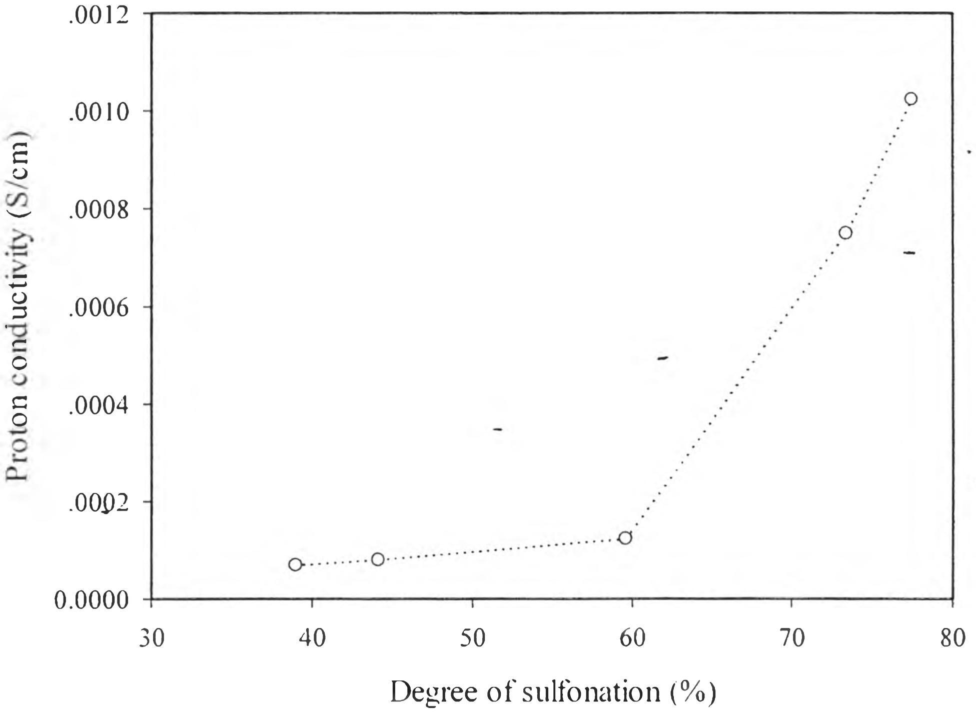

Figure D2 Effect of degree of sulfonation on the proton conductivity under dry state of S-PEEK.

Table D2 Proton conductivity of sulfonated poly(ether ether ketone) under dry state at 25 °C

Sample	DS (%)	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Water uptake (%)	Proton conductivity ($S.cm^{-1}$)
50_100_3	39.02	0.0154	11.3411	20.00	2.27	6.789×10^{-5}
50_150_3	44.14	0.0173	11.3411	19.32	9.69	7.896×10^{-5}
50_200_3	59.60	0.0131	11.3411	0.95	10.46	1.216×10^{-4}
50_200_5	73.32	0.0174	11.3411	2.05	10.85	7.484×10^{-4}
50_200_7	77.43	0.0181	11.3411	1.56	11.04	1.023×10^{-3}

D4 Proton conductivity under dry state of sulfonated poly(phenylene ether ether sulfone)

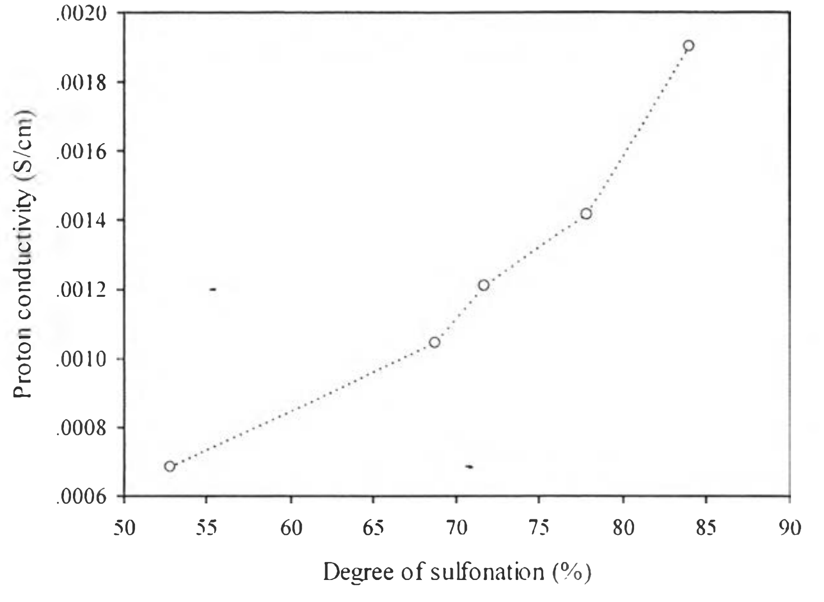

Figure D3 Proton conductivity under dry state of sulfonated poly(phenylene ether ether sulfone) under dry state at 25 °C.

Table D3 Proton conductivity of sulfonated poly(phenylene ether ether sulfone) under dry state at 25 °C

Sample	DS (%)	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Water uptake (%)	Proton conductivity ($S.cm^{-1}$)
25_100_12	52.81	0.0132	11.3411	1.70	6.63	6.847×10^{-4}
25_100_18	62.53	0.0223	11.3411	2.75	7.54	7.150×10^{-4}
25_100_24	68.73	0.0192	11.3411	1.62	8.30	1.045×10^{-3}
25_100_30	71.69	0.0151	11.3411	1.10	9.64	1.210×10^{-3}
25_100_36	77.88	0.0194	11.3411	1.21	9.71	1.414×10^{-3}
25_100_48	83.99	0.0192	11.3411	0.89	9.99	1.902×10^{-3}

D5 Complex impedance plane of sulfonated poly(ether ether ketone)

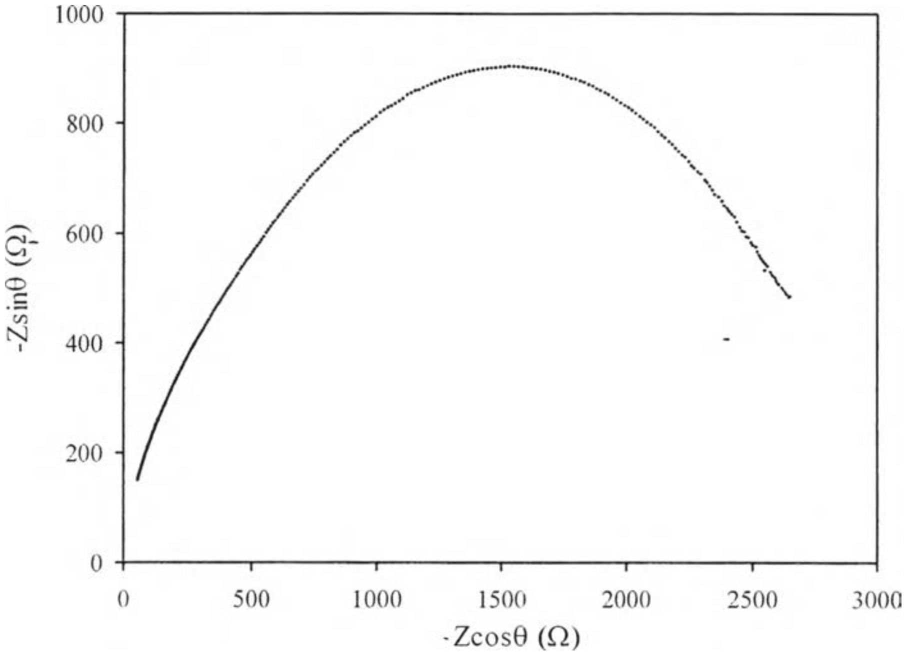

Figure D4 Proton conductivity of S-PEEK (DS=39.02%).

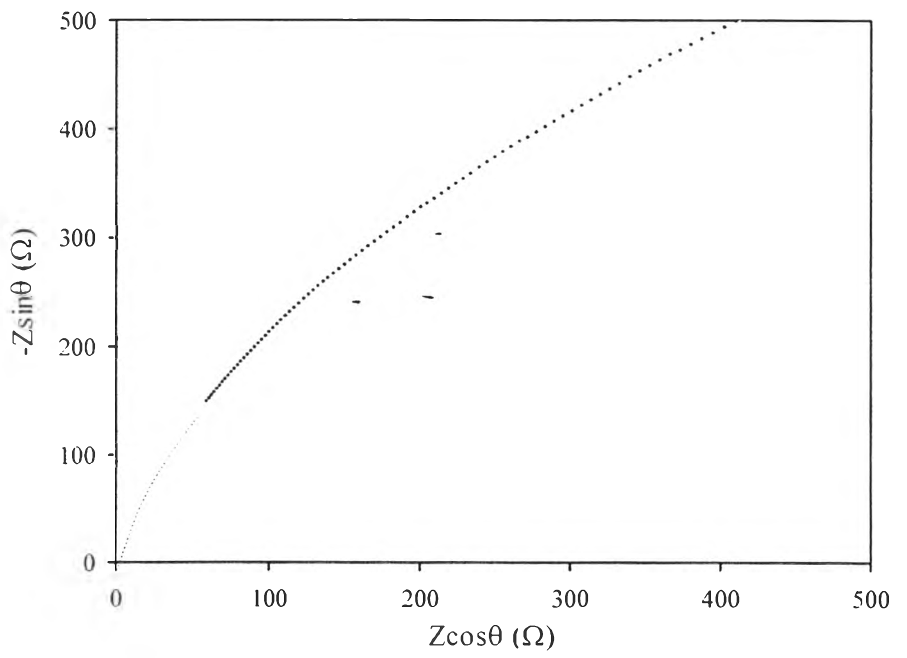

Figure D5 X-intercept at the high frequency of S-PEEK (DS=39.02%).

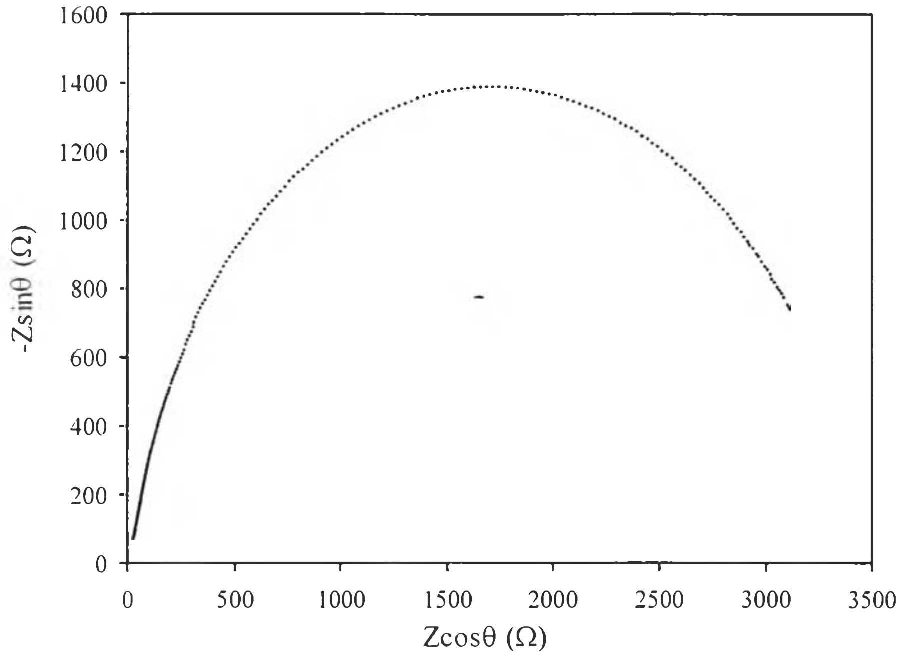

Figure D6 Proton conductivity of S-PEEK (DS=44.14%).

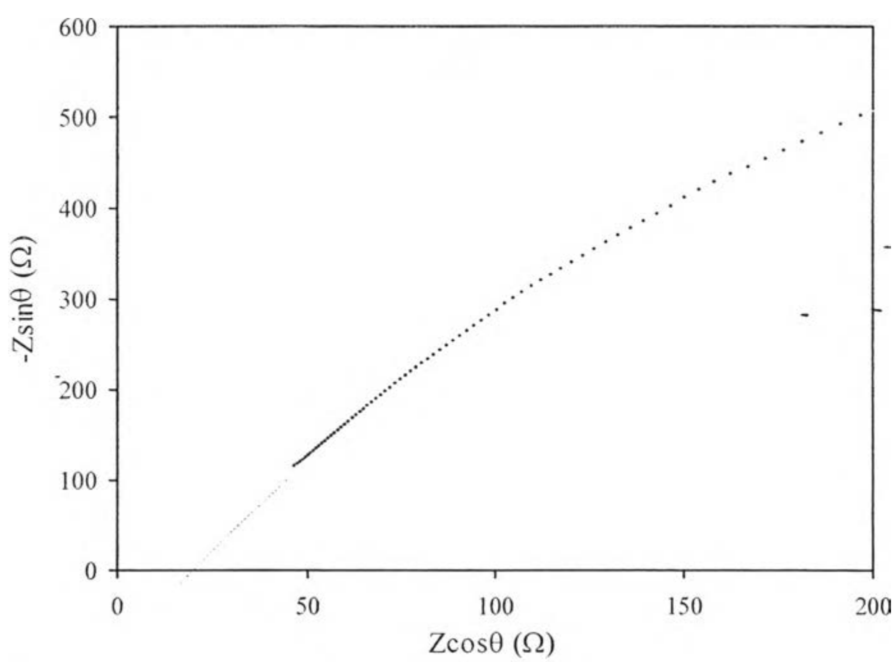

Figure D7 X-intercept at the high frequency of S-PEEK (DS=44.14%).

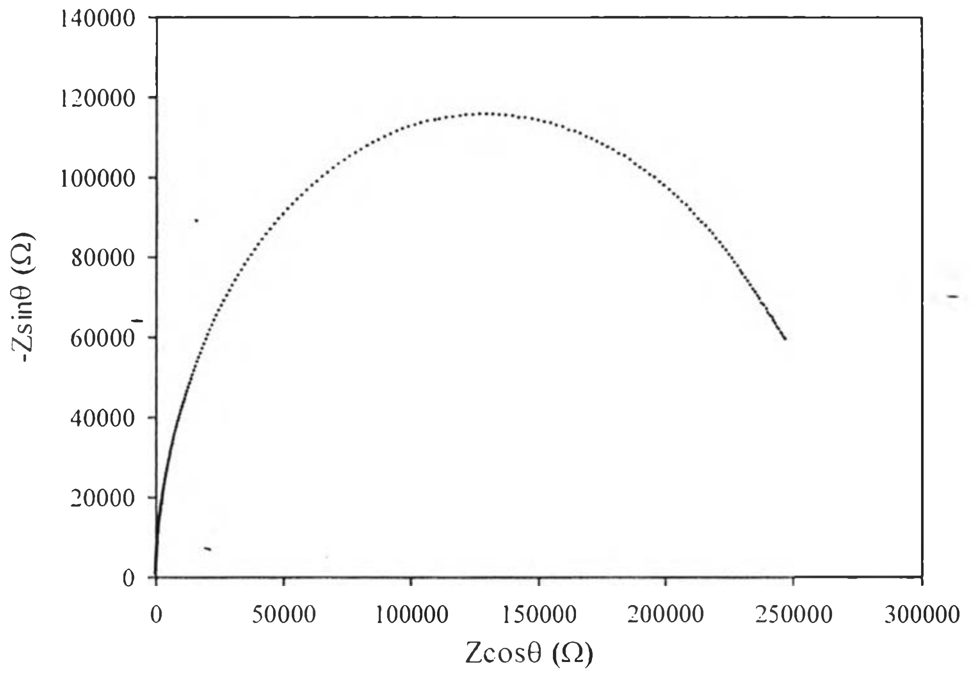

Figure D8 Proton conductivity of S-PEEK (DS=59.60%).

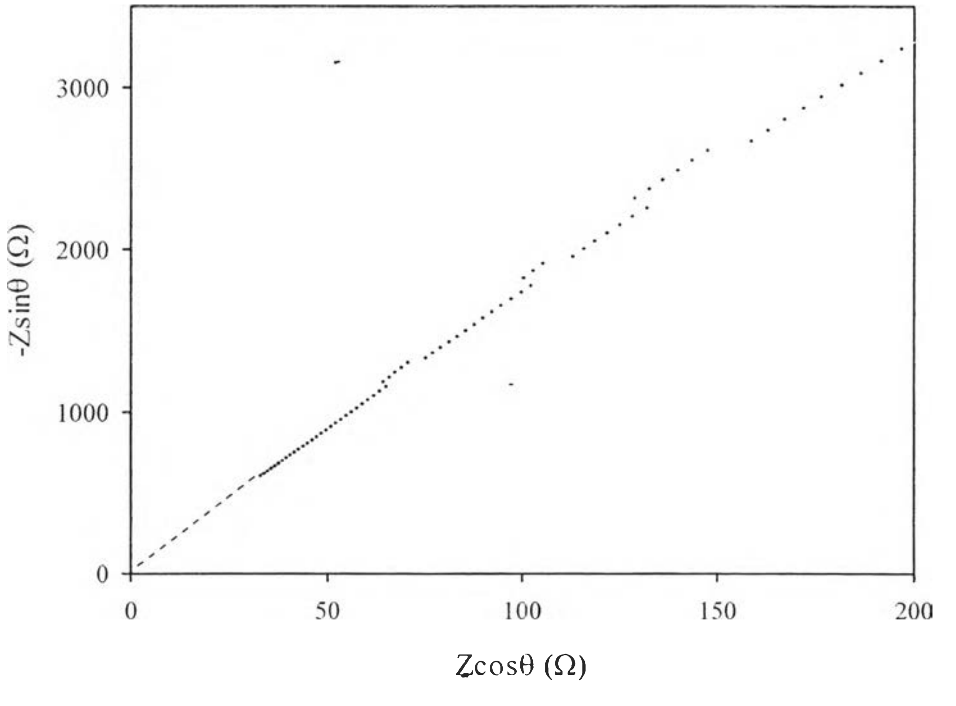

Figure D9 X-intercept at the high frequency of S-PEEK (DS=59.60%).

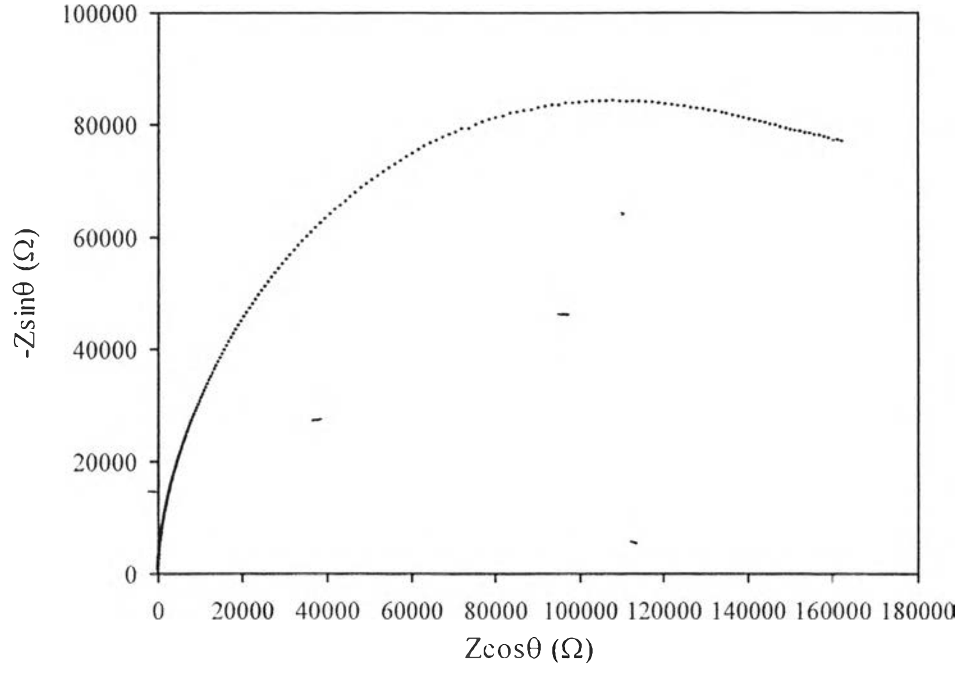

Figure D10 Proton conductivity of S-PEEK (DS=73.32%).

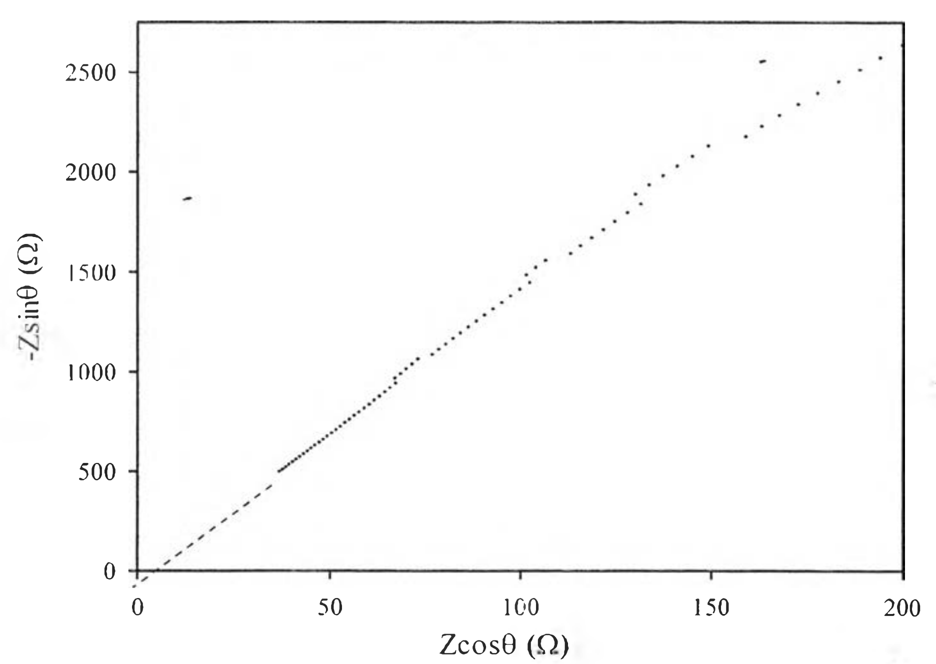

Figure D11 X-intercept at the high frequency of S-PEEK (DS=73.32%).

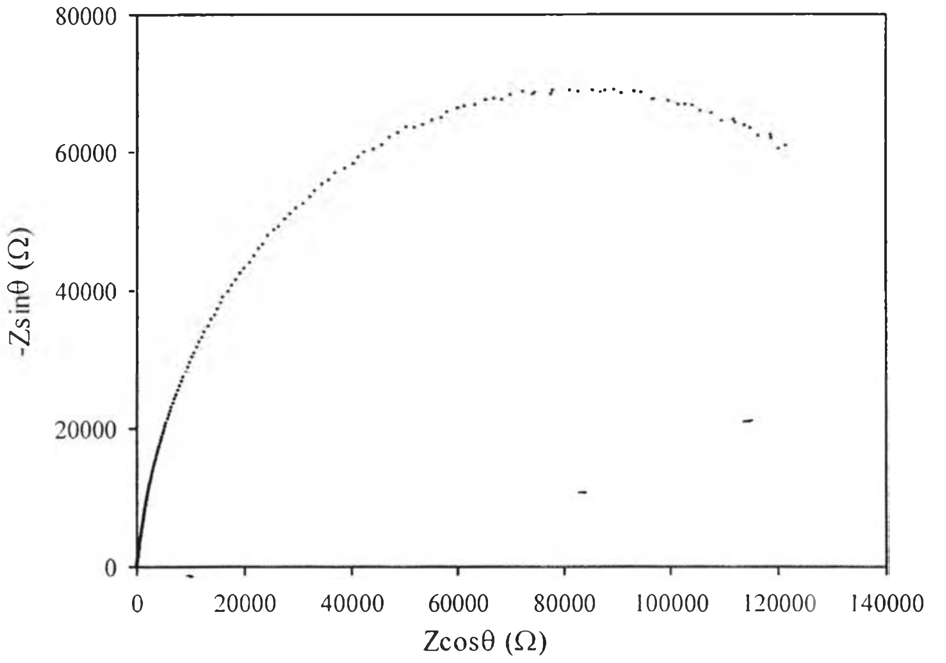

Figure D12 Proton conductivity of S-PEEK (DS=77.43%).

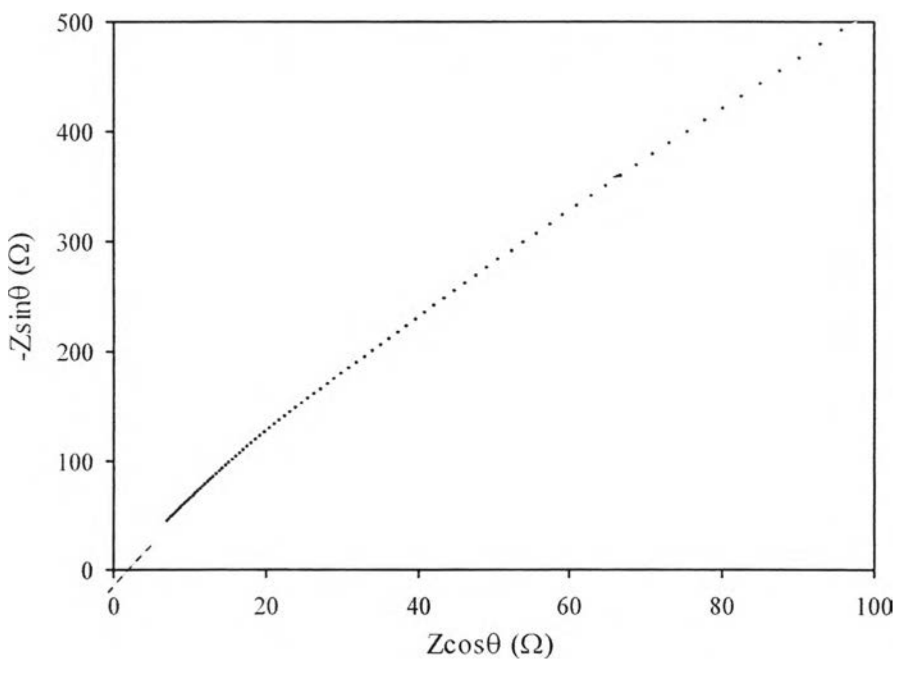

Figure D13 X-intercept at the high frequency of S-PEEK (DS=77.43%).

D6 Complex impedance plane of sulfonated poly(phenylene ether ether sulfone)

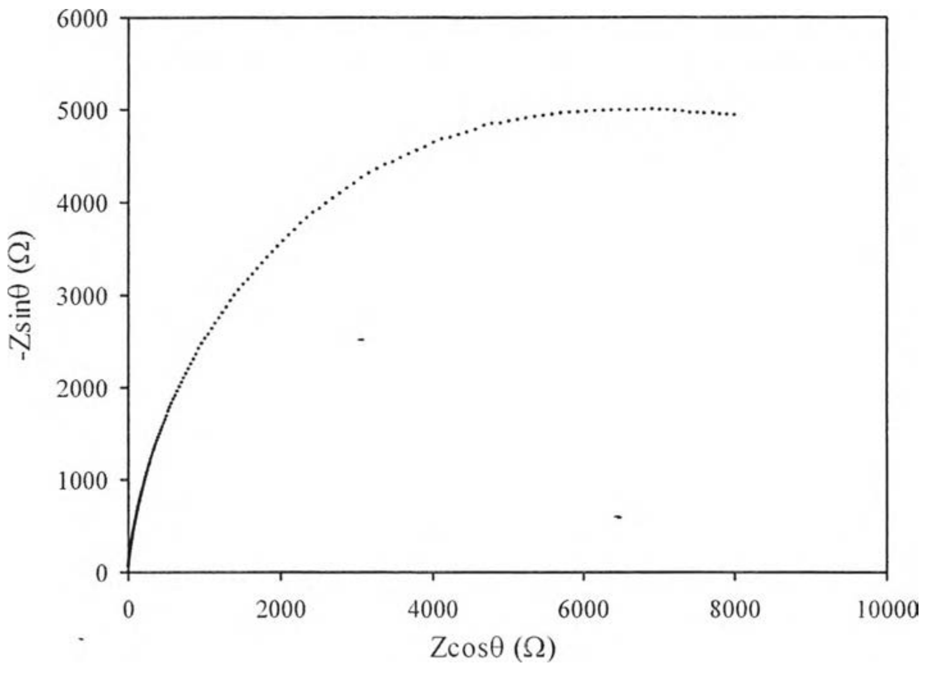

Figure D14 Nyquist plot of S-PPEES (DS=52.81%).

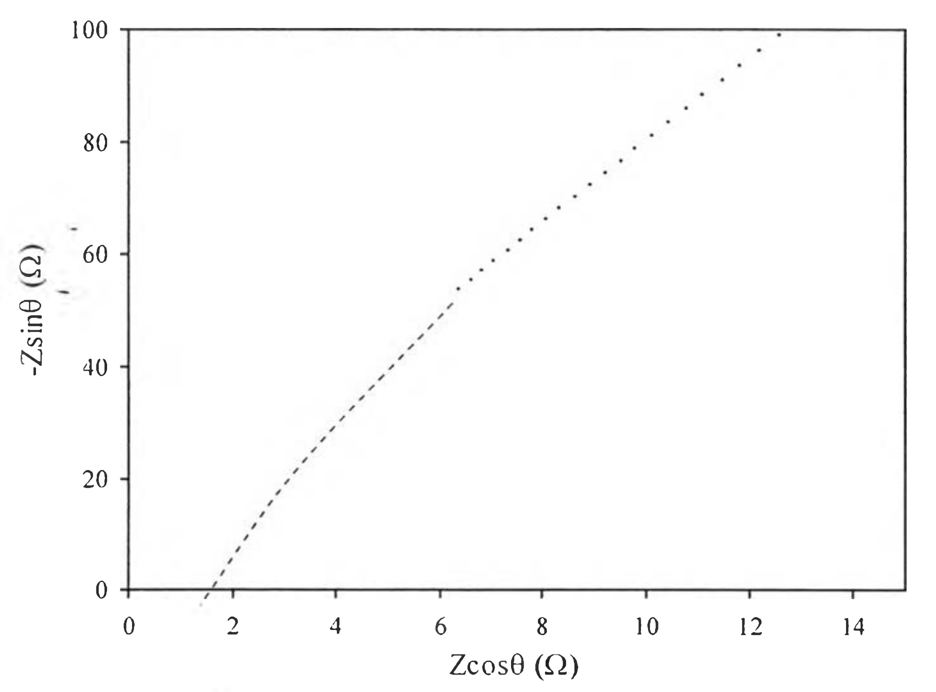

Figure D15 X-intercept at the high frequency of S-PPEES (DS=52.81%).

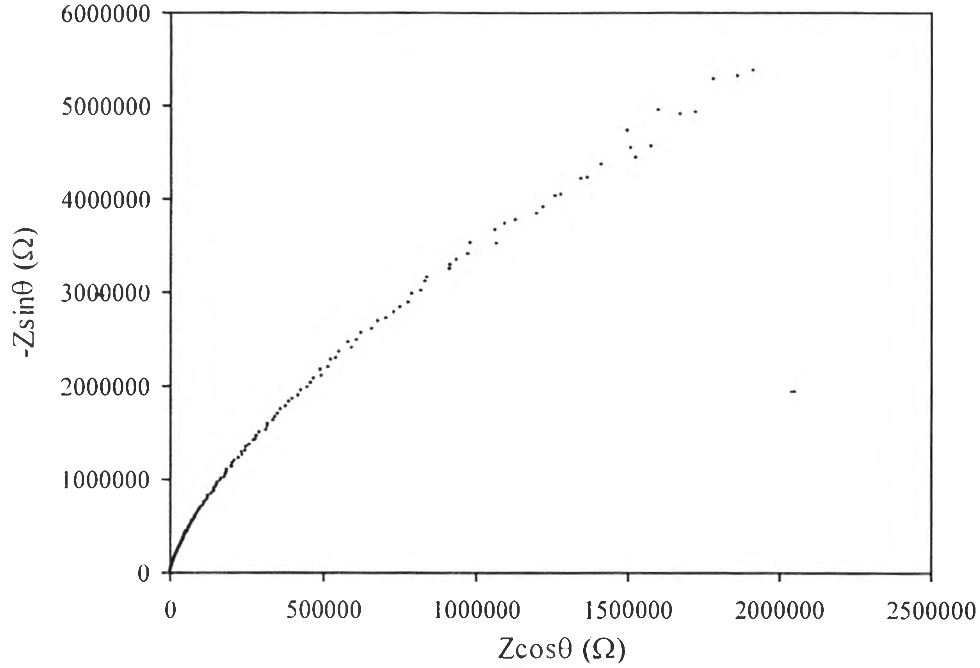

Figure D16 Proton conductivity of S-PPEES (DS=62.53%).

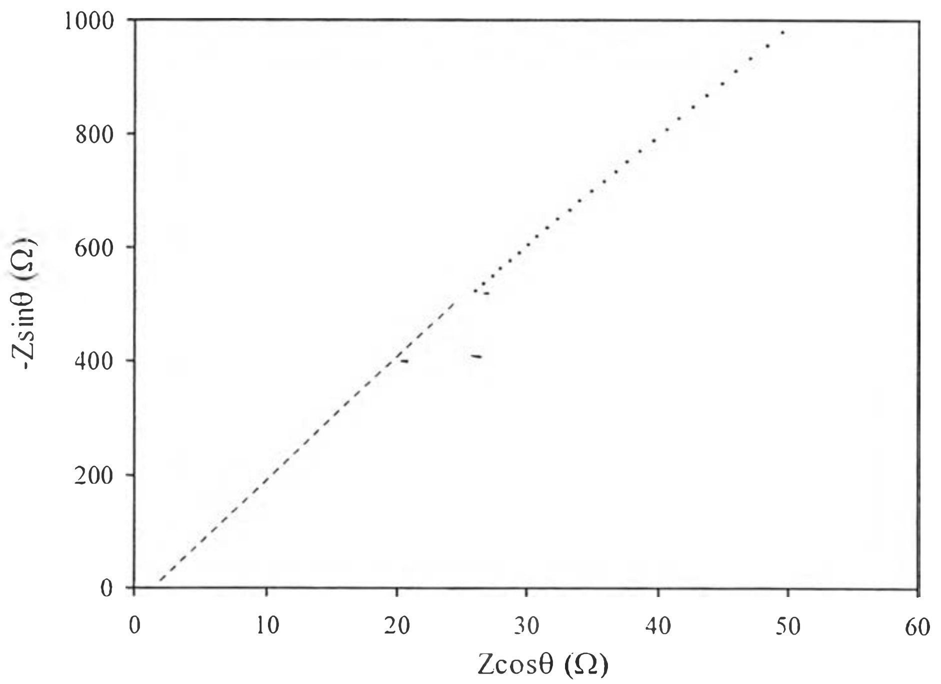

Figure D17 X-intercept at the high frequency of S-PPEES (DS=62.53%).

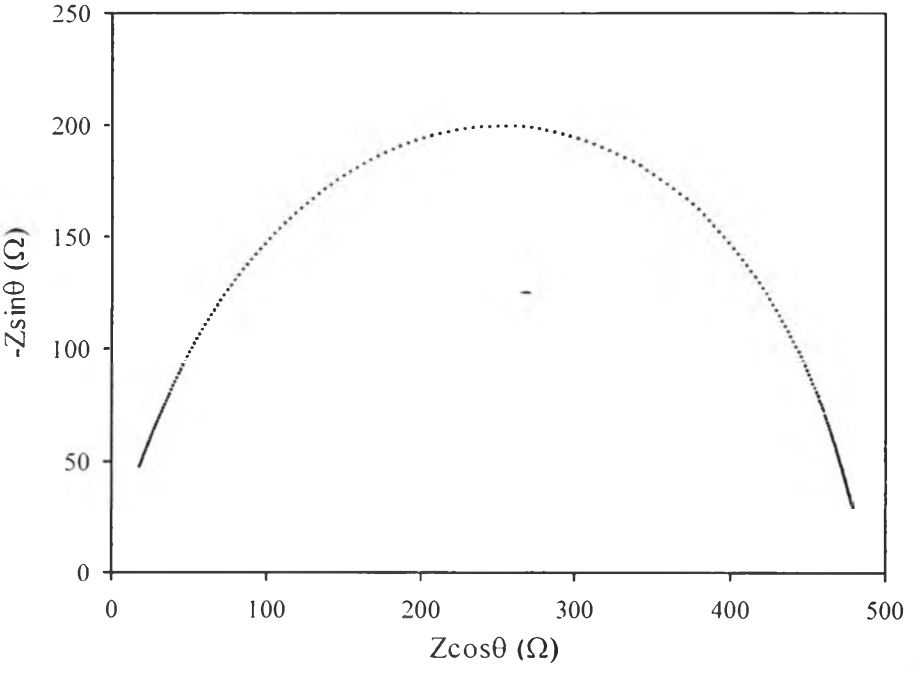

Figure D18 Nyquist plot of S-PPEES (DS=68.73%).

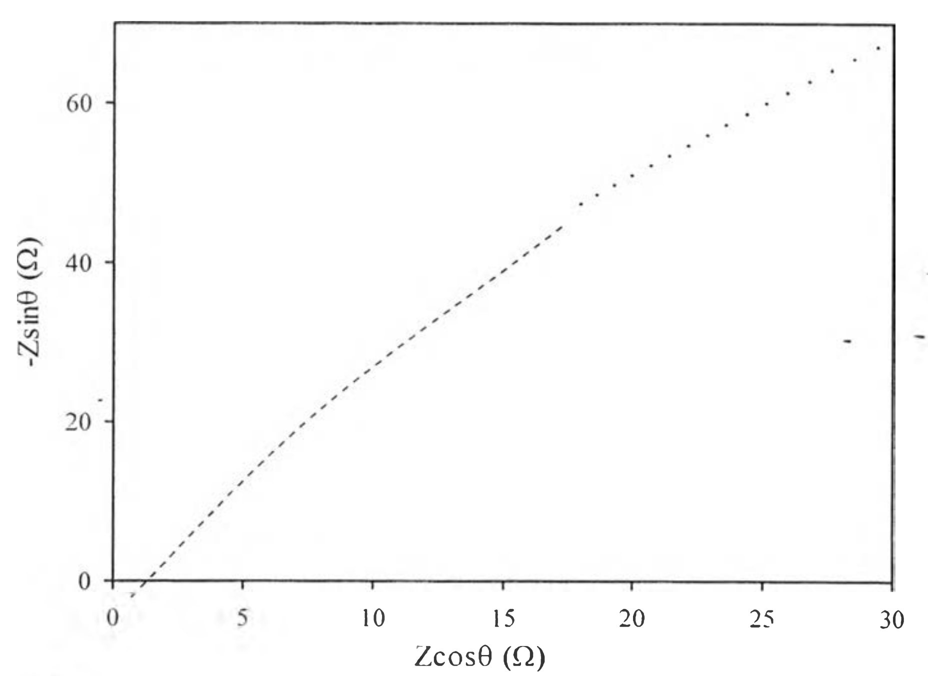

Figure D19 X-intercept at the high frequency of S-PPEES (DS=68.73%).

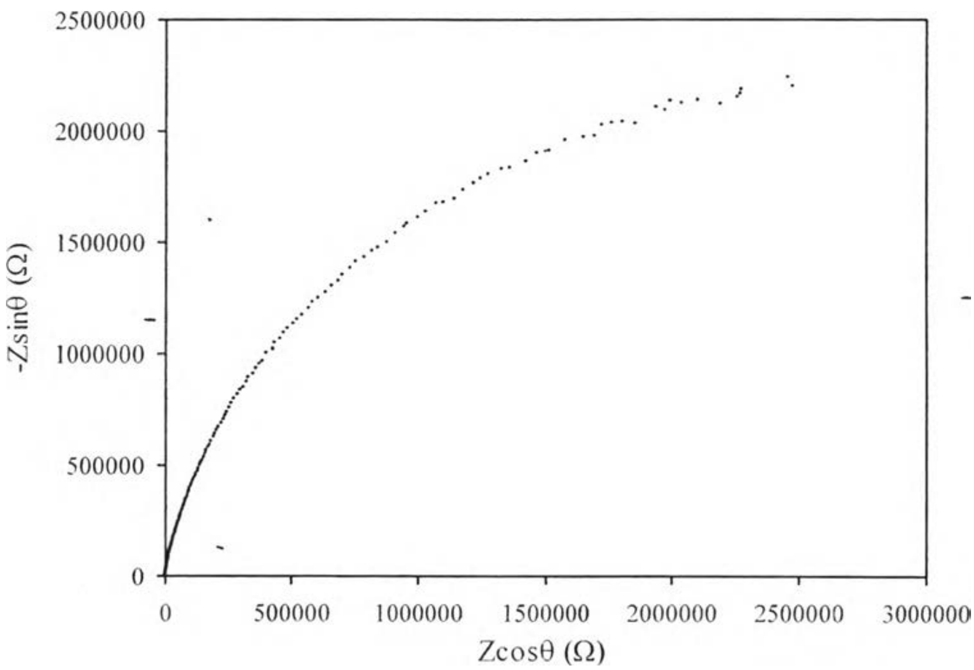

Figure D20 Nyquist plot of S-PPEES (DS=71.69%).

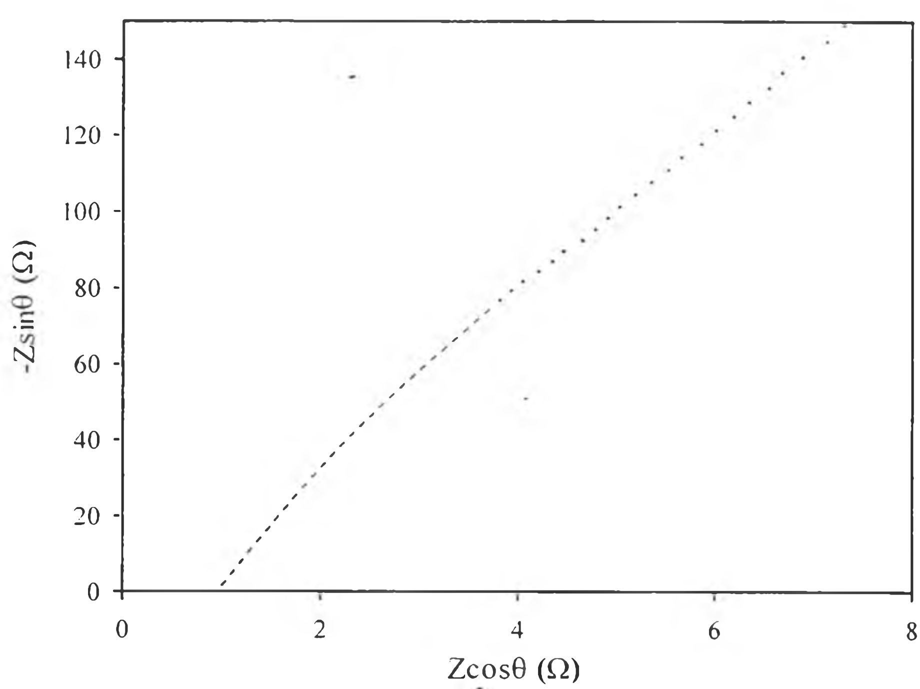

Figure D21 X-intercept at the high frequency of S-PPEES (DS=71.69%).

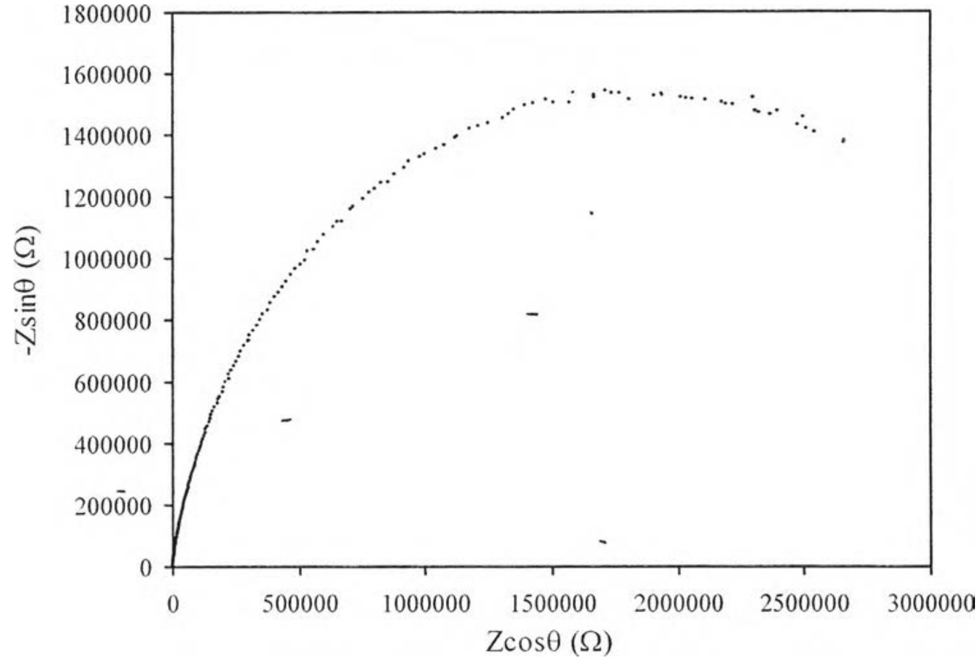

Figure D22 Nyquist plot of S-PPEES (DS=77.88%).

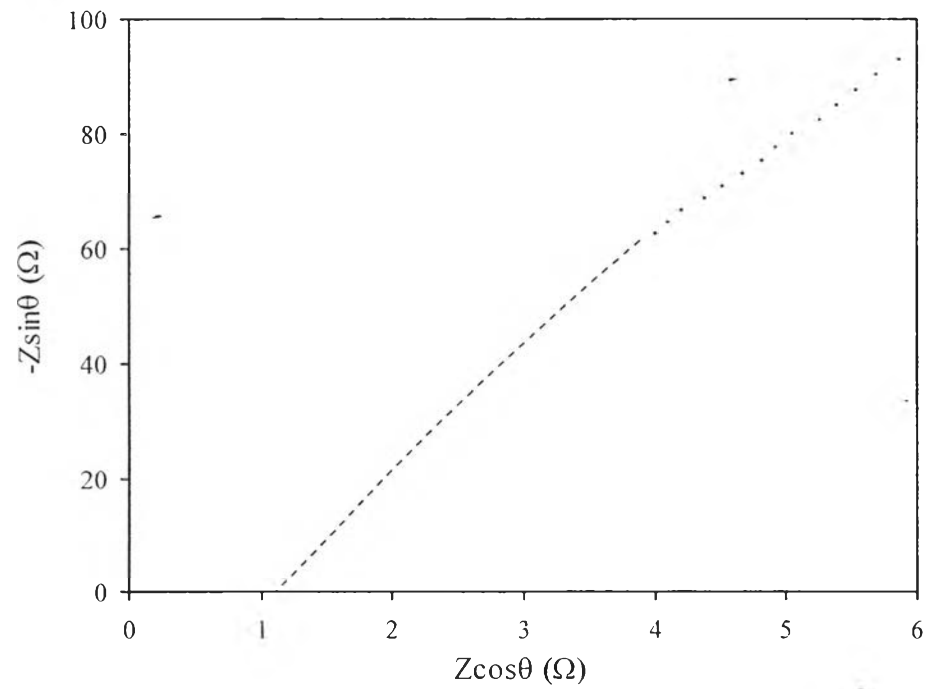

Figure D23 X-intercept at the high frequency of S-PPEES (DS=77.88%).

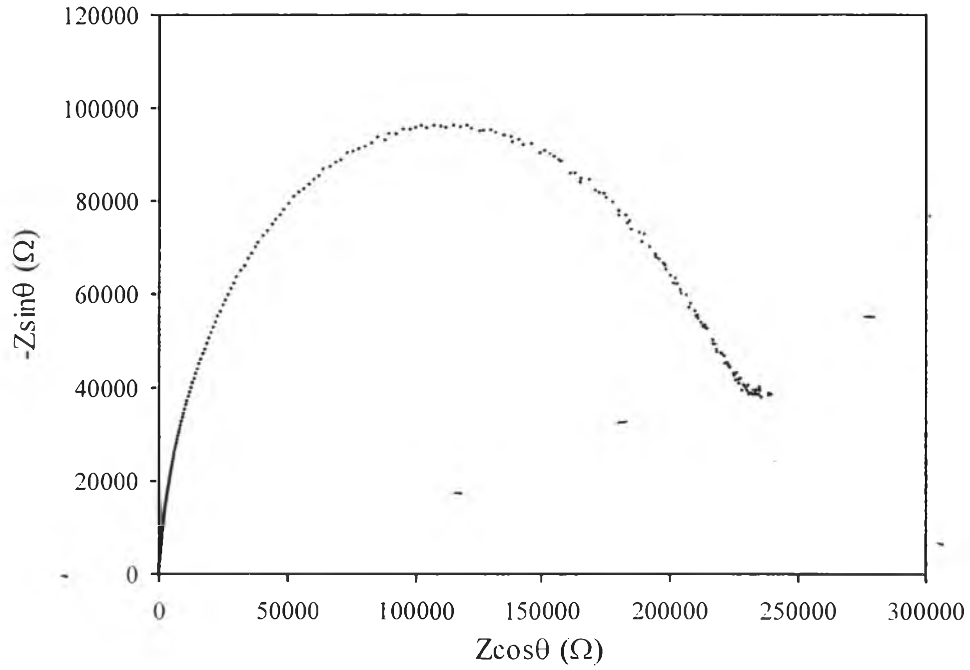

Figure D24 Nyquist plot of S-PPEES (DS=83.99%).

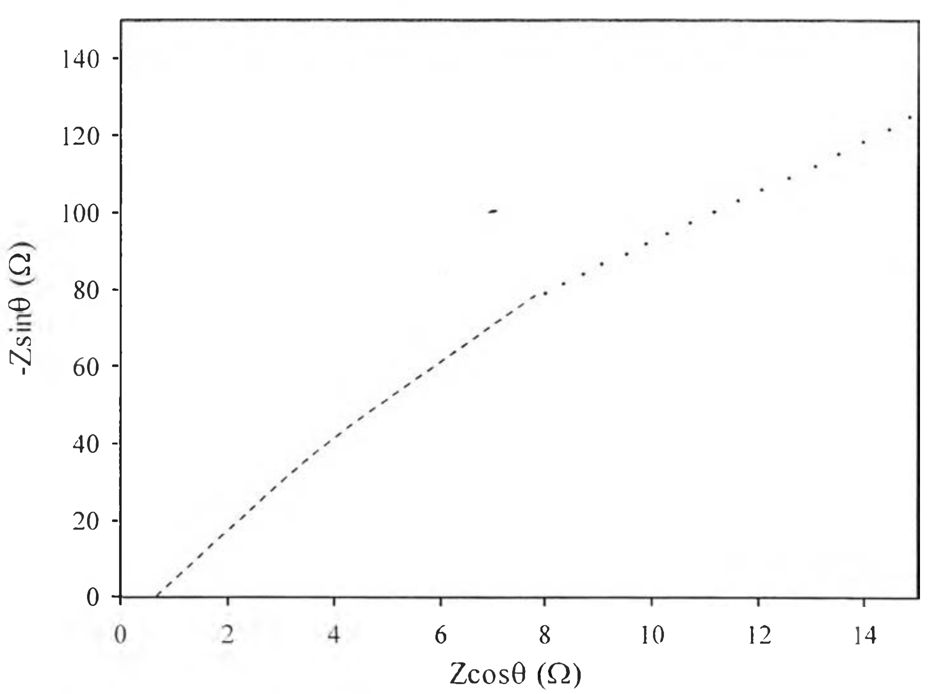

Figure D25 X-intercept at the high frequency of S-PPEES (DS=83.99%).

D7 Complex impedance plane of Nafion 117

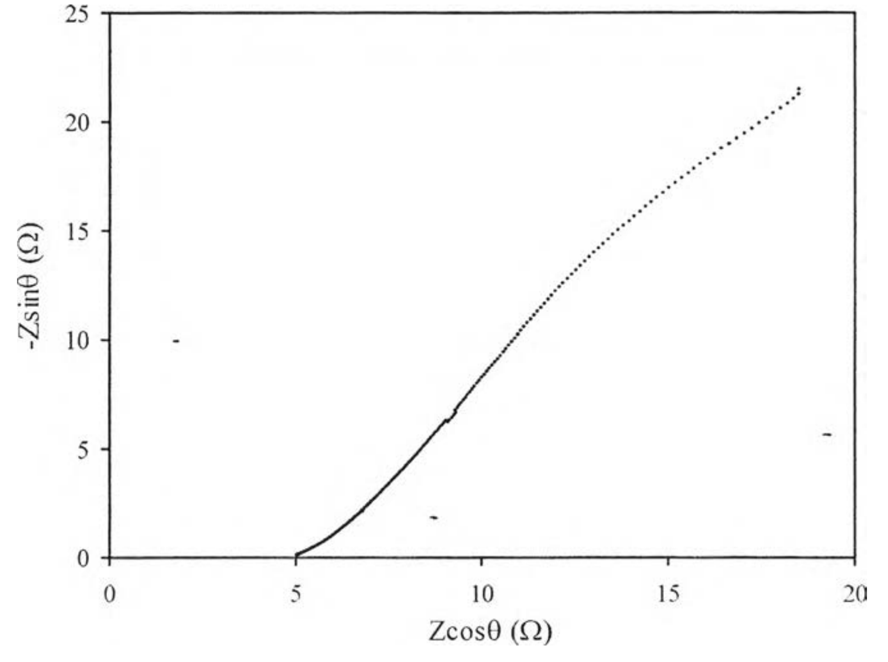

Figure D26 Proton conductivity of Nafion117.

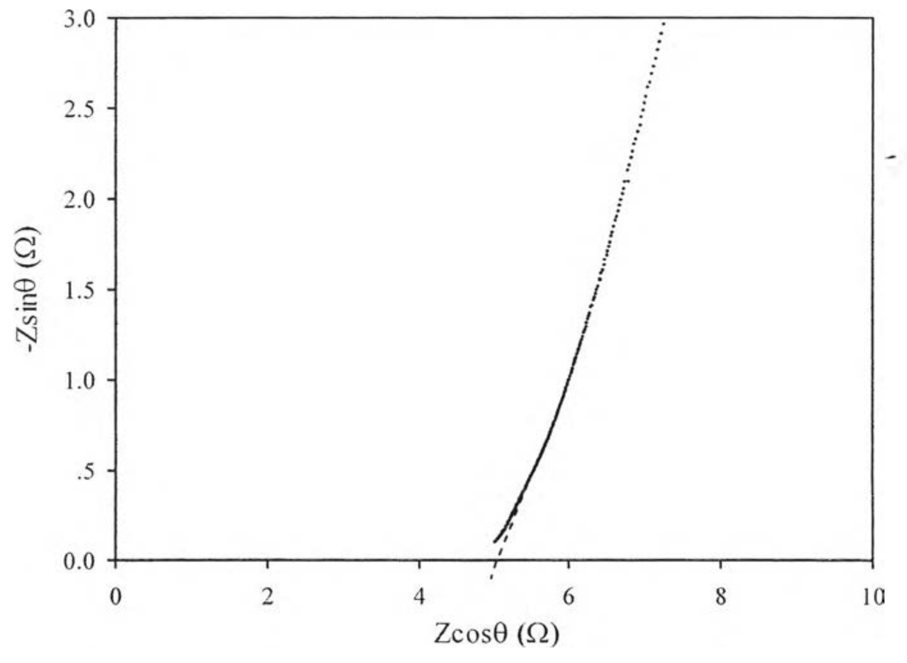

Figure D27 X-intercept at the high frequency of Nafion117.

Appendix E Proton Conductivity under Wet State

Proton conductivity of the membrane was determined by an impedance phase analyser HP 4194 under wet state at 25 °C. The 5 cm × 5 cm film after immersed in deionized water at room temperature for 24 h was measured at 1 V potential using the alternating current in the frequency range of 100 Hz – 2 MHz. The graphs show the relationship between the real impedance (Zcosθ) and the imaginary impedance (-Zsinθ). The proton conductivity (σ) was calculated using Eq. (E1):

$$\sigma = \frac{d}{R \times A} \text{ (S/cm)} \qquad \text{(E1)}$$

where σ is the proton conductivity (S/cm), d is the thickness of the membrane (cm), A is the surface area of membrane in contact with the electrodes (cm^2), and R refers to the measured resistance of the membrane (Ω) which was derived from the Re (Z) axis intersect of the high frequency on a complex impedance plane.

E1 Proton conductivity under wet state compared with previous work

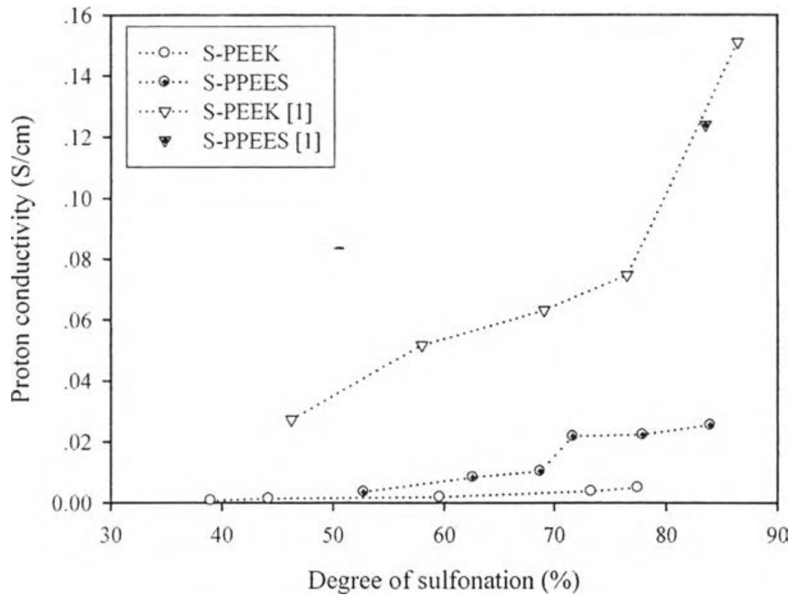

Figure E1 Comparison of proton conductivity under wet state at 25 °C.

[1] Macksasitorn (2012) sulfonated PEEK and PPEES at 25 °C

Table E1 Comparison of proton conductivity

Polymer	Degree of sulfonation (%)	Proton conductivity ($S.cm^{-1}$)	water uptake (%)	Reference
S-PEEK	46.21	2.72×10^{-2}	15.54	[1]
S-PEEK	57.99	5.17×10^{-2}	30.57	[1]
S-PEEK	69.07	6.31×10^{-2}	27.16	[1]
S-PEEK	76.49	7.47×10^{-2}	67.65	[1]
S-PEEK	86.49	1.51×10^{-1}	83.02	[1]
S-PEEK	39.02	7.1452×10^{-4}	30.38	
S-PEEK	44.14	1.2857×10^{-3}	31.16	
S-PEEK	59.60	1.8300×10^{-3}	39.24	
S-PEEK	73.32	3.7179×10^{-3}	48.97	
S-PEEK	77.43	4.8971×10^{-3}	53.61	
S-PPEES	83.57	1.24×10^{-1}	121.93	[1]
S-PPEES	52.81	3.556×10^{-3}	73.02	
S-PPEES	62.53	8.277×10^{-3}	79.72	
S-PPEES	68.73	1.026×10^{-2}	87.24	
S-PPEES	71.69	2.176×10^{-2}	92.04	
S-PPEES	77.88	2.229×10^{-2}	98.40	
S-PPEES	83.99	2.547×10^{-2}	107.89	

[1] Macksasitorn (2012) sulfonated PEEK and PPEES at 25 °C

E2 Proton conductivity under wet state compared in present work

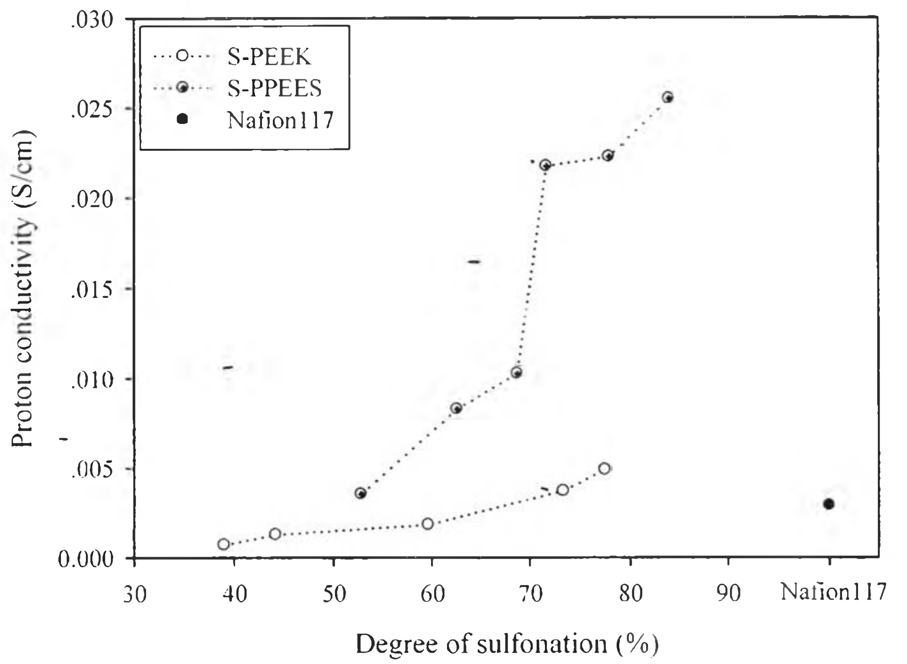

Figure E2 Effect of degree of sulfonation on the proton conductivity under wet state of S-PEEK, S-PPEES, and Nafion117.

Table E2 Proton conductivity of Nafion117 under wet state at 25 °C

Sample	DS (%)	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Water uptake (%)	Proton conductivity ($S.cm^{-1}$)
Nafion117	-	0.0193	11.3411	0.59	16.30	2.8942×10^{-3}

E3 Proton conductivity of sulfonated poly(ether ether ketone) under wet state

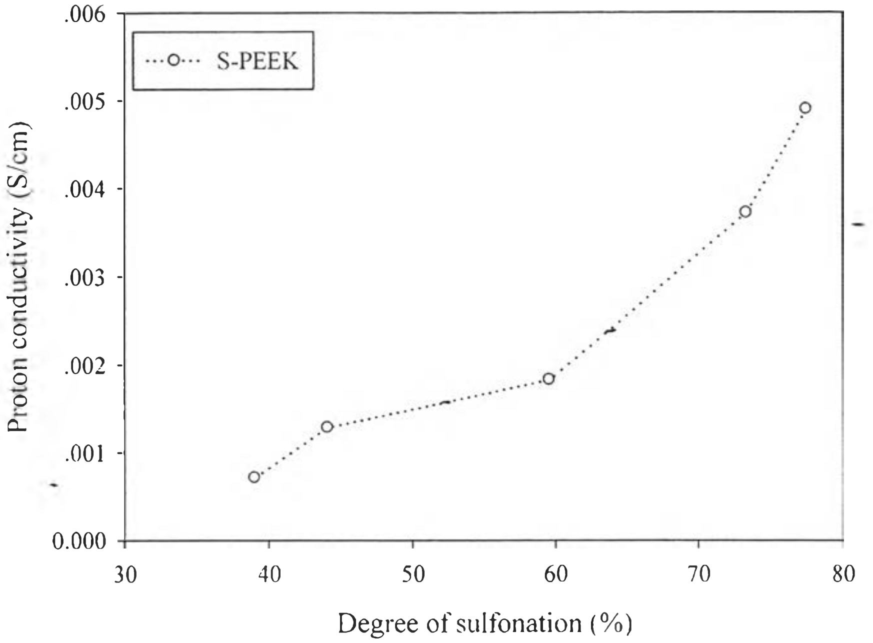

Figure E3 Effect of degree of sulfonation on the proton conductivity under wet state of S-PEEK.

Table E3 Proton conductivity of sulfonated poly(ether ether ketone) under wet state at 25 °C

Sample	DS (%)	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Water uptake (%)	Proton conductivity (S/cm)
50_100_3	39.02	0.0191	11.3411	2.357	30.38	7.1452×10^{-4}
50_150_3	44.14	0.0183	11.3411	1.255	31.16	1.2857×10^{-3}
50_200_3	59.60	0.0253	11.3411	1.219	39.24	1.8300×10^{-3}
50_200_5	73.32	0.0246	11.3411	0.585	48.97	3.7179×10^{-3}
50_200_7	77.43	0.0266	11.3411	0.480	53.61	4.8971×10^{-3}

E4 Proton conductivity of sulfonated sulfonated poly(phenylene ether ether sulfone) under wet state

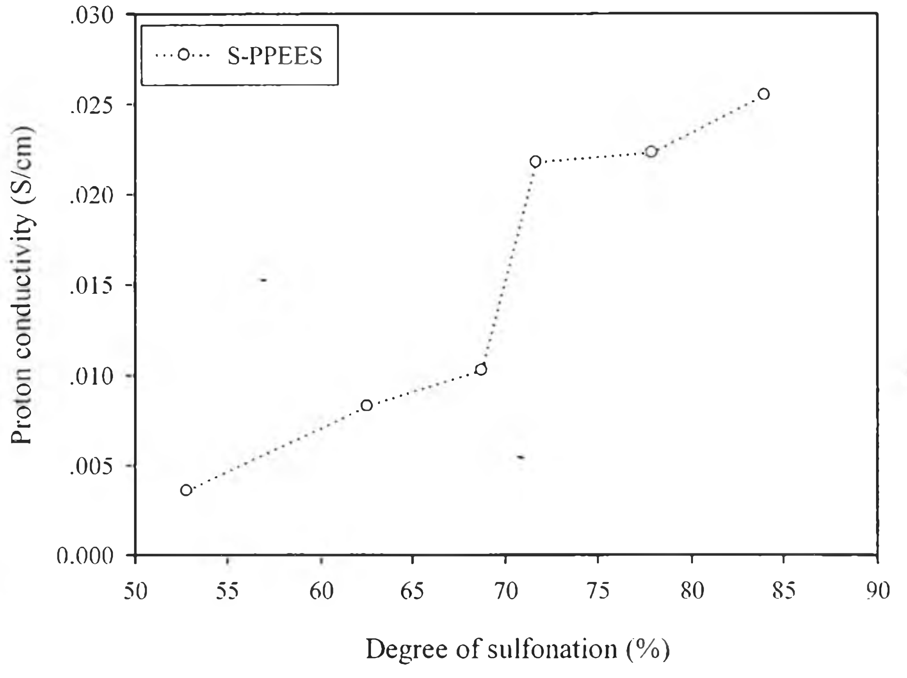

Figure E4 Effect of degree of sulfonation on the proton conductivity under wet state of S-PPEES.

Table E4 Proton conductivity of sulfonated poly(phenylene ether ether sulfone) under wet state at 25 °C

Sample	DS (%)	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Water uptake (%)	Proton conductivity ($S.cm^{-1}$)
25_100_12	52.81	0.0213	11.3411	5.28	73.02	3.556×10^{-3}
25_100_18	62.53	0.0268	11.3411	2.86	79.72	8.277×10^{-3}
25_100_24	68.73	0.0235	11.3411	2.02	87.24	1.026×10^{-2}
25_100_30	71.69	0.0227	11.3411	0.92	92.04	2.176×10^{-2}
25_100_36	77.88	0.0154	11.3411	0.61	98.40	2.229×10^{-2}
25_100_48	83.99	0.0255	11.3411	0.89	107.89	2.547×10^{-2}

E5 Complex impedance plane of sulfonated poly(ether ether ketone)

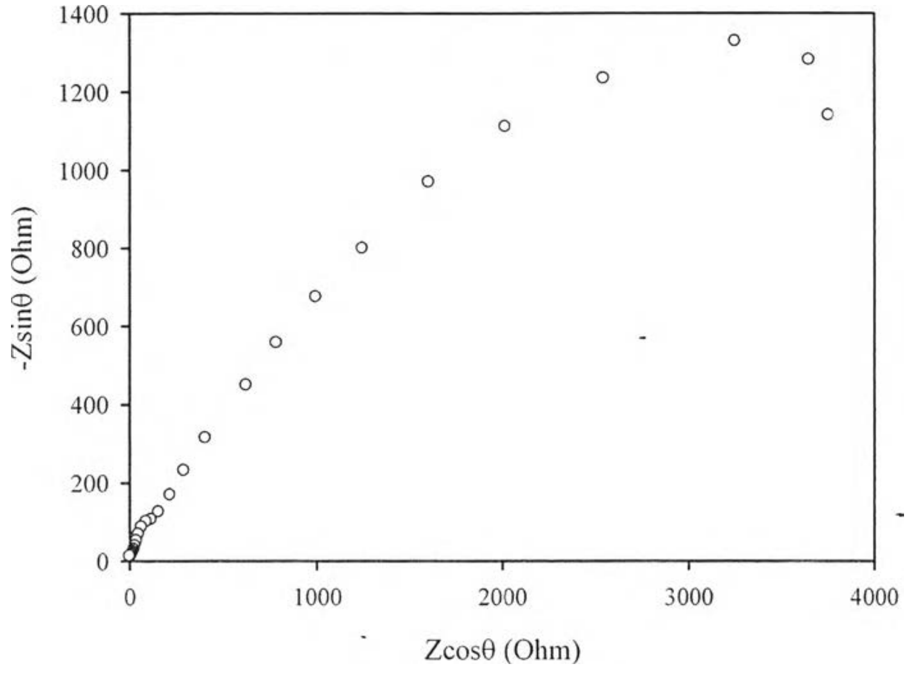

Figure E5 Nyquist plot of S-PEEK (DS=39.02%).

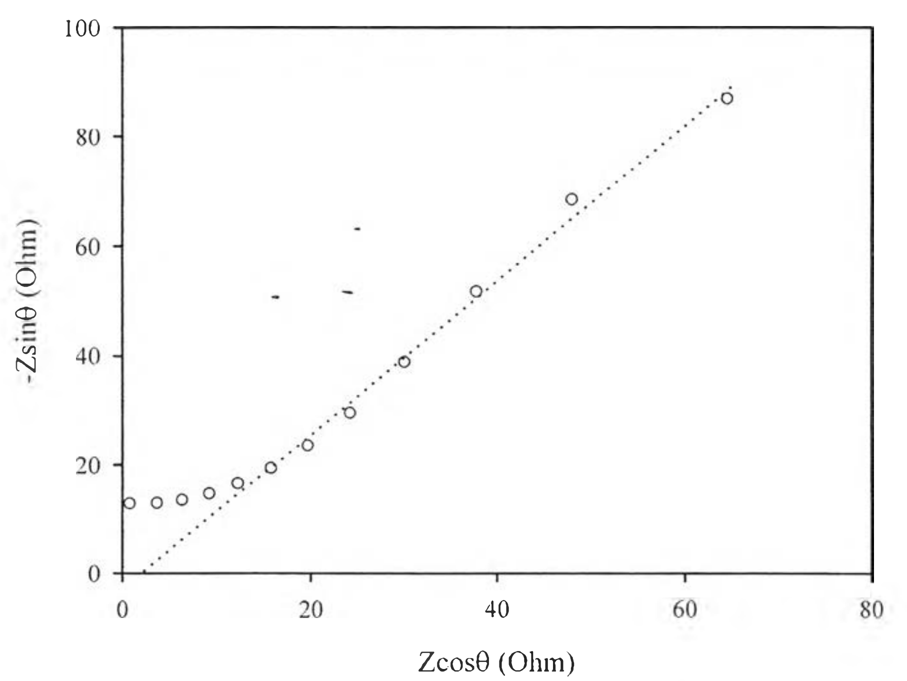

Figure E6 Nyquist plot of S-PEEK (DS=39.02%).

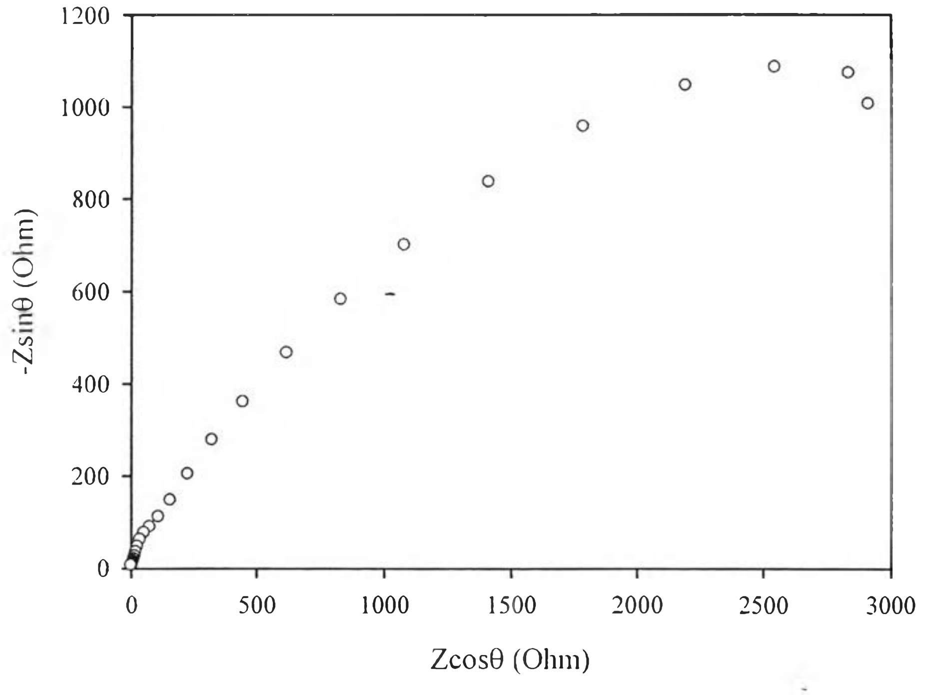

Figure E7 Nyquist plot of S-PEEK (DS=44.14%).

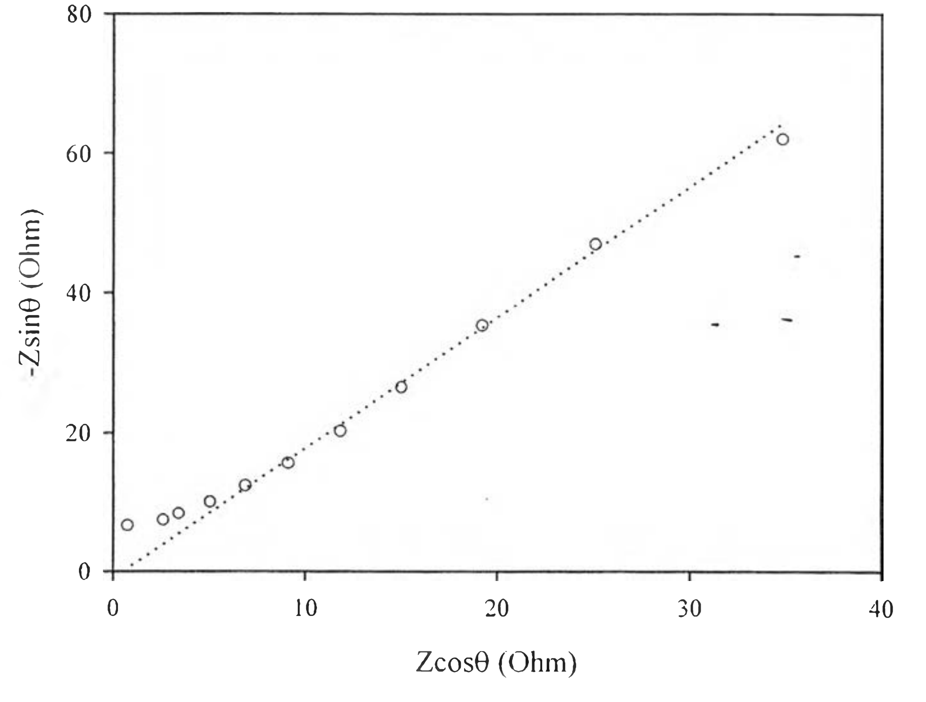

Figure E8 Nyquist plot of S-PEEK (DS=44.14%).

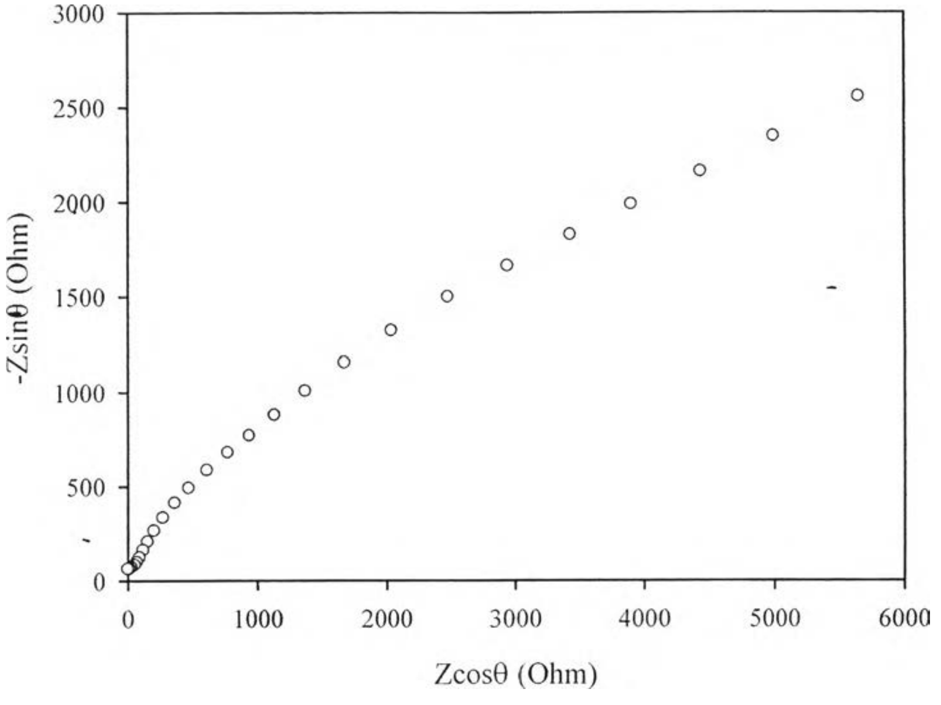

Figure E9 Nyquist plot of S-PEEK (DS=59.60%).

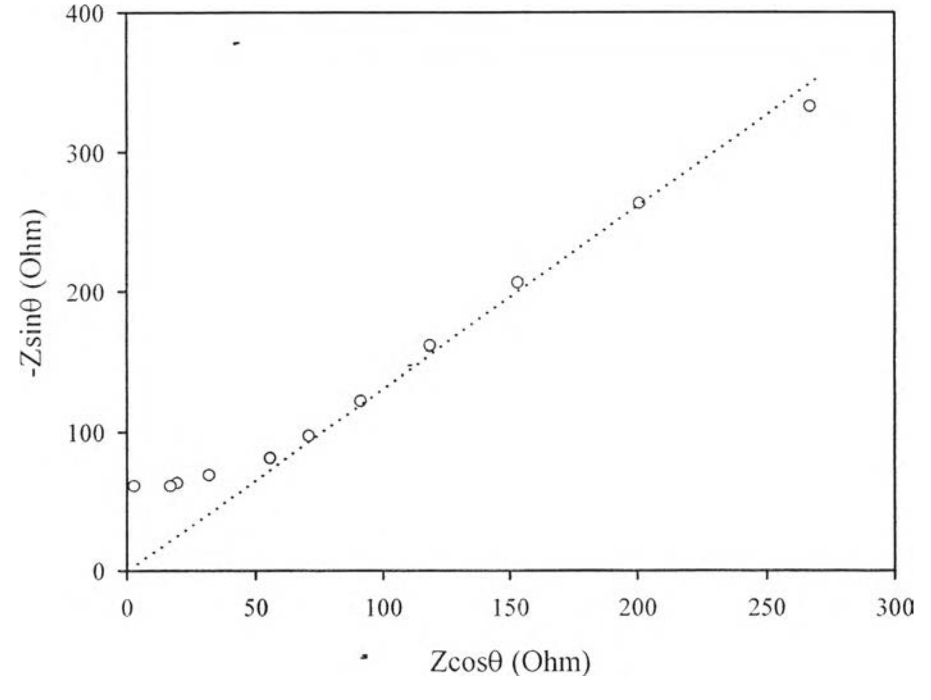

Figure E10 Nyquist plot of S-PEEK (DS=59.60%).

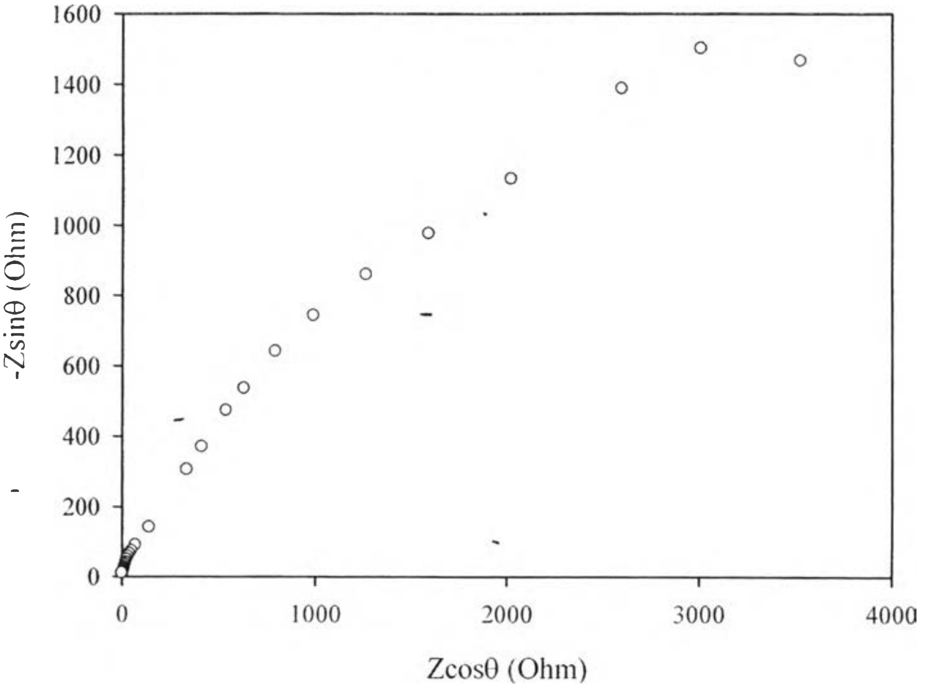

Figure E11 Nyquist plot of S-PEEK (DS=73.32%).

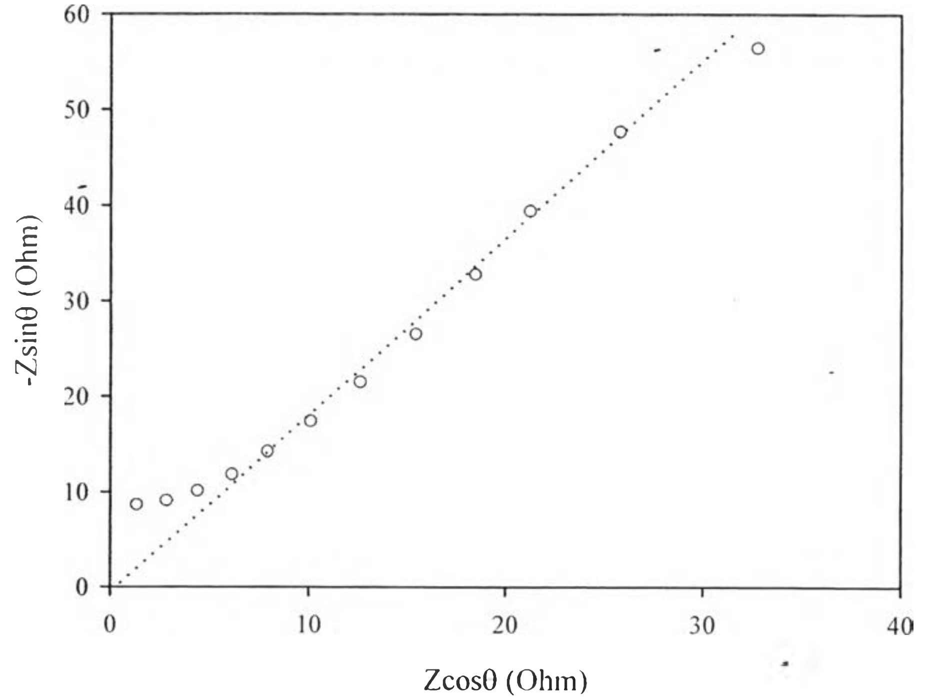

Figure E12 Nyquist plot of S-PEEK (DS=73.32%).

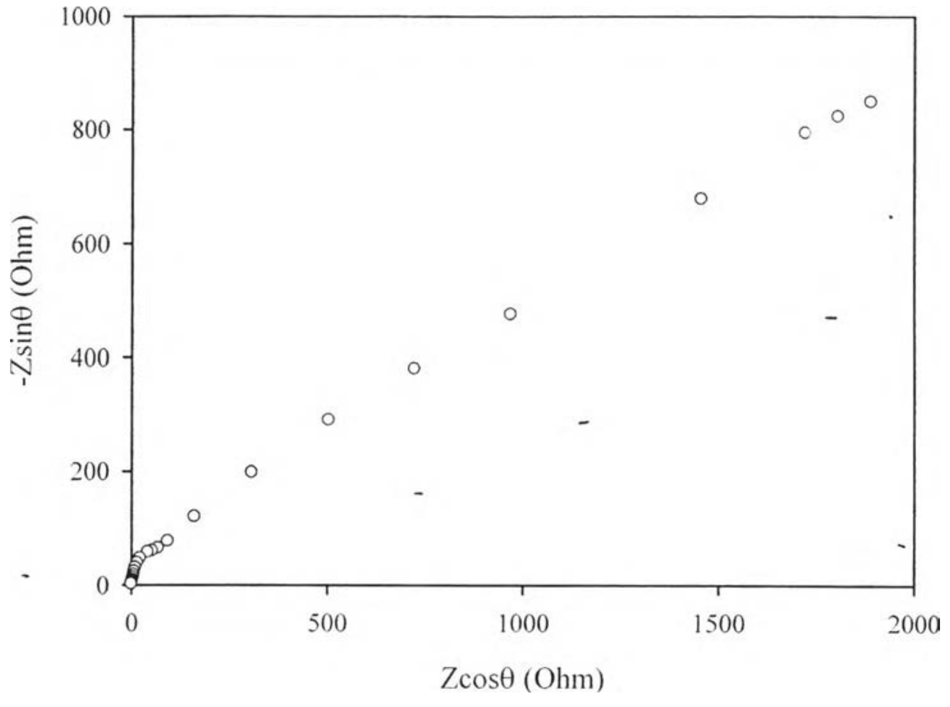

Figure E13 Nyquist plot of S-PEEK (DS=77.43%).

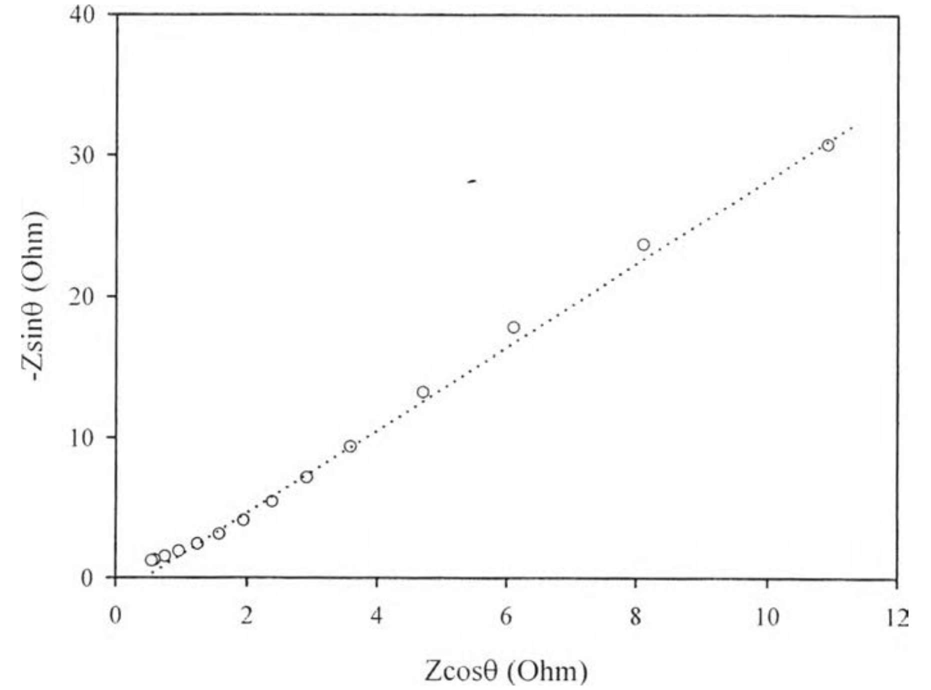

Figure E14 Nyquist plot of S-PEEK (DS=77.43%).

E5 Complex impedance plane of sulfonated poly(phenylene ether ether sulfone)

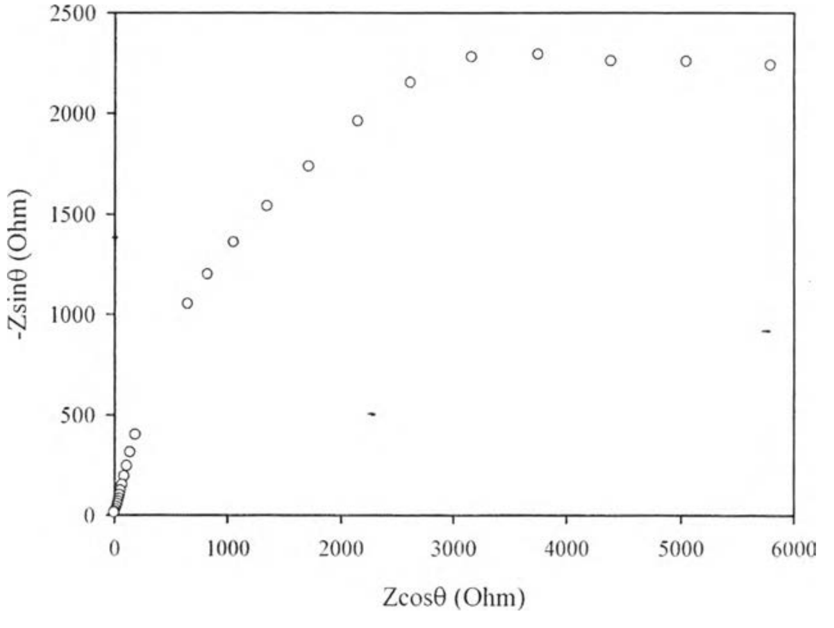

Figure E15 Nyquist plot of S-PPEES (DS=52.81%).

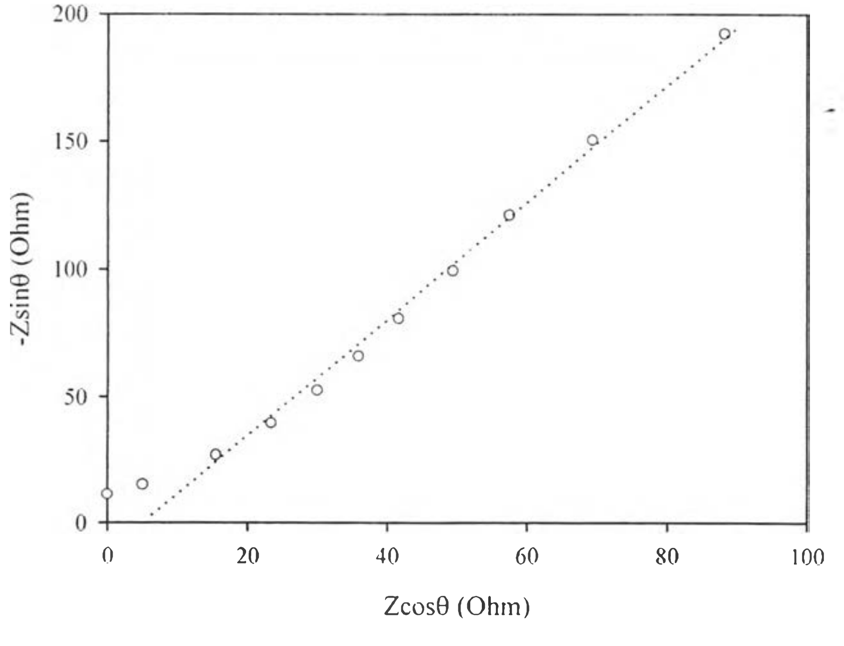

Figure E16 Nyquist plot of S-PPEES (DS=52.81%).

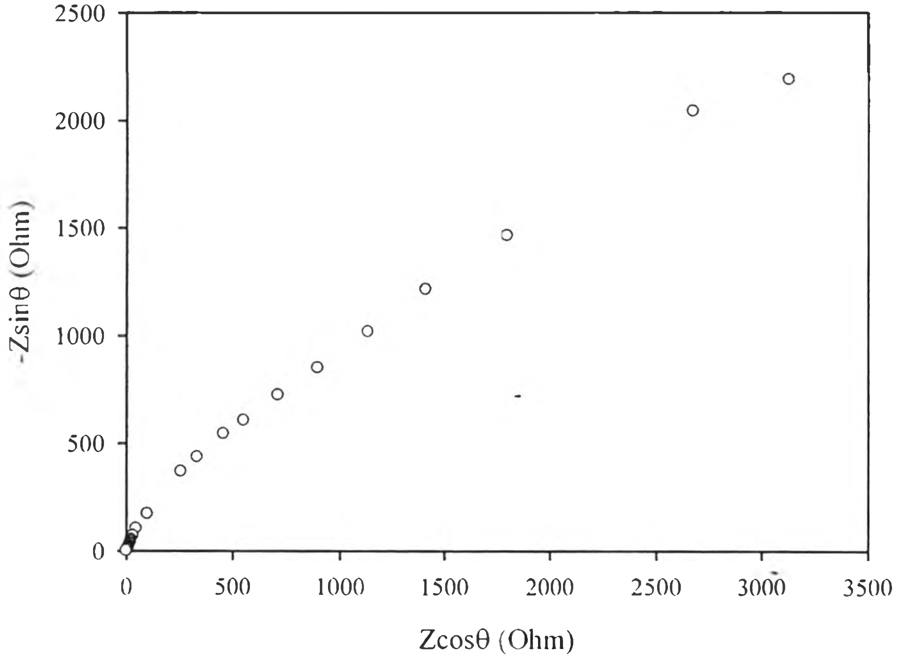

Figure E17 Nyquist plot of S-PPEES (DS=62.53%).

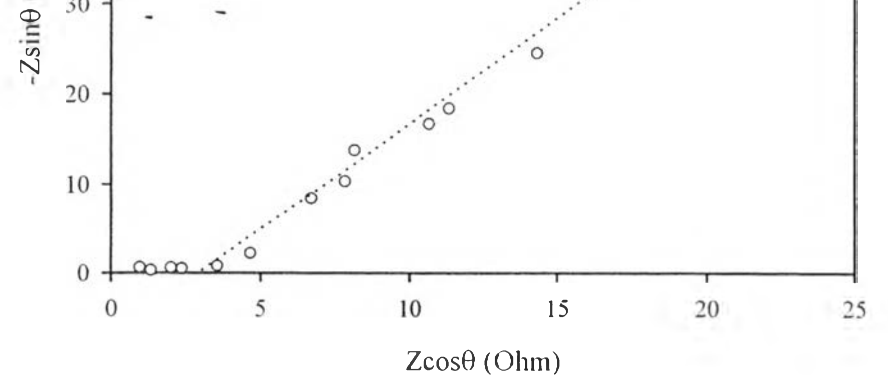

Figure E18 Nyquist plot of S-PPEES (DS=62.53%).

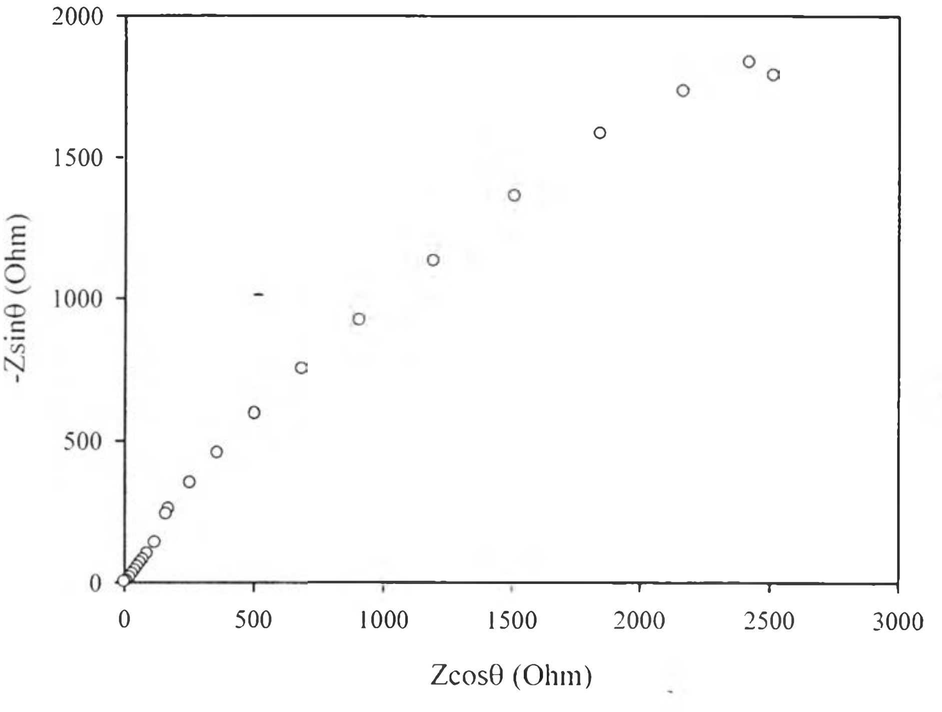

Figure E19 Nyquist plot of S-PPEES (DS=68.73%).

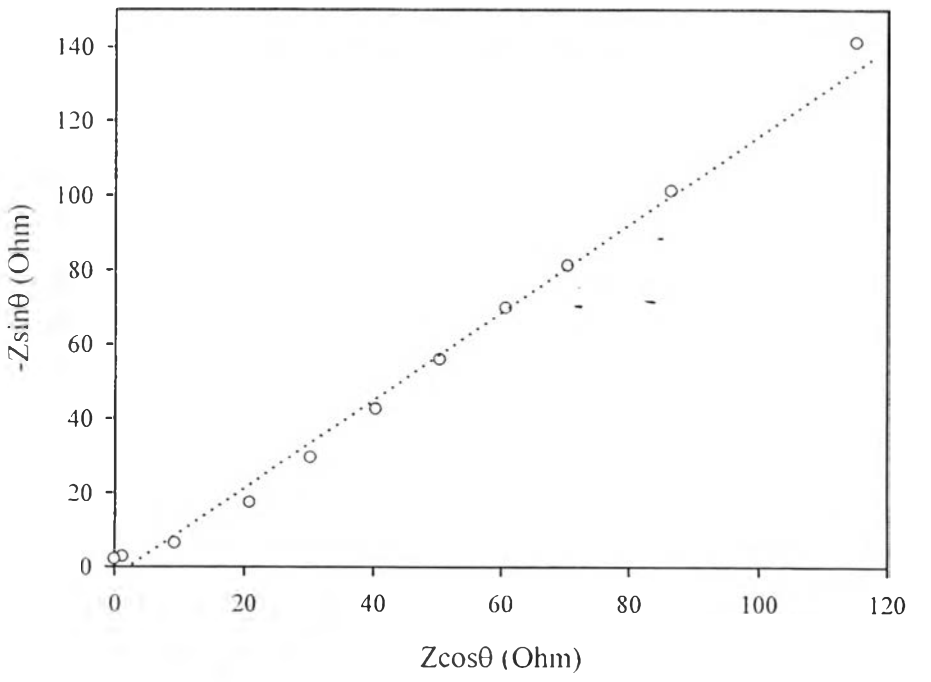

Figure E20 Nyquist plot of S-PPEES (DS=68.73%).

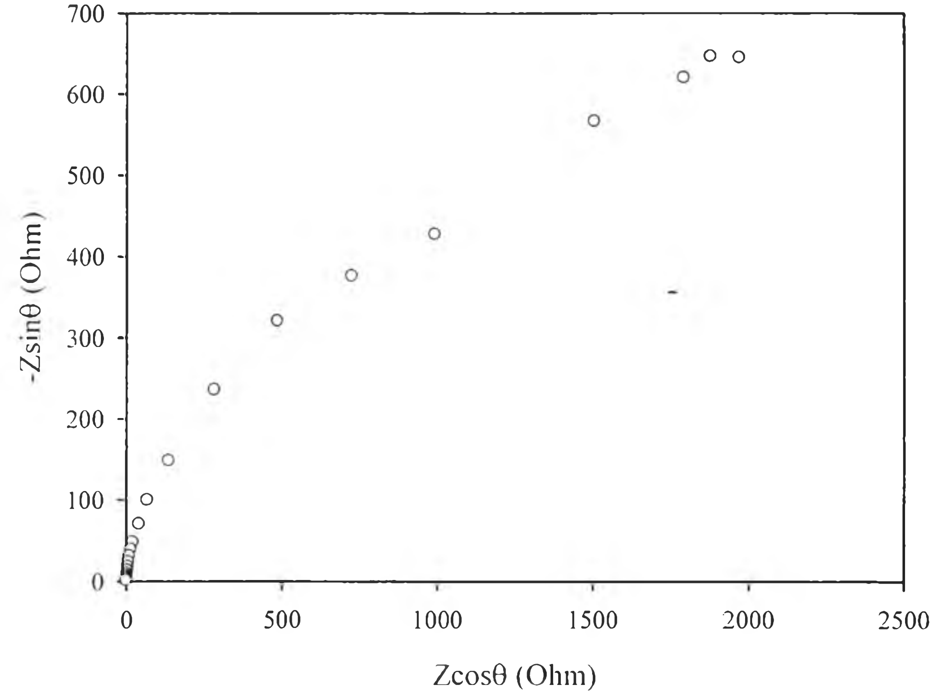

Figure E21 Nyquist plot of S-PPEES (DS=71.69%).

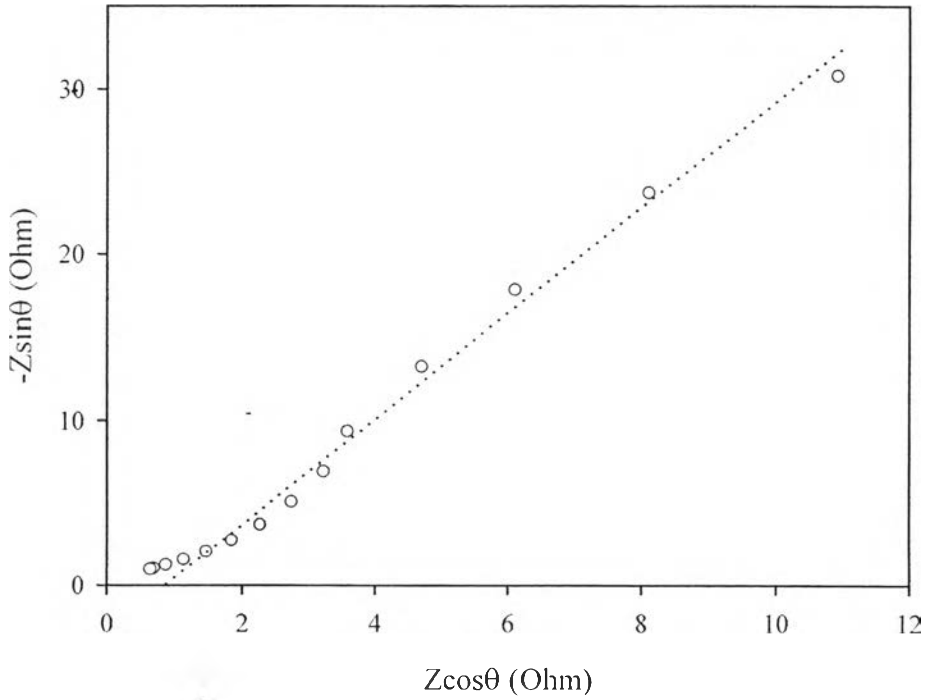

Figure E22 Nyquist plot of S-PPEES (DS=71.69%).

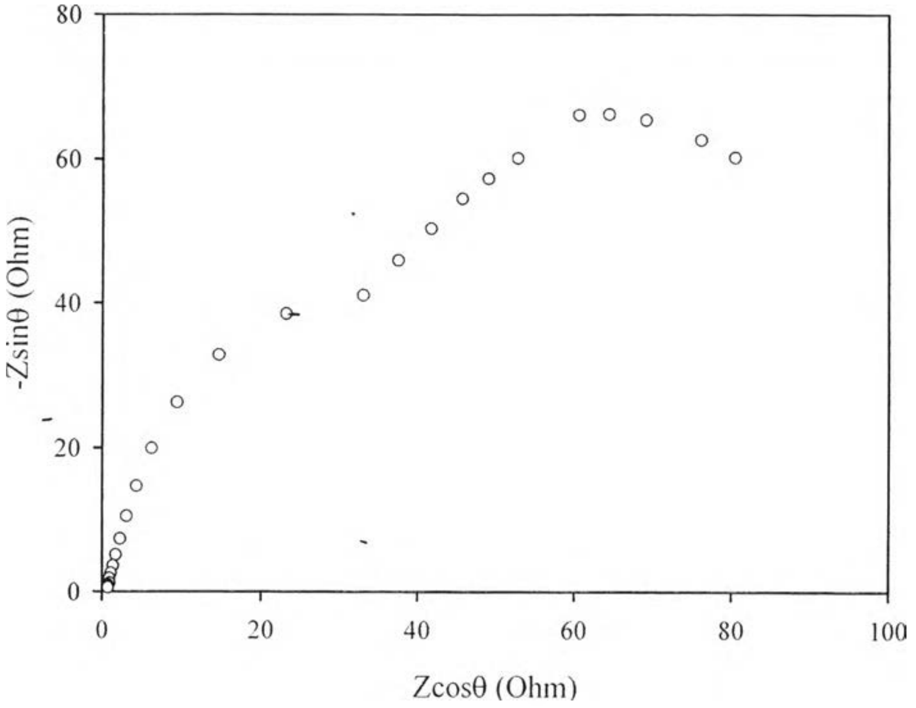

Figure E23 Nyquist plot of S-PPEES (DS=77.88%).

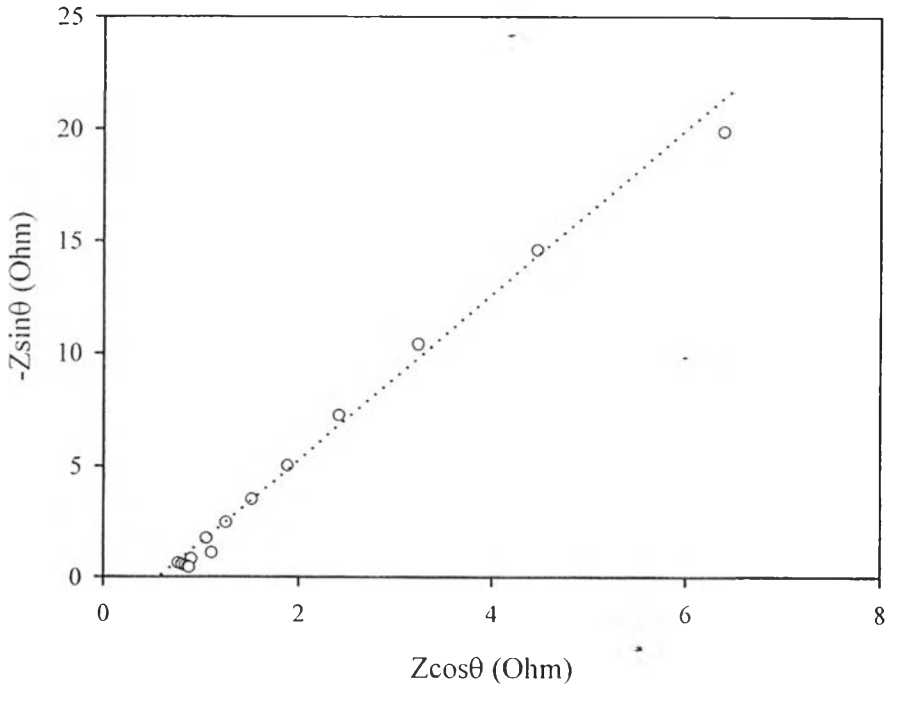

Figure E24 Nyquist plot of S-PPEES (DS=77.88%).

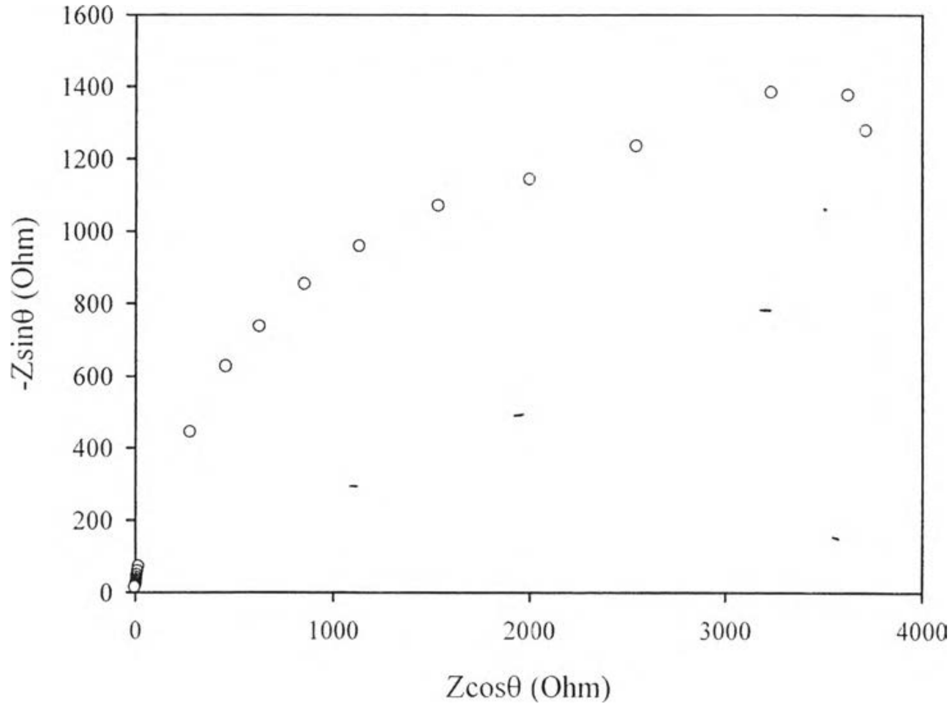

Figure E25 Nyquist plot of S-PPEES (DS=83.99%).

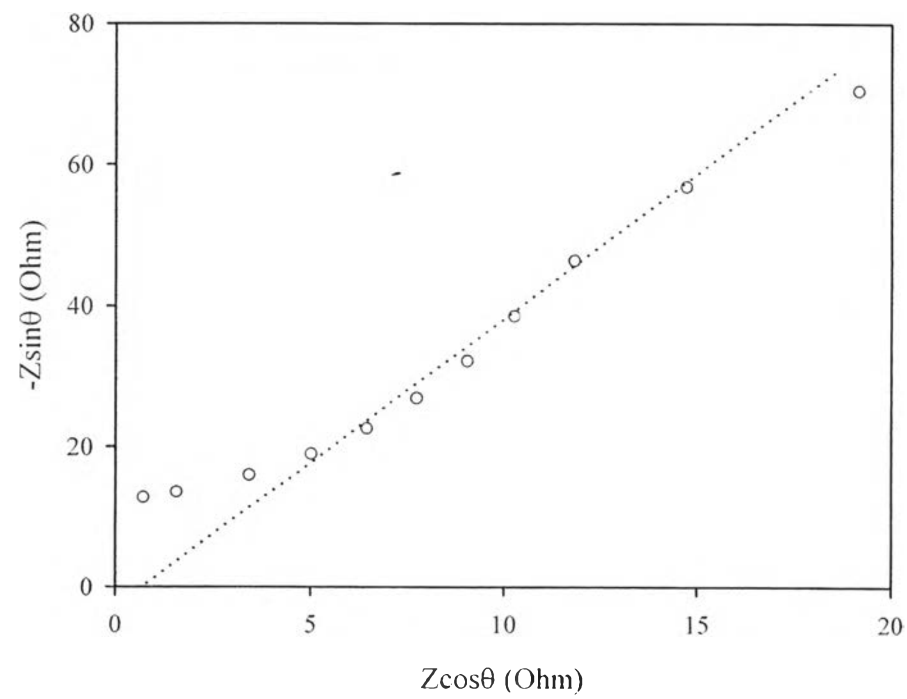

Figure E26 Nyquist plot of S-PPEES (DS=83.99%).

E6 Complex impedance plane of Nafion 117

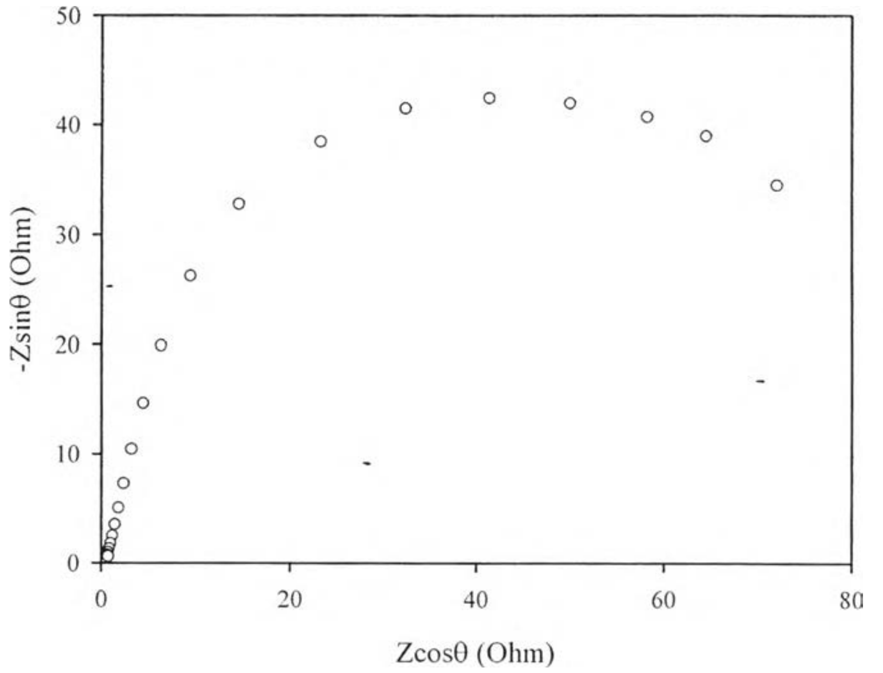

Figure E27 Nyquist plot of Nafion117.

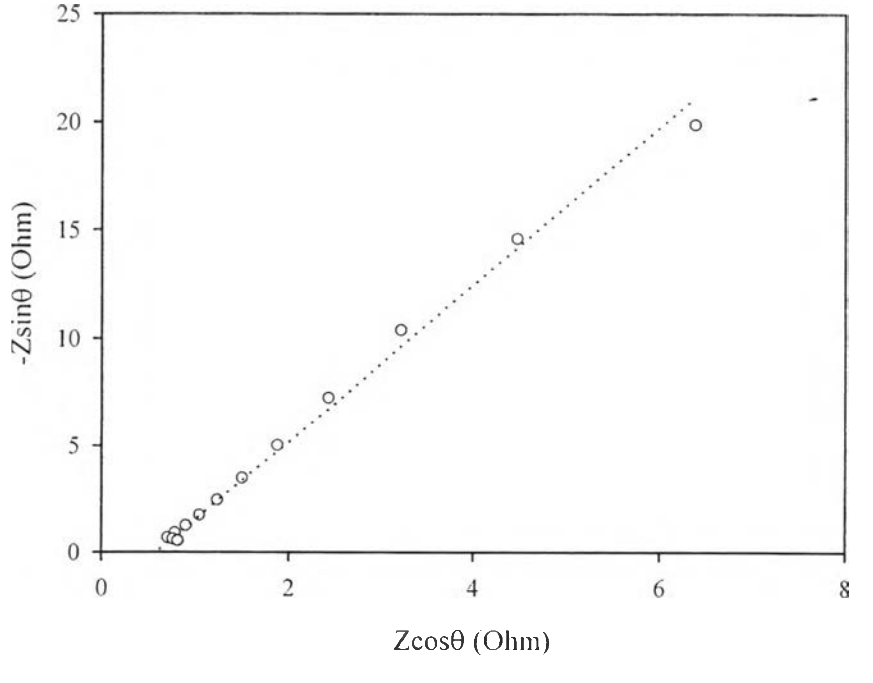

Figure E28 Nyquist plot of Nafion117.

E7 Comparison of Proton conductivity between dry and wet state

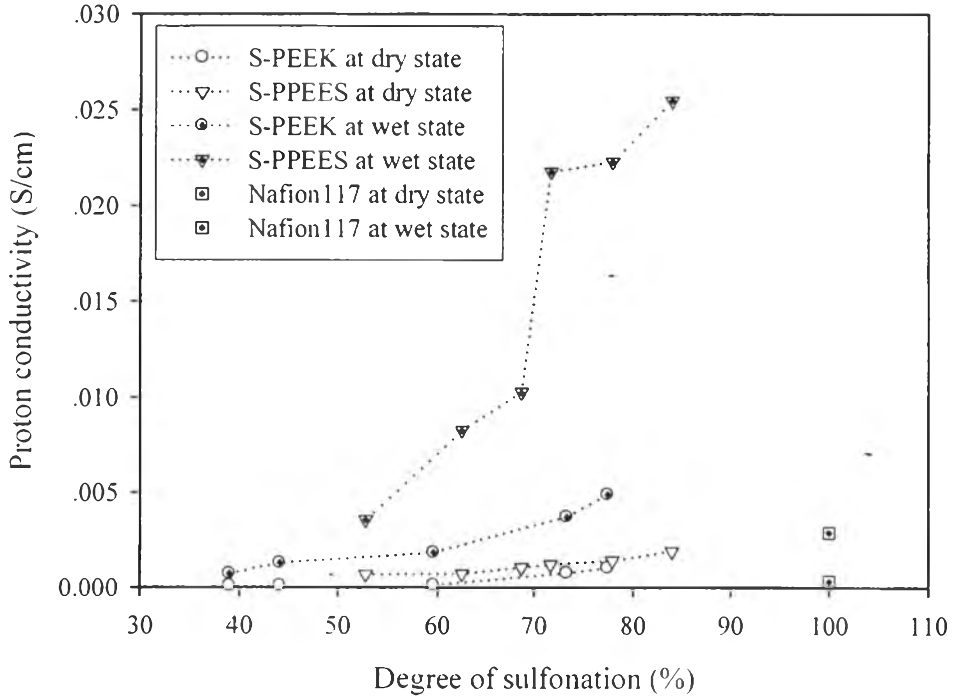

Figure E29 Comparison of proton conductivity between dry and wet state.

Appendix F Vanadium Permeability

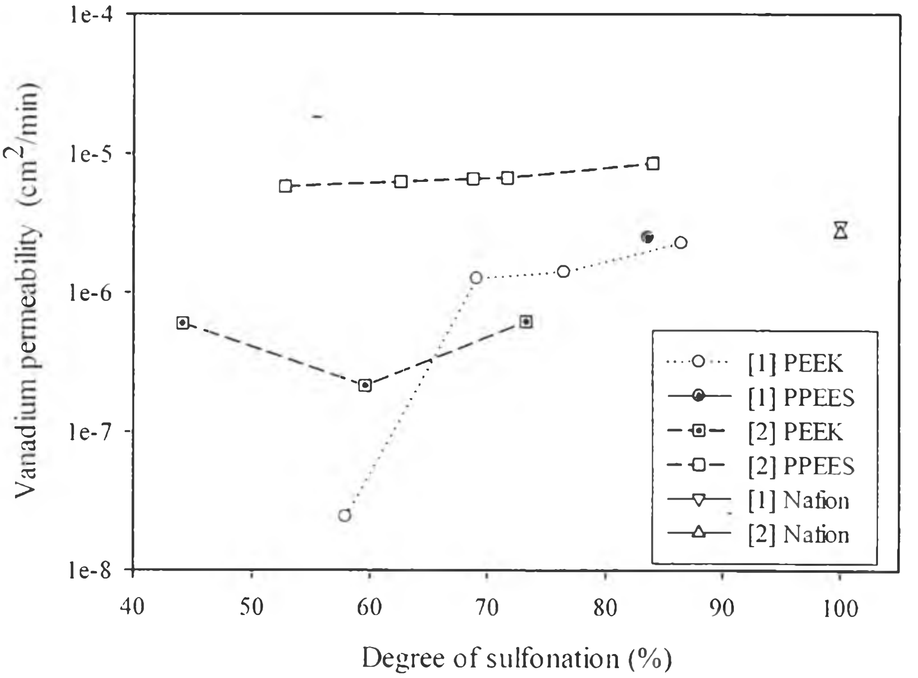

Figure F1 Comparison of vanadium permeability at 25 °C with previous work.

Remark:

[1] Macksasitorn (2012) sulfonated PEEK and PPEES at 25 °C.

[2] Watpathomsub (2014) sulfonated PEEK at 50 °C and PPEES at 25 °C.

Table F1 Comparison of vanadium permeability at 25 °C

Polymer	Degree of sulfonation (%)	Vanadium permeability (cm^2/min)	Reference
S-PEEK	46.21	0	[1]
S-PEEK	57.99	2.42×10^{-8}	[1]
S-PEEK	69.07	1.26×10^{-6}	[1]
S-PEEK	76.49	1.41×10^{-6}	[1]
S-PEEK	86.49	2.28×10^{-6}	[1]
S-PEEK	39.02	9.391×10^{-6}	[2]
S-PEEK	44.14	1.009×10^{-5}	[2]
S-PEEK	59.60	1.730×10^{-5}	[2]
S-PEEK	73.32	2.779×10^{-5}	[2]
S-PEEK	77.43	5.767×10^{-5}	[2]
S-PPEES	83.57	2.50×10^{-6}	[1]
S-PPEES	52.81	3.160×10^{-6}	[2]
S-PPEES	62.53	3.393×10^{-6}	[2]
S-PPEES	68.73	4.485×10^{-6}	[2]
S-PPEES	71.69	4.471×10^{-6}	[2]
S-PPEES	77.88	4.797×10^{-6}	[2]
S-PPEES	83.99	6.739×10^{-6}	[2]
Nafion117	-	3.08×10^{-6}	[1]
Nafion117	-	6.76×10^{-6}	[2]
Nafion117	-	3.69×10^{-6}	[3]
Nafion117	-	2.94×10^{-6}	[4]

Remark:

[1] Macksasitorn *et al.* (2012) sulfonated PEEK and PPEES at 25 °C.

[2] Watpathomsub *et al.* (2014) sulfonated PEEK at 50 °C and PPEES at 25 °C.

[3] Teng *et al.* (2009) investigated Nafion composite membrane for VRFB.

[4] Chen *et al.* (2010) investigated SPFEK composite membrane for VRFB.

F1 Calibration Curve

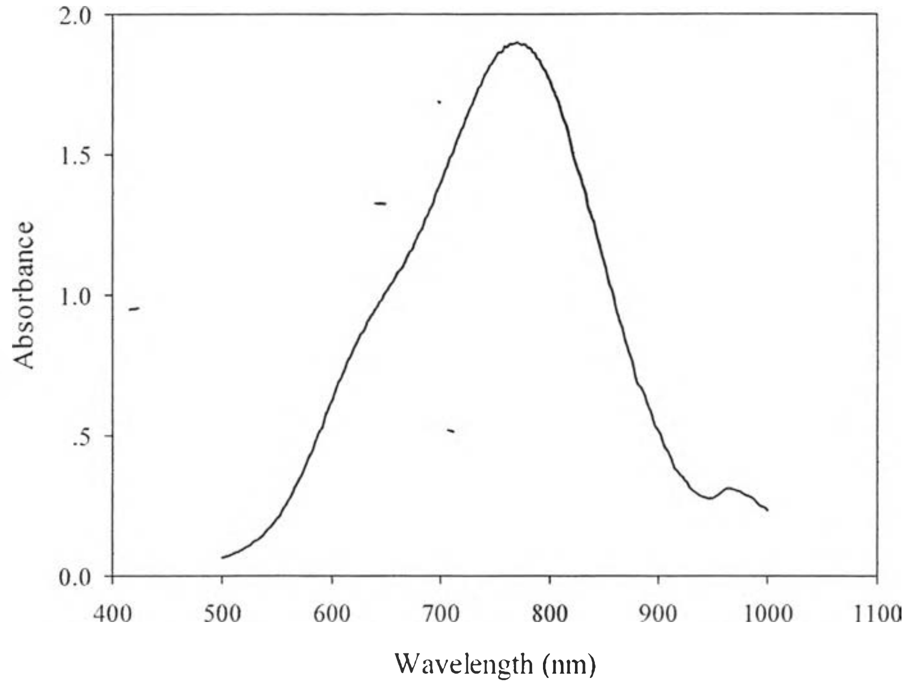

Figure F2 Wavelength profile of 0.1 M VO_2SO_4 in 0.2 M H_2SO_4.

Table F2 Absorbances at 760 nm at different vanadium concentrations

VO^{2+} concentration (mol/L)		0.01	0.05	0.10	0.20	0.30
Absorbance	1	0.2518	1.1355	1.8962	3.0344	3.7563
	2	0.2376	1.0525	1.7078	2.9400	3.6825
	3	0.2368	1.0031	1.6926	2.9737	3.8063
	4	0.2594	1.1657	1.9374	3.0522	3.8291
	5	0.2521	1.1350	1.8355	2.8494	3.8233
	6	0.2520	1.0529	1.9041	2.7044	3.6345
	7	0.2520	1.0040	1.9373	2.8820	3.6993
	8	0.2376	1.1335	1.8392	2.7007	3.8330
	9	0.2370	1.0528	1.9054	2.7248	3.8225
	10	0.2525	1.0048	1.8990	3.0698	3.9268

The vanadium permeability was measured by the method according to the literature (Macksasitorn *et al.*, 2012). The left reservoir was filled with 50 mL of 1M $VOSO_4$ in 2M H_2SO_4 solution, while the right reservoir was filled with 50 mL of 1M $MgSO_4$ in 2M H_2SO_4 solution. $MgSO_4$ was used to equalize the osmotic pressure. The two reservoirs were separated by the membrane which its area equal 5 cm^2.

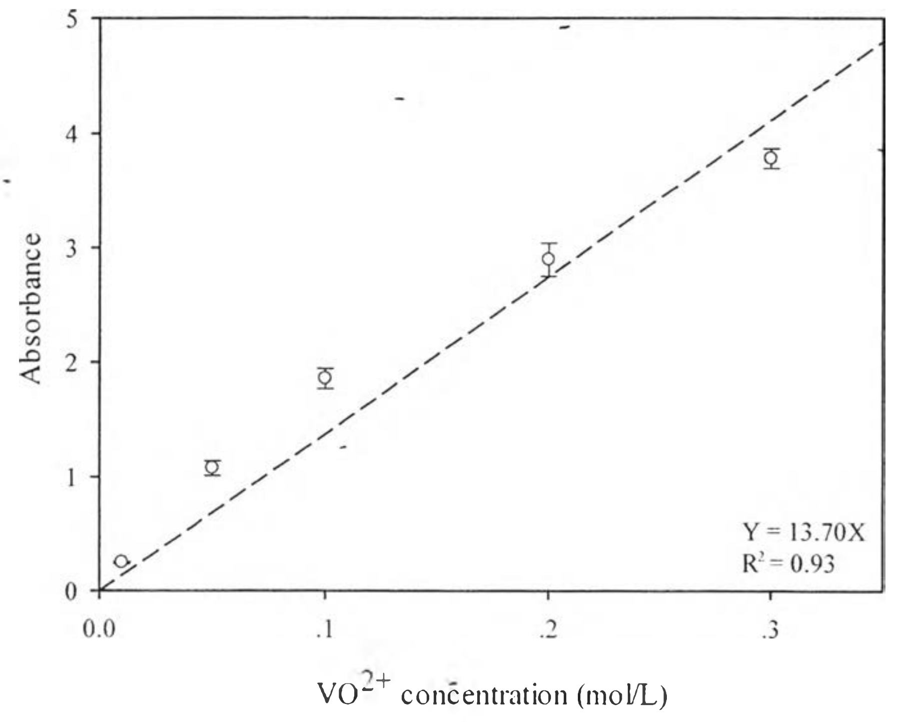

Figure F3 Calibration curve.

Both solutions were continuously magnetic stirred at room temperature. The 0.4 mL of solution from the right reservoir was taken at a regular time interval and 1M $MgSO_4$ in 2M H_2SO_4 was added in right reservoir to hold constant volume. Then, vanadium concentrations were analyzed by a UV-VIS spectrometer (Nanoquant, Infinite M200).

The vanadium permeability was calculated with the following Eq. F1:

$$V_R \frac{d\,C_R(t)}{dt} = A\frac{P}{L}(C_L - C_R(t)) \quad \text{(F1)}$$

where V_R is the volume of the right-hand reservoir (cm^3), C_L is the vanadium ion concentration in the left-hand reservoir (M), $C_R(t)$ is the vanadium ion concentration in the right-hand reservoir as a function of time (M), P is the permeability of vanadium ions (cm^2/min) , A is the area of the membrane (cm^2). L is the membrane thickness (cm).

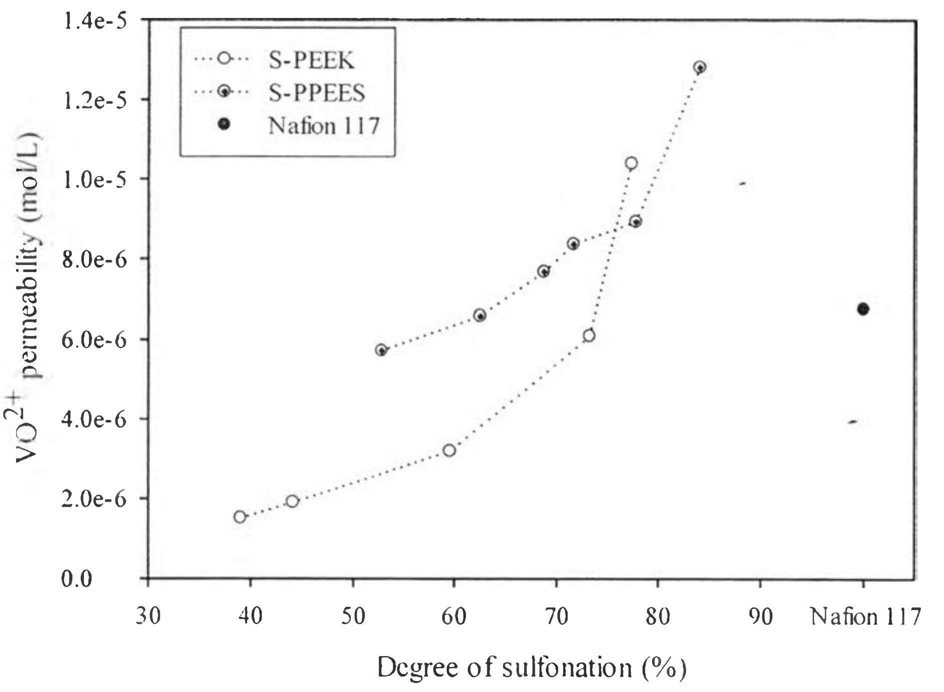

Figure F4 Vanadium permeability of S-PEEK, S-PPEES and Nafion117 at 25 °C.

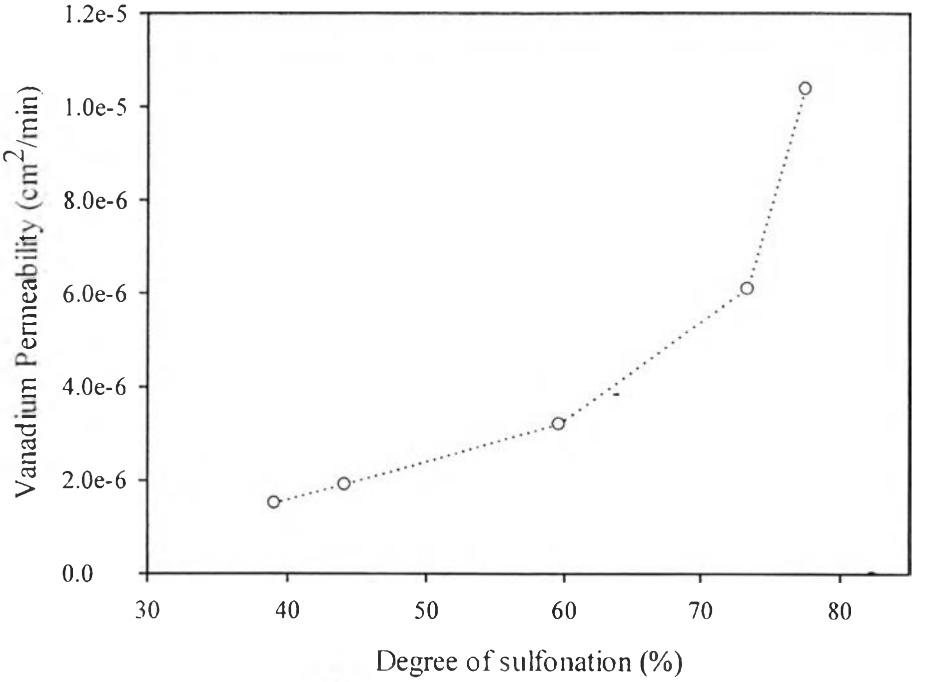

Figure F5 Vanadium permeability of S-PEEK at 25 °C.

Table F3 Vanadium permeability of S-PEEK at 25 °C

Sample	Degree of sulfonation (%)	Thickness (cm)	Slope (mol/L.min)	Vanadium permeability (cm^2/min)
50_100_3	39.02	0.0161	9.391×10^{-6}	1.512×10^{-6}
50_150_3	44.14	0.0189	1.009×10^{-5}	1.908×10^{-6}
50_200_3	59.60	0.0185	1.730×10^{-5}	3.199×10^{-6}
50_200_5	73.32	0.0219	2.779×10^{-5}	6.088×10^{-6}
50_200_7	77.43	0.0180	5.767×10^{-5}	1.038×10^{-5}

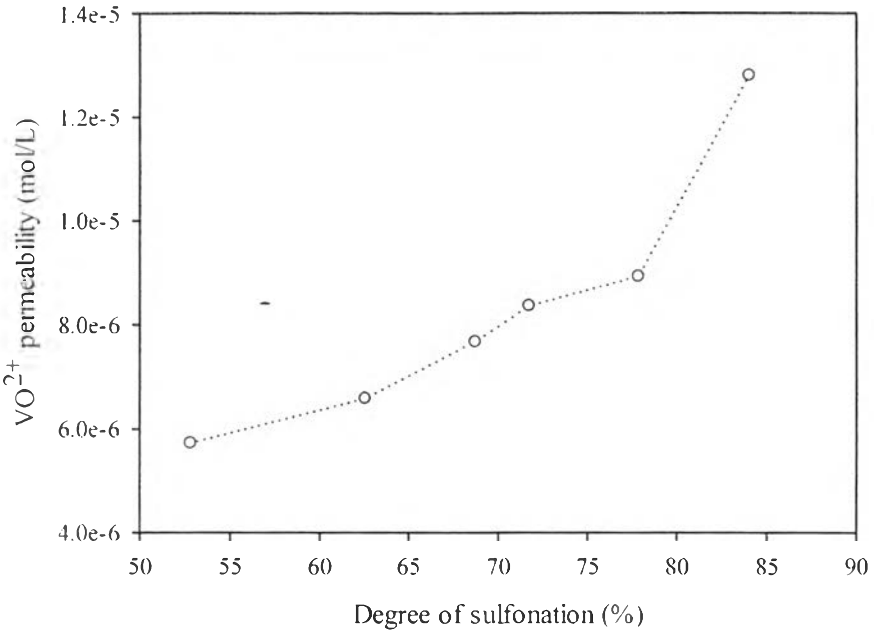

Figure F6 Vanadium permeability of S-PPEES at 25 °C.

Table F4 Vanadium permeability of S-PPEES at 25 °C

Sample	Degree of sulfonation (%)	Thickness (cm)	Slope (mol/L.min)	Vanadium permeability (cm^2/min)
25_100_12	52.81	0.0181	3.160×10^{-5}	5.720×10^{-6}
25_100_18	62.53	0.0194	3.393×10^{-5}	6.582×10^{-6}
25_100_24	68.73	0.0171	4.485×10^{-5}	7.670×10^{-6}
25_100_30	71.69	0.0191	4.471×10^{-5}	8.361×10^{-6}
25_100_36	77.88	0.0186	4.797×10^{-5}	8.922×10^{-6}
25_100_48	83.99	0.0190	6.739×10^{-5}	1.280×10^{-5}

Table F5 Vanadium permeability of Nafion at 25 °C

Sample	Thickness (cm)	Slope (mol/L.min)	Vanadium permeability (cm^2/min)
Nafion	0.0180	3.412×10^{-5}	6.757×10^{-6}

F2 Vanadium permeability raw data of S-PEEK

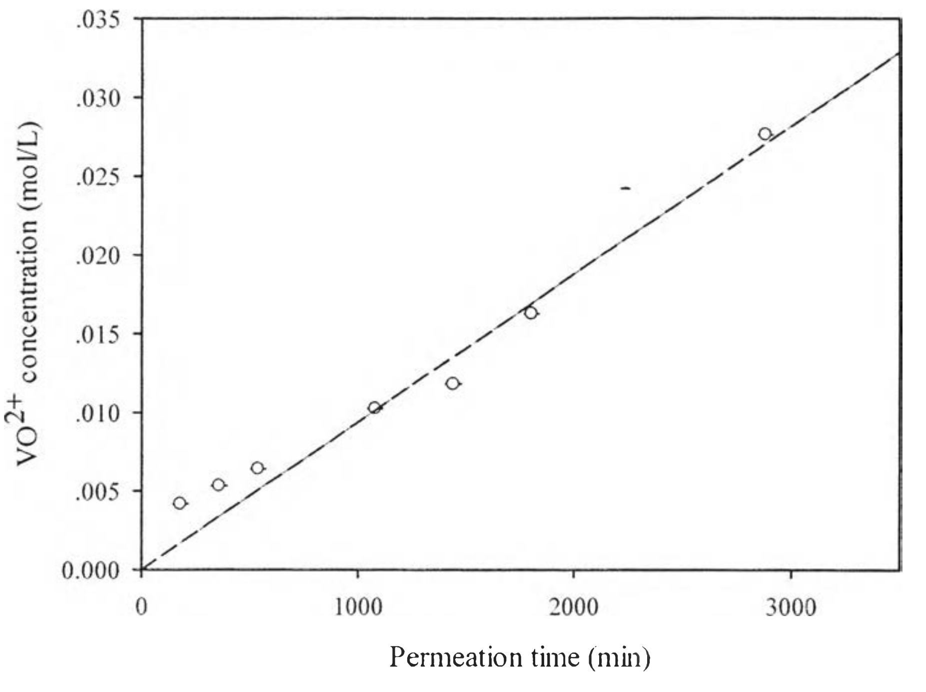

Figure F7 Vanadium (IV) concentration in right reservoir with various time of S-PEEK (DS=39.02%).

Table F6 Vanadium permeability data of S-PEEK (DS=39.02%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.0573	0.0570	0.0572	0.0042	0.0042	0.0042
6	360	0.0729	0.0732	0.0731	0.0053	0.0053	0.0053
9	540	0.0878	0.0881	0.0878	0.0064	0.0064	0.0064
12	720	0.1951	0.1952	0.1954	0.0142	0.0142	0.0143
18	1080	0.1403	0.1405	0.1407	0.0102	0.0102	0.0103
24	1440	0.1616	0.1619	0.1619	0.0118	0.0118	0.0118
30	1800	0.2227	0.2230	0.2228	0.0162	0.0163	0.0163
39	2340	0.5640	0.5636	0.5630	0.0411	0.0411	0.0411
48	2880	0.3786	0.3786	0.3787	0.0276	0.0276	0.0276

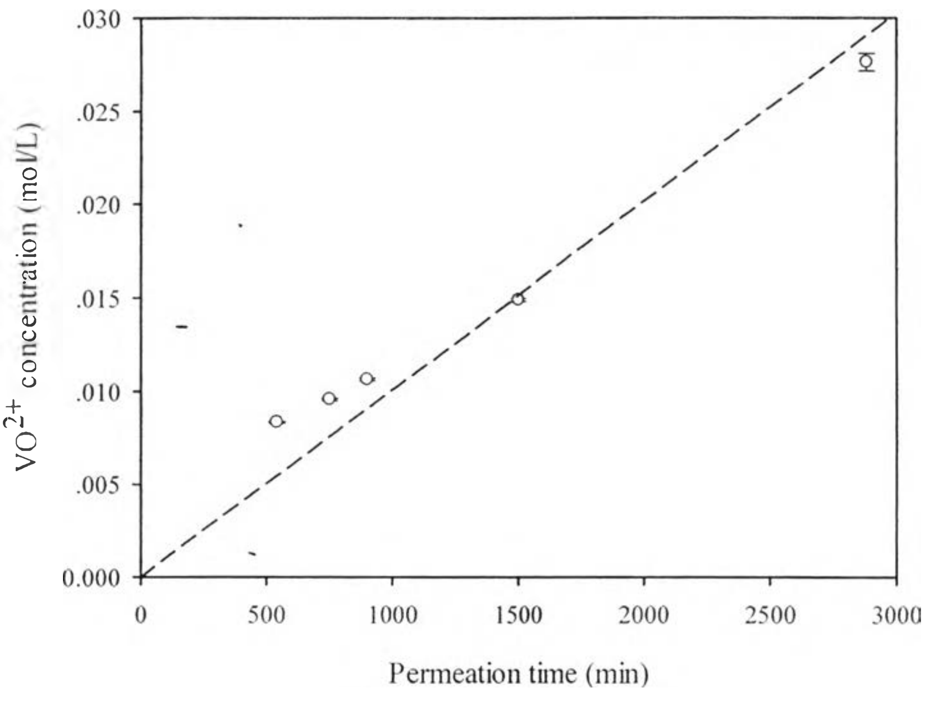

Figure F8 Vanadium (IV) concentration in right reservoir with various time of S-PEEK (DS=44.14%).

Table F7 Vanadium permeability data of S-PEEK (DS=44.14%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1016	0.1011	0.1008	0.0074	0.0074	0.0074
9	540	0.1148	0.1144	0.1136	0.0084	0.0083	0.0083
12.5	750	0.1320	0.1312	0.1304	0.0096	0.0096	0.0095
15	900	0.1470	0.1456	0.1451	0.0107	0.0106	0.0106
25	1500	0.2052	0.2044	0.2032	0.0150	0.0149	0.0148
48	2880	0.3861	0.3777	0.3731	0.0282	0.0276	0.0272

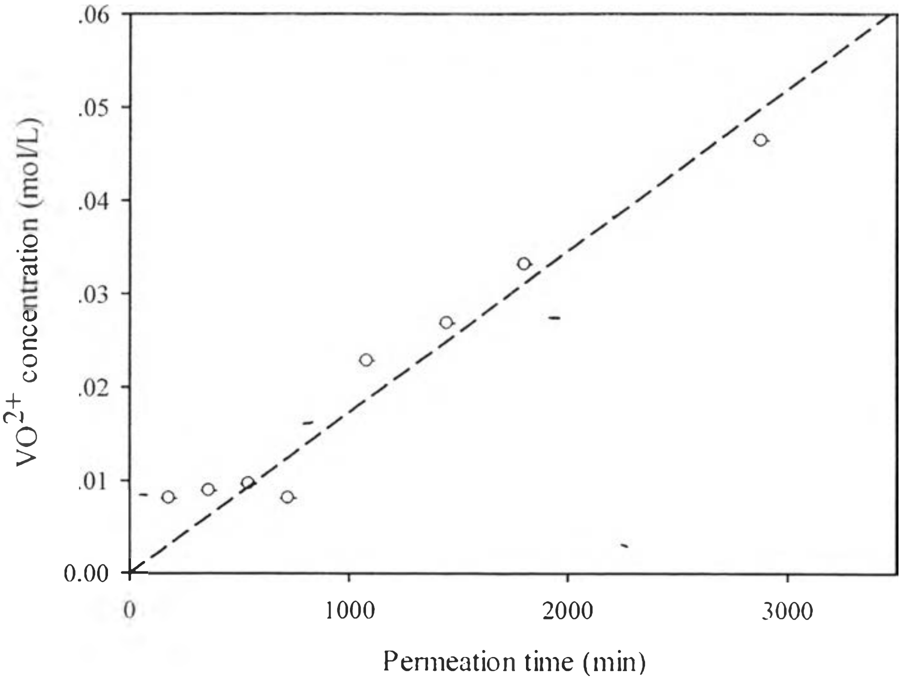

Figure F9 Vanadium (IV) concentration in right reservoir with various time of S-PEEK (DS=59.60%).

Table F8 Vanadium permeability data of S-PEEK (DS=59.60%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1109	0.1110	0.1110	0.0081	0.0081	0.0081
6	360	0.1220	0.1224	0.1223	0.0089	0.0089	0.0089
9	540	0.1318	0.1324	0.1325	0.0096	0.0097	0.0097
12	720	0.1109	0.1112	0.1115	0.0081	0.0081	0.0081
18	1080	0.3123	0.3125	0.3124	0.0228	0.0228	0.0228
24	1440	0.3677	0.3678	0.3677	0.0268	0.0268	0.0268
30	1800	0.4547	0.4546	0.4545	0.0332	0.0332	0.0332
39	2340	0.3451	0.3455	0.3456	0.0252	0.0252	0.0252
48	2880	0.6364	0.6365	0.6363	0.0464	0.0464	0.0464

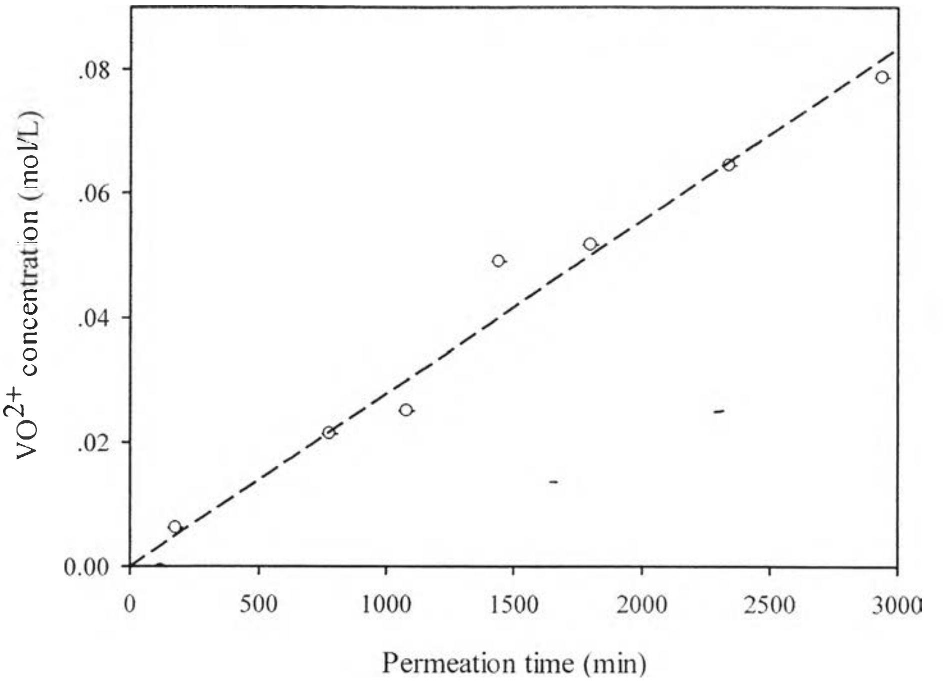

Figure F10 Vanadium (IV) concentration in right reservoir with various time of S-PEEK (DS=73.32%).

Table F9 Vanadium permeability data of S-PEEK (DS=73.32%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.0847	0.0850	0.0850	0.0062	0.0062	0.0062
13	780	0.2929	0.2925	0.2935	0.0214	0.0213	0.0214
18	1080	0.3430	0.3435	0.3439	0.0250	0.0251	0.0251
24	1440	0.6714	0.6712	0.6710	0.0490	0.0490	0.0489
30	1800	0.7082	0.7073	0.7078	0.0517	0.0516	0.0516
39	2340	0.8832	0.8833	0.8834	0.0644	0.0644	0.0644
49	2940	1.0787	1.0785	1.0787	0.0787	0.0787	0.0787

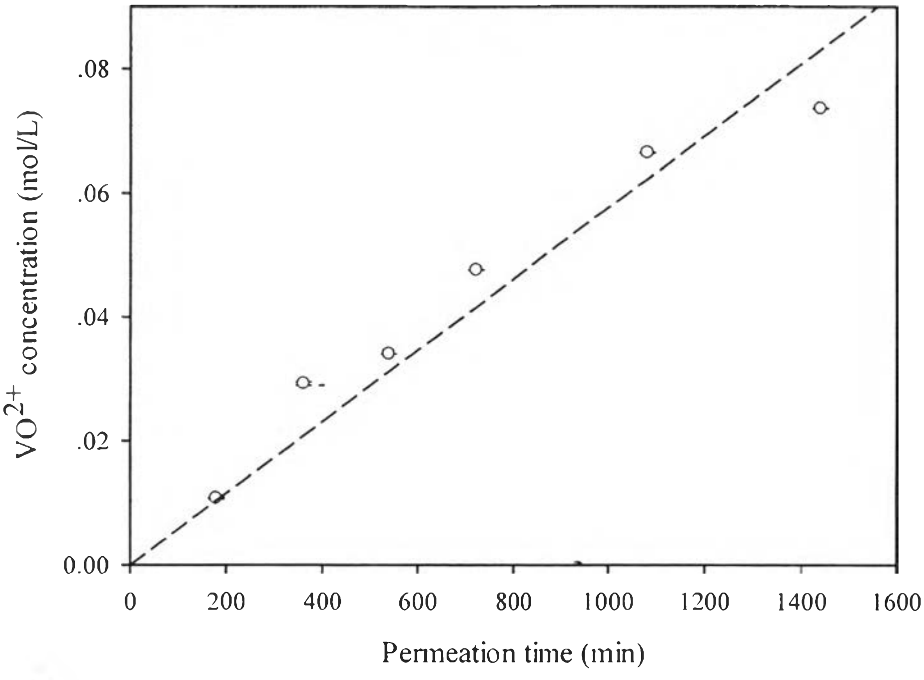

Figure F11 Vanadium (IV) concentration in right reservoir with various time of S-PEEK (DS=77.43%).

Table F10 Vanadium permeability data of S-PEEK (DS=77.43%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1492	0.1464	0.1466	0.0109	0.0107	0.0107
6	360	0.3955	0.4015	0.4023	0.0289	0.0293	0.0293
9	540	0.4657	0.4657	0.4659	0.0340	0.0340	0.0340
12	720	0.6521	0.6521	0.6517	0.0476	0.0476	0.0475
18	1080	0.9126	0.9113	0.9117	0.0666	0.0665	0.0665
24	1440	1.0103	1.0090	1.0087	0.0737	0.0736	0.0736

F3 Vanadium permeability raw data of S-PPEES

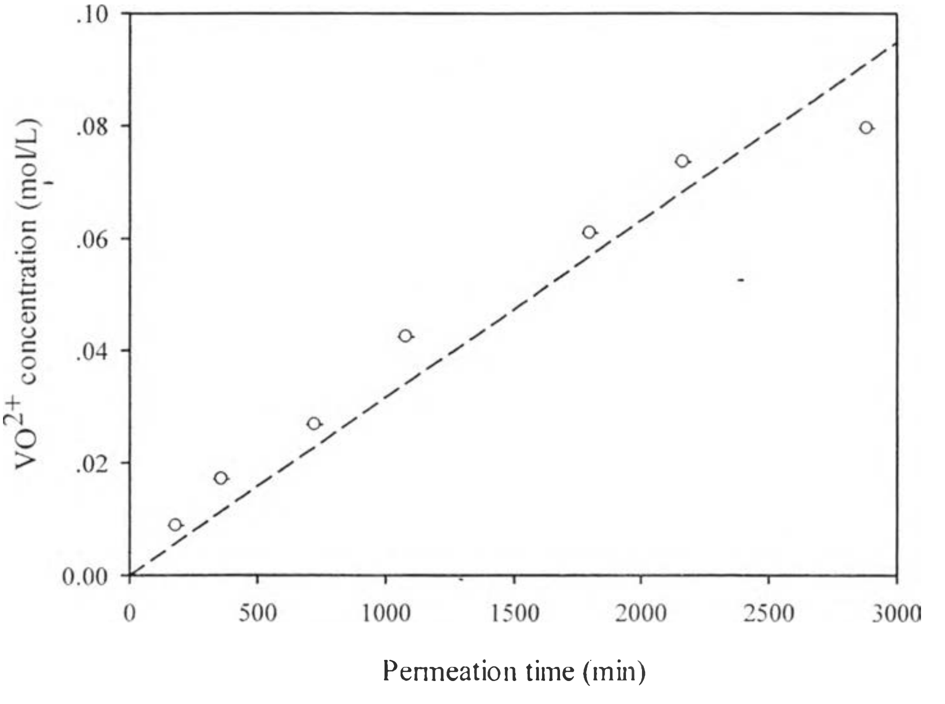

Figure F12 Vanadium (IV) concentration in right reservoir with various time of S-PPEES (DS=52.81%).

Table F11 Vanadium permeability data of S-PPEES (DS=52.81%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1207	0.1209	0.1208	0.0088	0.0088	0.0088
6	360	0.2337	0.2339	0.2340	0.0170	0.0171	0.0171
12	720	0.3659	0.3667	0.3669	0.0267	0.0268	0.0268
18	1080	0.5816	0.5814	0.5818	0.0424	0.0424	0.0424
30	1800	0.8354	0.8353	0.8361	0.0609	0.0609	0.0610
36	2160	1.0073	1.0082	1.0082	0.0735	0.0735	0.0735
48	2880	1.0899	1.0903	1.0900	0.0795	0.0795	0.0795

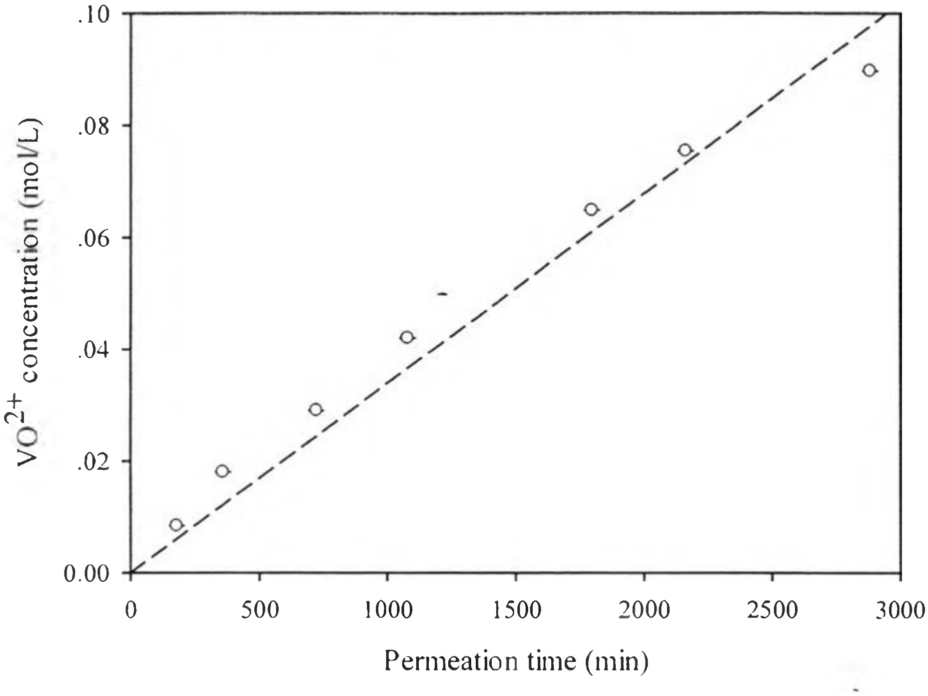

Figure F13 Vanadium (IV) concentration in right reservoir with various time of S-PPEES (DS=62.53%).

Table F12 Vanadium permeability data of S-PPEES (DS=62.53%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1151	0.1163	0.1159	0.0084	0.0085	0.0085
6	360	0.2463	0.2468	0.2468	0.0180	0.0180	0.0180
12	720	0.3978	0.3980	0.3981	0.0290	0.0290	0.0290
18	1080	0.5752	0.5756	0.5755	0.0420	0.0420	0.0420
30	1800	0.8889	0.8893	0.8890	0.0648	0.0649	0.0649
36	2160	1.0342	1.0345	1.0343	0.0754	0.0755	0.0755
48	2880	1.2293	1.2301	1.2291	0.0897	0.0897	0.0897

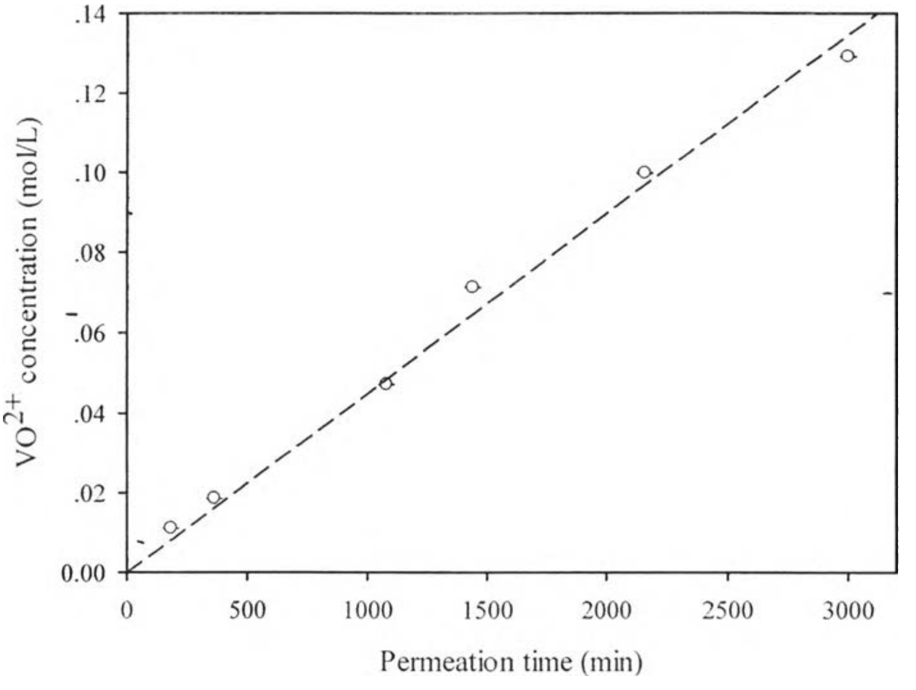

Figure F14 Vanadium (IV) concentration in right reservoir with various time of S-PPEES (DS=68.73%).

Table F13 Vanadium permeability data of S-PPEES (DS=68.73%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1514	0.1514	0.1513	0.0110	0.0110	0.0110
6	360	0.2549	0.2551	0.2547	0.0186	0.0186	0.0186
18	1080	0.6472	0.6470	0.6465	0.0472	0.0472	0.0472
24	1440	0.9780	0.9772	0.9766	0.0713	0.0713	0.0712
36	2160	1.3701	1.3685	1.3669	0.0999	0.0998	0.0997
50	3000	1.7706	1.7717	1.7703	0.1292	0.1292	0.1291

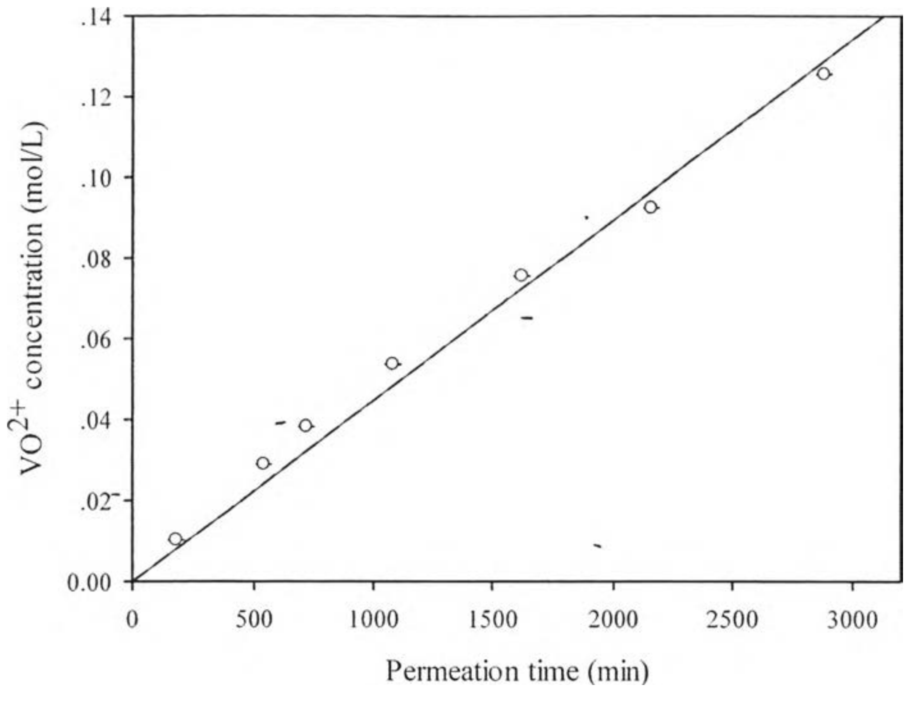

Figure F15 Vanadium (IV) concentration in right reservoir with various time of S-PPEES (DS=71.69%).

Table F14 Vanadium permeability data of S-PPEES (DS=71.69%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1409	0.1410	0.1409	0.0103	0.0103	0.0103
9	540	0.3969	0.3978	0.3979	0.0290	0.0290	0.0290
12	720	0.5232	0.5241	0.5243	0.0382	0.0382	0.0382
18	1080	0.7368	0.7364	0.7349	0.0538	0.0537	0.0536
27	1620	1.0348	1.0368	1.0364	0.0755	0.0756	0.0756
36	2160	1.2674	1.2672	1.2675	0.0925	0.0924	0.0925
48	2880	1.7193	1.7195	1.7224	0.1254	0.1254	0.1257

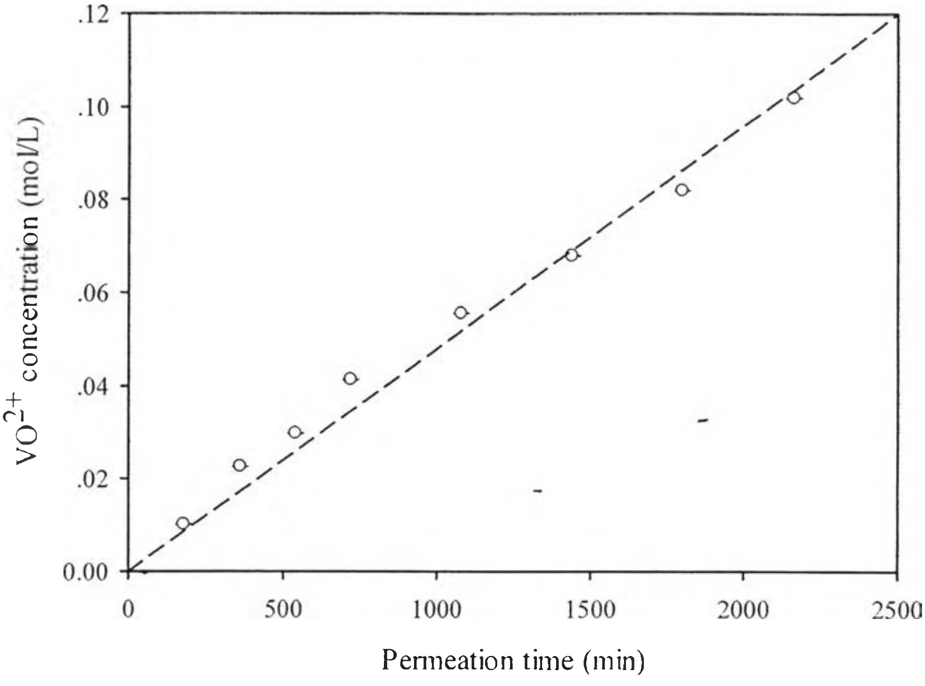

Figure F16 Vanadium (IV) concentration in right reservoir with various time of S-PPEES (DS=77.88%).

Table F15 Vanadium permeability data of S-PPEES (DS=77.88%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1387	0.1390	0.1393	0.0101	0.0101	0.0102
6	360	0.3096	0.3096	0.3100	0.0226	0.0226	0.0226
9	540	0.4082	0.4079	0.4078	0.0298	0.0298	0.0297
12	720	0.5669	0.5670	0.5669	0.0414	0.0414	0.0414
18	1080	0.7617	0.7616	0.7617	0.0556	0.0556	0.0556
24	1440	0.9312	0.9306	0.9303	0.0679	0.0679	0.0679
30	1800	1.1233	1.1230	1.1233	0.0819	0.0819	0.0819
36	2160	1.3966	1.3975	1.3984	0.1019	0.1019	0.1020

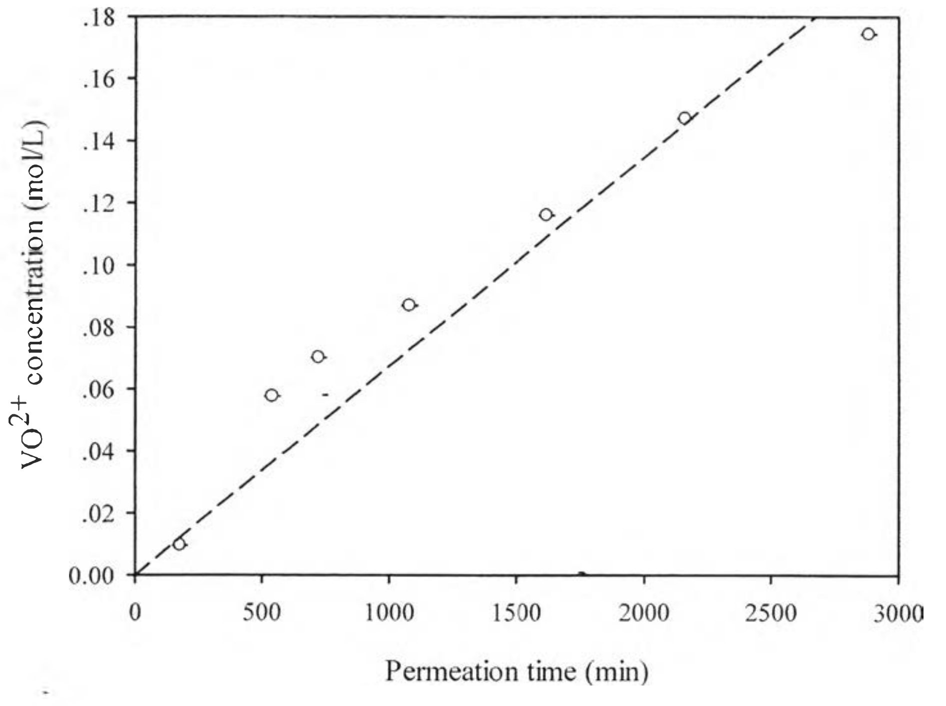

Figure F17 Vanadium (IV) concentration in right reservoir with various time of S-PPEES (DS=83.99%).

Table F16 Vanadium permeability data of S-PPEES (DS=83.99%)

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1316	0.1313	0.1320	0.0096	0.0096	0.0096
9	540	0.7891	0.7892	0.7895	0.0576	0.0576	0.0576
12	720	0.9623	0.9616	0.9606	0.0702	0.0701	0.0701
18	1080	1.1947	1.1938	1.1896	0.0872	0.0871	0.0868
27	1620	1.5921	1.5918	1.5902	0.1161	0.1161	0.1160
36	2160	2.0213	2.0162	2.0149	0.1475	0.1471	0.1470
48	2880	2.3937	2.3920	2.3885	0.1746	0.1745	0.1742

F4 Vanadium permeability of Nafion117

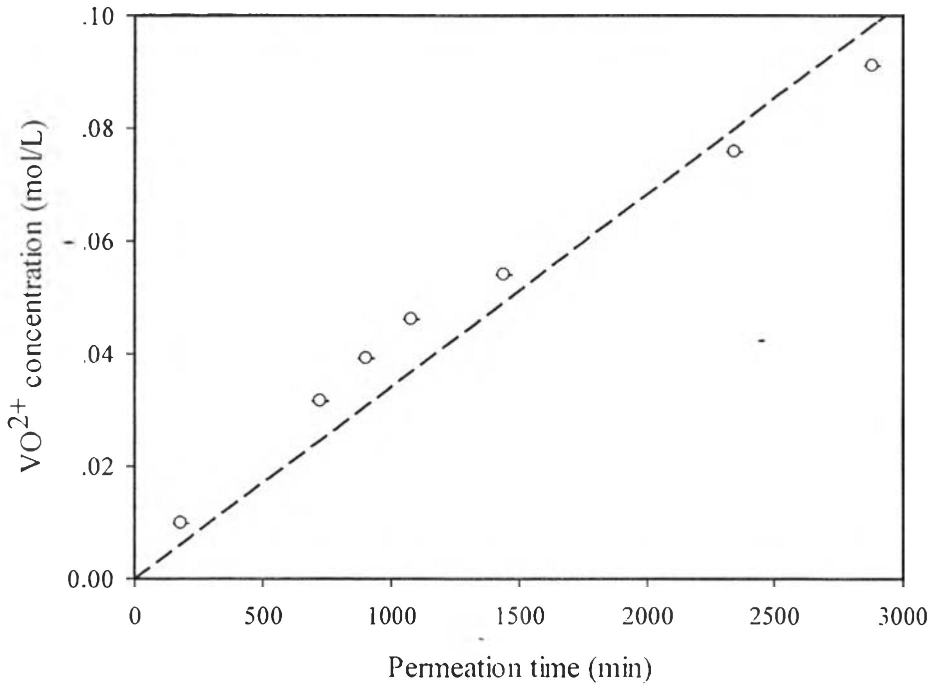

Figure F18 Vanadium (IV) concentration in right reservoir with various time of Nafion117.

Table F17 Vanadium permeability data of Nafion117

Permeation time		Absorbance			Concentration		
h	min	A_1	A_2	A_3	C_1	C_2	C_3
3	180	0.1349	0.1350	0.1351	0.0098	0.0098	0.0099
12	720	0.4342	0.4324	0.4327	0.0317	0.0315	0.0316
15	900	0.5370	0.5370	0.5369	0.0392	0.0392	0.0392
18	1080	0.6327	0.6318	0.6319	0.0462	0.0461	0.0461
24	1440	0.7403	0.7401	0.7404	0.0540	0.0540	0.0540
39	2340	1.0380	1.0380	1.0381	0.0757	0.0757	0.0757
48	2880	1.2485	1.2478	1.2487	0.0911	0.0910	0.0911

Appendix G Ion Exchange Capacity

The IEC is defined as mmol of sulfonic acid groups for 1 g of dry polymer determined through the acid–base titration. The sulfonic acid groups were titrated with NaOH solution. The membranes was dried at 100 °C for 24 h, weighed and then immersed overnight in a known volume 0.1 M NaCl solution to exchange the H^+ to Na^+ ions. The H^+ containing solution was determined by back titration with a 0.01 M NaOH solution until pH was neutral with phenolphthalein as an indicator. IEC was calculated according to the following Eq. G1:

$$\text{IEC}\ (\text{mmol}\cdot \text{g}^{-1}) = \frac{V_{eq} . C_{NaOH}}{W_d} \qquad \text{(G1)}$$

where V_{eq} is the equivalent volume of NaOH solution and W_d refers to the weight of the dry membrane.sds

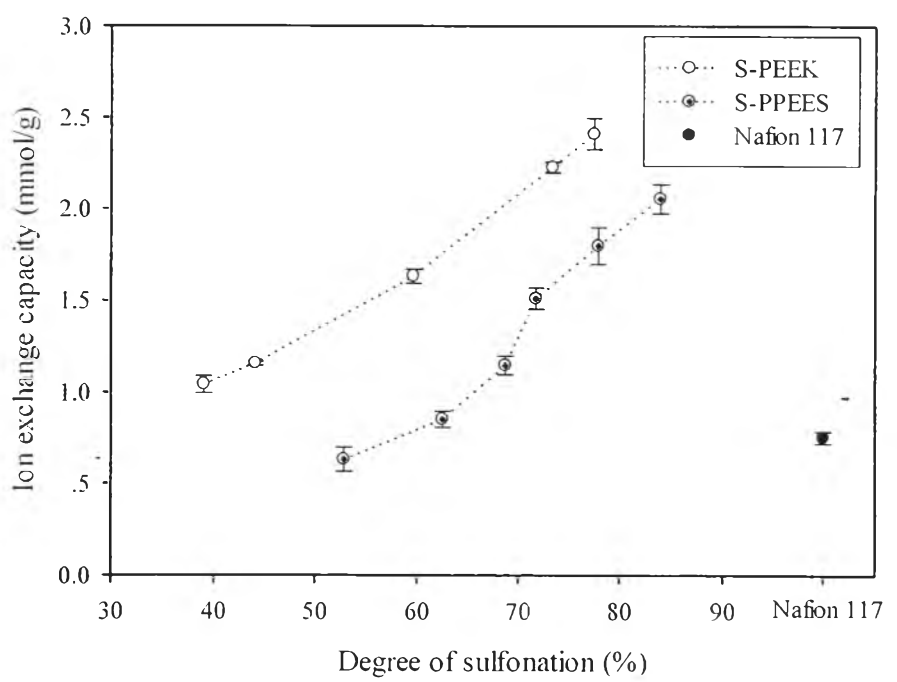

Figure G1 Ion exchange capacity versus degree of sulfonation of S-PEEK, S-PPEES, and Nafion117.

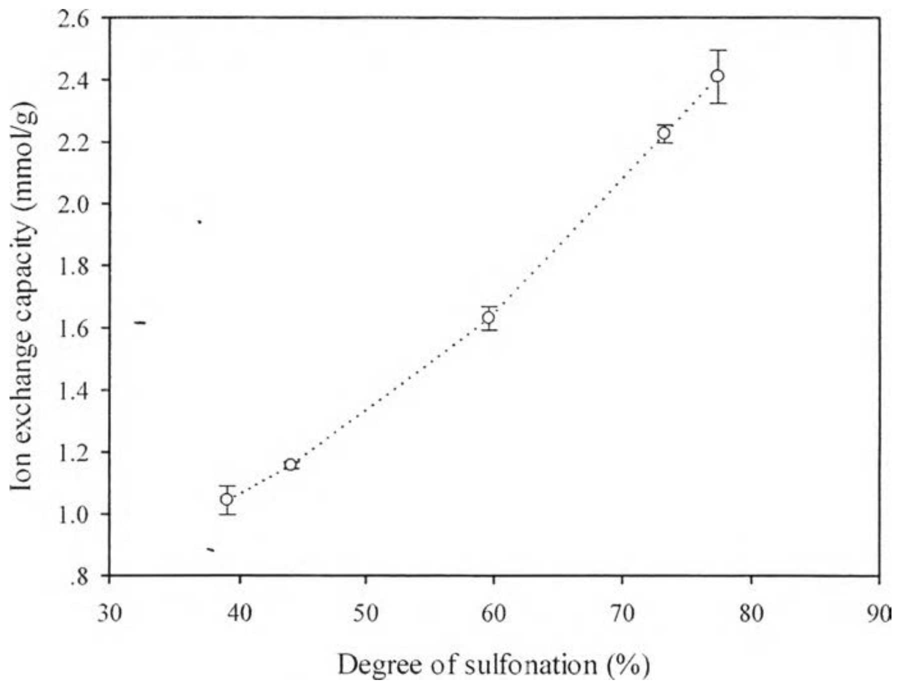

Figure G2 Ion exchange capacity versus degree of sulfonation of S-PEEK.

Table G1 Ion exchange capacity versus sulfonation time of S-PEEK

Sample	DS (%)	Ion Exchange Capacity (mmol/g)			
		IEC_1	IEC_2	IEC_3	Average
50_100_3	39.02	1.094	1.004	1.030	1.043 ± 0.046
50_150_3	44.14	1.162	1.144	1.162	1.156 ± 0.010
50_200_3	59.60	1.586	1.652	1.652	1.630 ± 0.038
50_200_5	73.32	2.193	2.243	2.243	2.226 ± 0.029
50_200_7	77.43	2.313	2.441	2.475	2.410 ± 0.085

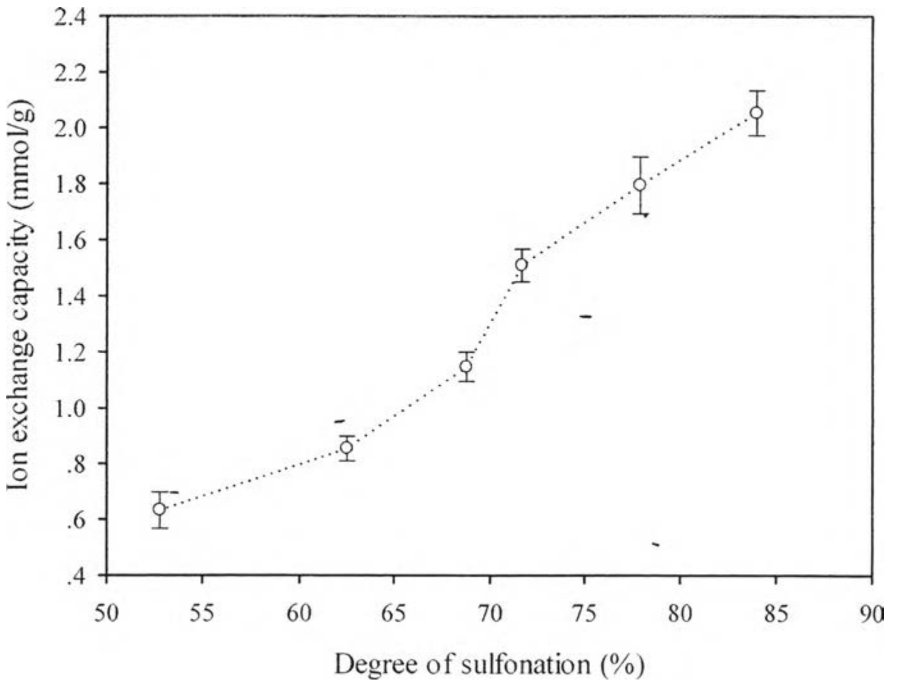

Figure G3 Ion exchange capacity versus degree of sulfonation of S-PPEES.

Table G2 Ion exchange capacity versus degree of sulfonation of S-PPEES

Sample	DS (%)	Ion Exchange Capacity (mmol/g)			
		IEC_1	IEC_2	IEC_3	Average
25_100_12	52.81	0.690	0.561	0.647	0.633 ± 0.066
25_100_18	62.53	0.804	0.870	0.886	0.853 ± 0.043
25_100_24	68.73	1.177	1.087	1.177	1.147 ± 0.052
25_100_30	71.69	1.573	1.458	1.497	1.509 ± 0.058
25_100_36	77.88	1.699	1.786	1.901	1.795 ± 0.101
25_100_48	83.99	2.133	2.053	1.972	2.053 ± 0.081

Table G3 Ion exchange capacity versus degree of sulfonation of Nafion117

Sample	Ion Exchange Capacity (mmol/g)			
	IEC_1	IEC_2	IEC_3	Average
Nafion 117	0.724	0.749	0.790	0.754 ± 0.033

Appendix H Water Uptake

The 0.180 cm thick membrane was cut to 1.5×1.5 cm^2 dimension. Then, the membrane was dried at 100 °C for 24 h, weighed, and soaked in deionized water at room temperature for 24 h. After that, the membrane was taken out and the water adhering to the surface was quickly wiped off using absorbent paper. The membrane was weighed again. Then, the water uptake was calculated as following Eq. H1:

$$\text{water uptake } (\%) = \left(\frac{W_w - W_d}{W_d}\right) \times 100 \qquad \text{(H1)}$$

where W_w and W_d refer to the weight of the wet and dry samples, respectively.

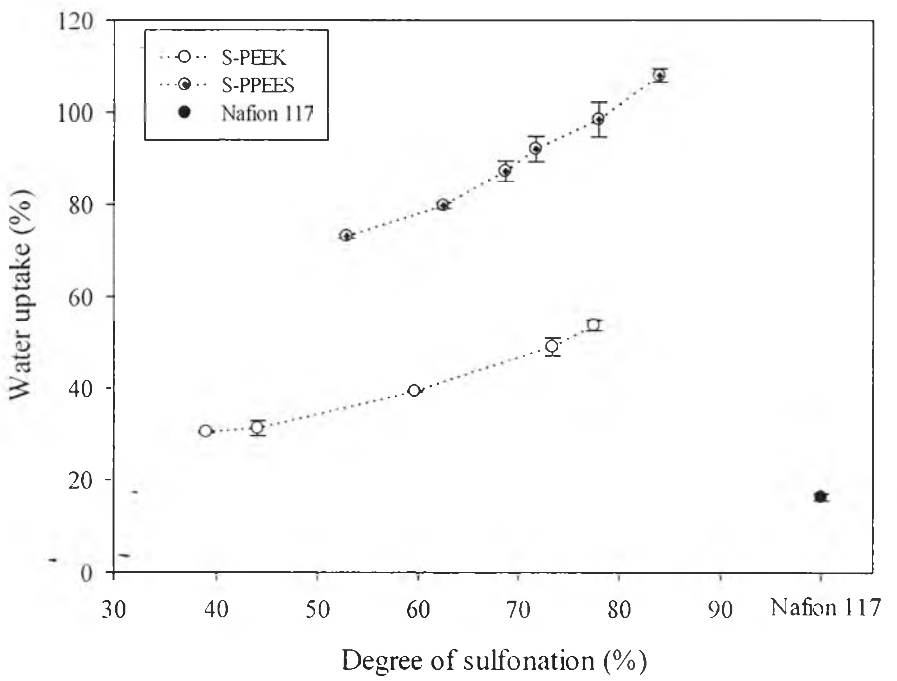

Figure H1 Water uptake of S-PEEK, S-PPEES and Nafion117.

H1 Sulfonated poly(ether ether ketone)

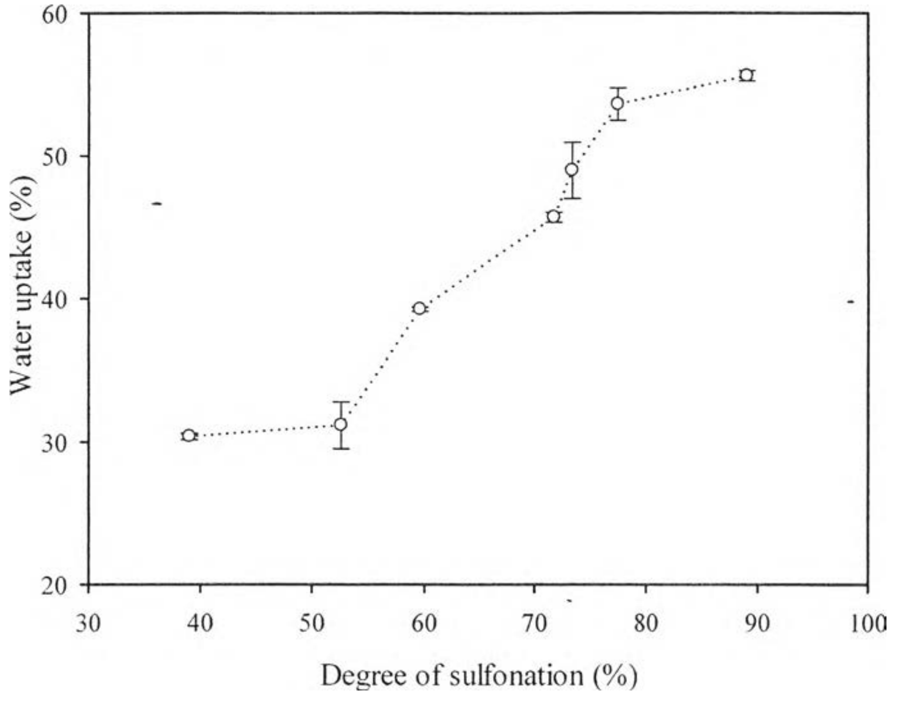

Figure H2 Water uptake of sulfonated poly (ether ether ketone) at different degree of sulfonation.

Table H1 Water uptake of sulfonated poly(ether ether ketone)

Sample	Degree of sulfonation (%)	Water Uptake (%)			
		1	2	3	Average
50_100_3	39.02	30.64	30.30	30.20	30.38 ± 0.23
50_150_3	44.14	32.64	29.38	31.44	31.16 ± 1.65
50_200_3	59.60	39.34	39.06	39.34	39.24 ± 0.16
50_200_5	73.32	50.50	46.73	49.67	48.97 ± 1.98
50_200_7	77.43	54.45	52.30	54.09	53.61 ± 1.15

Table H2 Water uptake data of sulfonated poly (ether ether ketone)

Sample	Wet weight (g)			Dry weight (g)		
	W_{w1}	W_{w2}	W_{w3}	W_{d1}	W_{d2}	W_{d3}
50_100_3	0.0388	0.0387	0.0388	0.0297	0.0297	0.0298
50_150_3	0.0256	0.0251	0.0255	0.0193	0.0194	0.0194
50_200_3	0.0503	0.0502	0.0503	0.0361	0.0361	0.0361
50_200_5	0.0456	0.0449	0.0455	0.0303	0.0306	0.0304
50_200_7	0.0434	0.0431	0.0433	0.0281	0.0283	0.0281

H2 Sulfonated poly(phenylene ether ether sulfone)

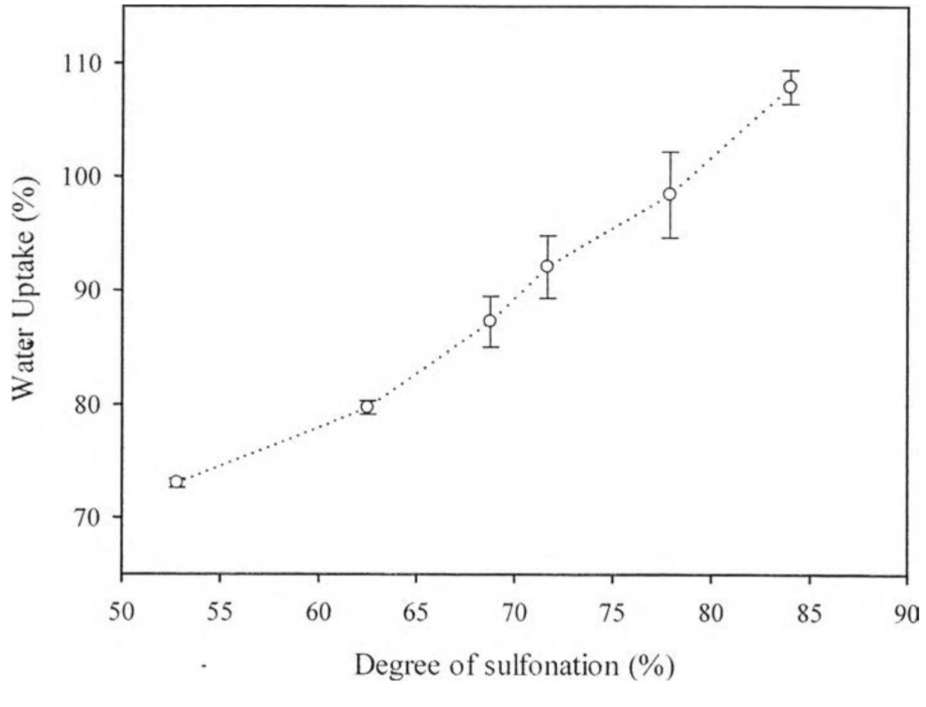

Figure H3 Water uptake of sulfonated poly(phenylene ether ether sulfone) at different degree of sulfonation.

Table H3 Water uptake of sulfonated poly(phenylene ether ether sulfone)

Sample	Degree of sulfonation (%)	Water Uptake (%)			
		1	2	3	Average
25_100_12	52.81	72.58	73.20	73.29	73.02 ± 0.39
25_100_18	62.53	80.27	79.80	79.08	79.72 ± 0.60
25_100_24	68.73	89.61	86.96	85.16	87.24 ± 2.24
25_100_30	71.69	94.99	91.57	89.57	92.04 ± 2.74
25_100_36	77.88	95.17	97.46	102.56	98.40 ± 3.78
25_100_48	83.99	106.76	107.32	109.58	107.89 ± 1.49

Table H4 Water uptake data of sulfonated poly (ether ether ketone)

Sample	Wet weight (g)			Dry weight (g)		
	W_{w1}	W_{w2}	W_{w3}	W_{d1}	W_{d2}	W_{d3}
25_100_12	0.0535	0.0530	0.0532	0.0310	0.0306	0.0307
25_100_18	0.1444	0.1442	0.1438	0.0801	0.0802	0.0803
25_100_24	0.0821	0.0817	0.0811	0.0433	0.0437	0.0438
25_100_30	0.0661	0.0659	0.0654	0.0339	0.0344	0.0345
25_100_36	0.8490	0.8550	0.8710	0.4350	0.4330	0.4300
25_100_48	0.8560	0.8500	0.8530	0.4140	0.4100	0.4070

H3 Nafion117

Table H5 Water uptake of Nafion117

Sample	Water Uptake (%)			
	1	2	3	Average
Nafion117	15.66	17.20	16.04	16.30 ± 0.80

Table H6 Water uptake data of Nafion117

Wet weight (g)			Dry weight (g)		
W_{w1}	W_{w2}	W_{w3}	W_{d1}	W_{d2}	W_{d3}
0.096	0.0981	0.0767	0.083	0.0837	0.0661

Appendix I Mechanical Properties

The tensile properties of thin film were investigated on a universal testing machine (Lloyd, SMT2-500N) under ASTM D882 with 500 N capacity at 23 ± 2 °C and 50 RH. The initial gauge separation and cross speed was set to 50 mm with 25 mm/min, respectively. A specimen with a guage length of 30 mm, a width of 10 mm and, nominal thickness was not greater than 0.250 mm. The parameters consist of the Young's modulus, tensile strength, and elongation at break were measured and reported. All these tests were conducted at ambient temperature and an average value of five repeated tests was taken for each material.

I1 Mechanical properties of S-PEEK, S-PPEES, and Nafion117

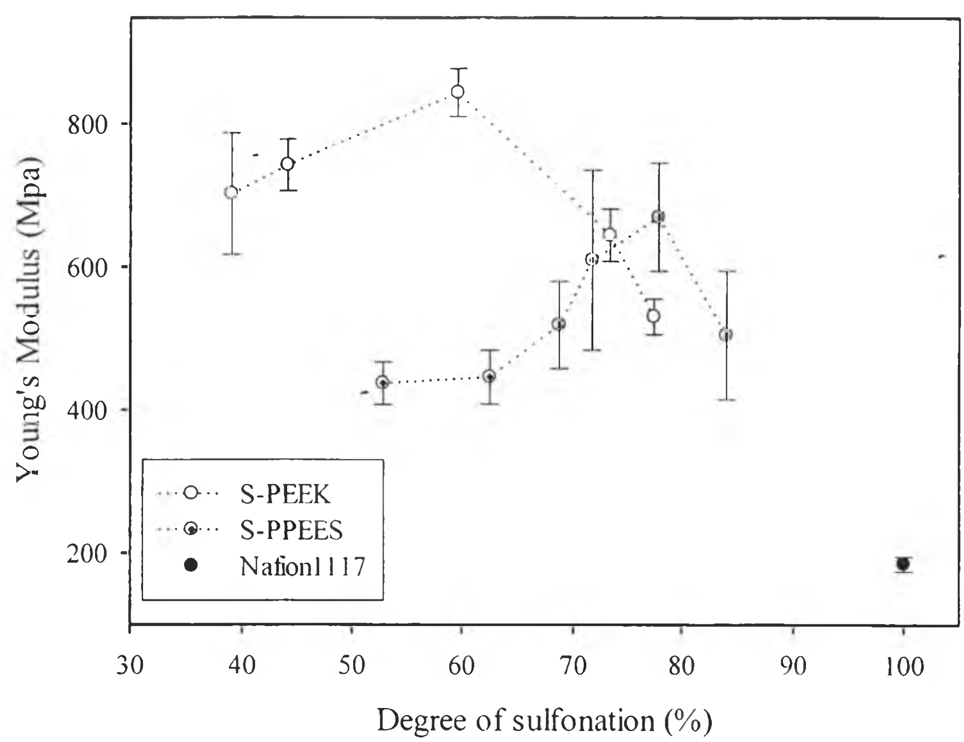

Figure I1 Young's modulus of S-PEEK, S-PPEES, and Nafion117.

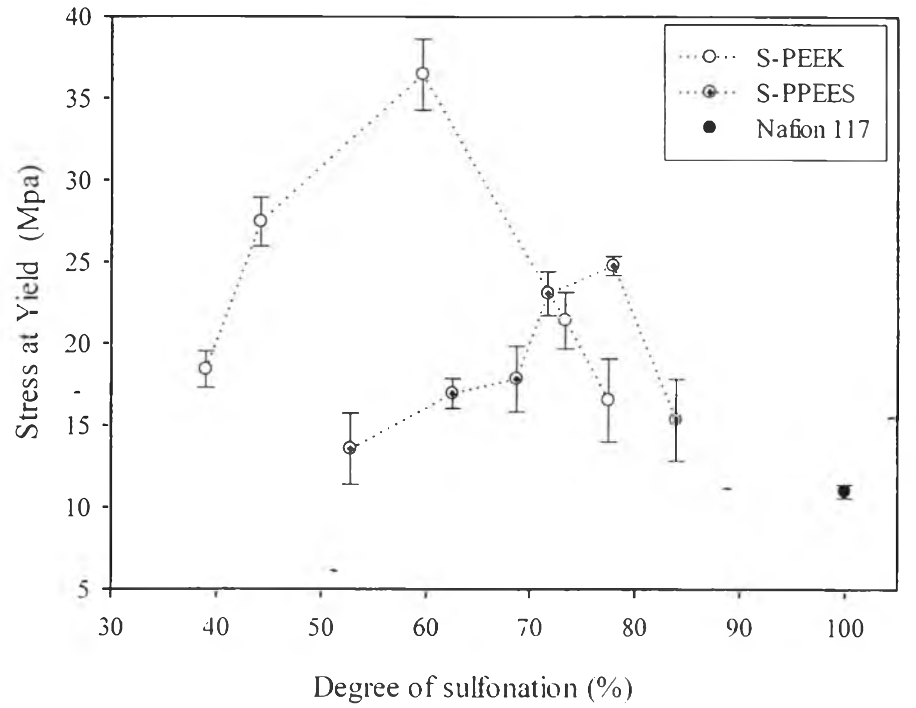

Figure I2 Stress at yield of S-PEEK, S-PPEES, and Nafion117.

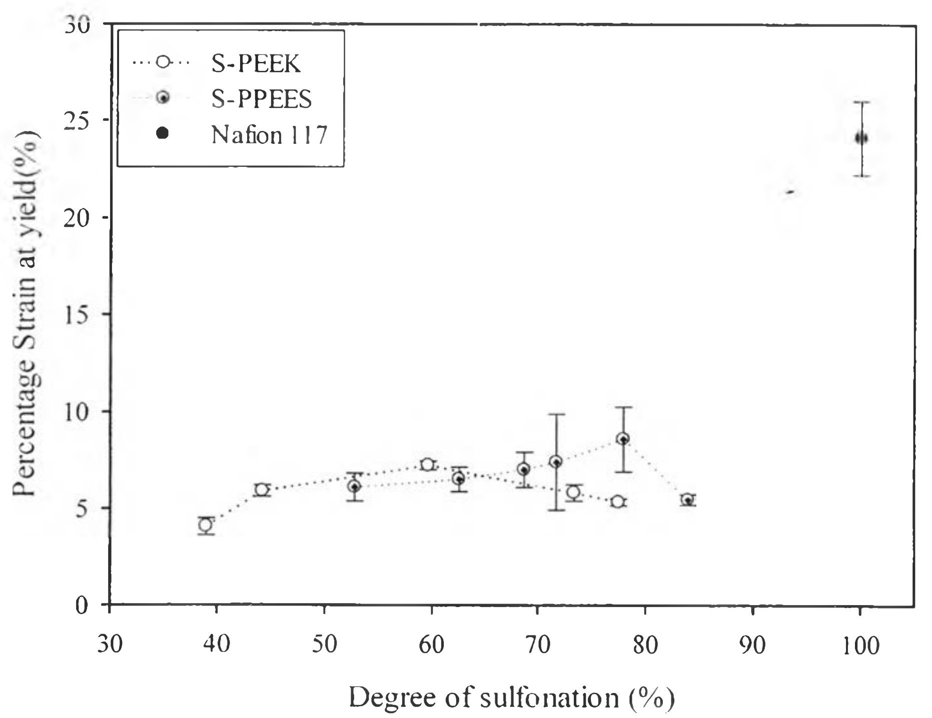

Figure I3 Percentage strain at yield of S-PEEK, S-PPEES, and Nafion117.

Table I1 Mechanical properties of sulfonated poly(ether ether ketone)

Sample	Degree of sulfonation (%)	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
50_100_3	39.02	720.3 ± 78.3	19.40 ± 2.21	4.317 ± 0.632
50_150_3	44.14	742.6 ± 36.1	27.46 ± 1.50	5.916 ± 0.298
50_200_3	59.60	850.3 ± 29.7	36.33 ± 1.79	7.229 ± 0.174
50_200_5	73.32	642.9 ± 26.2	21.29 ± 1.42	5.925 ± 0.373
50_200_7	77.43	530.6 ± 24.9	16.52 ± 2.53	5.341 ± 0.188

Table I2 Mechanical properties of sulfonated poly(phenylene ether ether sulfone)

Sample	Degree of sulfonation (%)	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
25_100_12	52.81	437.1 ± 29.6	13.56 ± 2.16	6.115 ± 0.722
25_100_18	62.53	446.0 ± 37.7	16.94 ± 0.91	6.525 ± 0.827
25_100_24	68.73	519.2 ± 61.2	17.83 ± 2.00	7.014 ± 0.895
25_100_30	71.69	609.8 ± 125.8	23.06 ± 1.36	7.398 ± 2.477
25_100_36	77.88	669.9 ± 75.5	24.78 ± 0.59	8.589 ± 1.668
25_100_48	83.99	504.7 ± 90.4	15.32 ± 2.50	5.475 ± 0.274

Table I3 Mechanical properties of Nafion117

Sample	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Nafion 117	185.0 ± 10.2	10.99 ± 0.41	24.12 ± 1.91

I2 Mechanical properties raw data of S-PEEK

Table I4 Mechanical properties of S-PEEK (DS=39.02%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	607.3	17.14	4.278
Sample 2	Grip	727.6	18.75	3.549
Sample 3	Grip	771.9	19.29	4.347
Sample 4	Grip	774.2	22.41	5.095

Table I5 Mechanical properties of S-PEEK (DS=44.14%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	773.1	28.40	6.086
Sample 2	Grip	751.9	28.25	6.090
Sample 3	Grip	702.8	25.73	5.571

Table I6 Mechanical properties of S-PEEK (DS=59.60%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Guage length	806.1	34.59	7.288
Sample 2	Grip	867.9	38.83	7.001
Sample 3	Guage length	860.0	35.92	7.417
Sample 4	Guage length	867.2	35.96	7.208

Table I7 Mechanical properties of S-PEEK (DS=73.32%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Guage length	680.8	23.32	6.271
Sample 2	*Grip	515.7	21.35	6.307
Sample 3	Grip	607.2	19.92	5.400
Sample 4	Guage length	645.4	20.99	5.831
Sample 5	Grip	643.0	20.11	6.302
Sample 6	*Grip	417.8	14.15	5.006
Sample 7	Grip	637.9	22.09	5.822

Table I8 Mechanical properties of S-PEEK (DS=77.43%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	516.1	19.43	5.130
Sample 2	Guage length	559.4	14.83	5.401
Sample 3	Grip	516.4	15.31	5.491
Sample 4	*Grip	953.6	19.99	3.760
Sample 5	*Grip	507.4	19.64	6.429
Sample 6	*Grip	432.8	10.98	4.016

I3 Mechanical properties raw data of S-PPEES

Table I9 Mechanical properties of S-PPEES (DS=52.81%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	406.2	11.46	5.944
Sample 2	Guage length	465.2	13.44	6.907
Sample 3	Grip	439.9	15.78	5.494

Table I10 Mechanical properties of S-PPEES (DS=62.53%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	437.4	15.74	6.620
Sample 2	*Grip	987.9	14.79	5.177
Sample 3	Grip	468.0	17.47	6.049
Sample 4	Grip	396.8	17.79	7.373
Sample 5	Guage length	481.7	16.76	6.059

Table I11 Mechanical properties of S-PPEES (DS=68.73%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	467.2	17.32	7.557
Sample 2	Grip	491.7	18.00	7.954
Sample 3	Guage length	510.8	15.59	6.523
Sample 4	Guage length	606.9	20.41	6.022

Table I12 Mechanical properties of S-PPEES DS=71.69%

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	496.4	22.86	8.523
Sample 2	Grip	459.9	22.92	11.04
Sample 3	Grip	689.5	21.59	5.15
Sample 4	Grip	750.2	22.65	5.192
Sample 5	Grip	653.1	25.29	7.086

Table I13 Mechanical properties of S-PPEES (DS=77.88%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Guage length	588.2	25.25	8.859
Sample 2	Guage length	684.3	24.12	10.105
Sample 3	Guage length	737.2	24.96	6.802

Table I14 Mechanical properties of S-PPEES (DS=83.99%)

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	Grip	601.3	18.02	5.531
Sample 2	*Grip	8939.9	29.53	14.78
Sample 3	*Grip	1069.8	32.86	8.809
Sample 4	Grip	490.5	14.88	5.178
Sample 5	Grip	422.2	13.07	5.717

I4 Mechanical properties raw data of Nafion117

Table I15 Mechanical properties of Nafion117

Sample	Break position	Young's Modulus (MPa)	Stress at Yield (MPa)	Percentage Strain at Yield (%)
Sample 1	-	181.7	11.04	25.06
Sample 2	-	176.8	10.55	21.92
Sample 3	*Grip	216.0	11.88	78.40
Sample 4	Grip	196.4	11.37	25.37
Sample 5	*Slip	198.9	20.28	154.7
Sample 6	*Slip	143.8	14.23	70.08
Sample 7	*Guage length	53.10	26.55	218.7
Sample 8	*Grip	150.5	9.485	9.666

Remark: Some conditions (*) were not calculated for average evaluation.

Appendix J Selectivity

The selectivity of S-PEEK, S-PPEES, and Nafion 117 is defined the ratio of proton conductivity to vanadium permeability.

Table J1 Selectivity of sulfonated poly(ether ether ketone)

Sample	Degree of sulfonation (%)	Proton conductivity (S/cm)	Vanadium permeability (cm^2/min)	Selectivity (S min/cm^3)
50_100_3	39.02	6.789×10^{-5}	1.512×10^{-6}	44.89
50_150_3	44.14	7.896×10^{-5}	1.908×10^{-6}	41.38
50_200_3	59.60	1.216×10^{-4}	3.199×10^{-6}	38.01
50_200_5	73.32	7.484×10^{-4}	6.088×10^{-6}	122.93
50_200_7	77.43	1.023×10^{-4}	1.038×10^{-5}	98.55

Table J2 Selectivity of sulfonated poly(phenylene ether ether sulfone)

Sample	Degree of sulfonation (%)	Proton conductivity (S/cm)	Vanadium permeability (cm^2/min)	Selectivity (S min/cm^3)
25_100_12	52.81	6.847×10^{-4}	5.720×10^{-6}	119.70
25_100_18	62.53	7.150×10^{-4}	6.582×10^{-6}	108.63
25_100_24	68.73	1.045×10^{-3}	7.670×10^{-6}	136.25
25_100_30	71.69	1.210×10^{-3}	8.361×10^{-6}	144.72
25_100_36	77.88	1.414×10^{-3}	8.922×10^{-6}	158.48
25_100_48	83.99	1.902×10^{-3}	1.280×10^{-5}	148.59

Table J3 Selectivity of of Nafion117

Sample	Proton conductivity (S/cm)	Vanadium permeability (cm^2/min)	Selectivity (S min/cm^3)
Nafion117	3.17×10^{-4}	6.760×10^{-6}	46.95

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 silt and scattering silt of 0.5° together with 0.3 mm of receiving silt were used. The samples were 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 50, with a scan speed of 1°/min, and a scan step of 0.02°.

K1 Sulfonated poly(ether ether ketone)

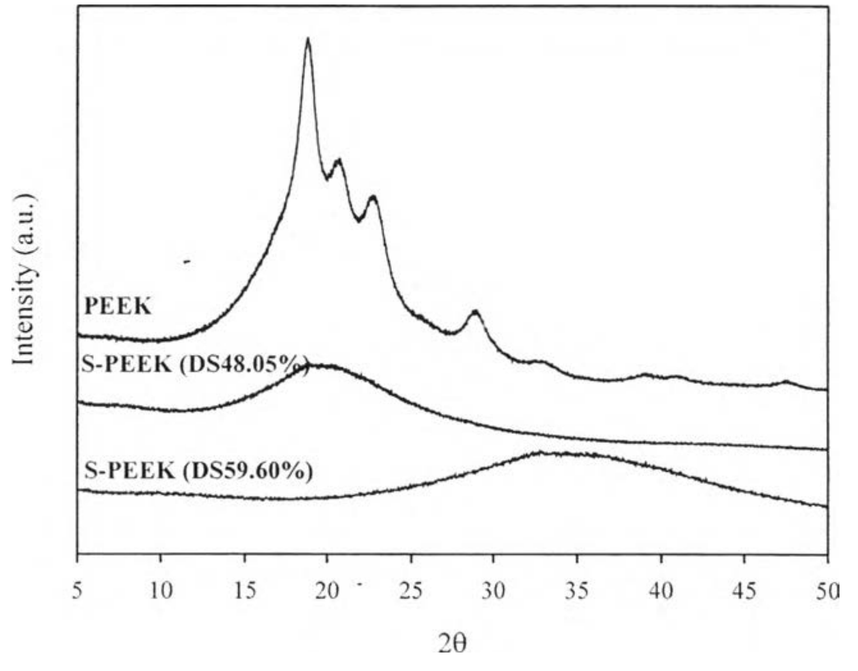

Figure K1 XRD pattern of poly(ether ether ketone) and sulfonated poly(ether ether ketone) at various degrees of sulfonation.

K2 Sulfonated poly(phenylene ether ether sulfone)

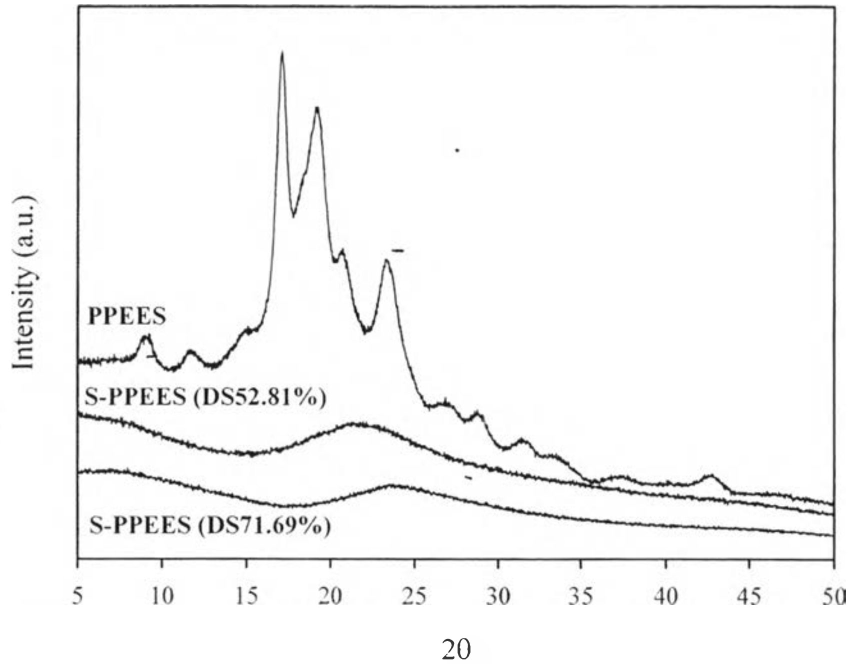

Figure K2 XRD pattern of poly(phenylene ether ether sulfone) and sulfonated poly(phenylene ether ether sulfone) at various degrees of sulfonation.

Figures K1 and K2 show a broad amorphous scattering of XRD pattern for both of polymers after sulfonation. Both of PEEK and PPEES exhibit a more amorphous structure with increasing DS. The increasing DS induces more SO_3H groups on the polymer backbone with resulting in changing the chain conformation and the decreasing the chain free volume, and thus facilitates orientation of the amorphous structure [Reyna-Valencia et al., 2005; Zaidi, 2003].

K3 Comparison between S-PEEK and S-PPEES

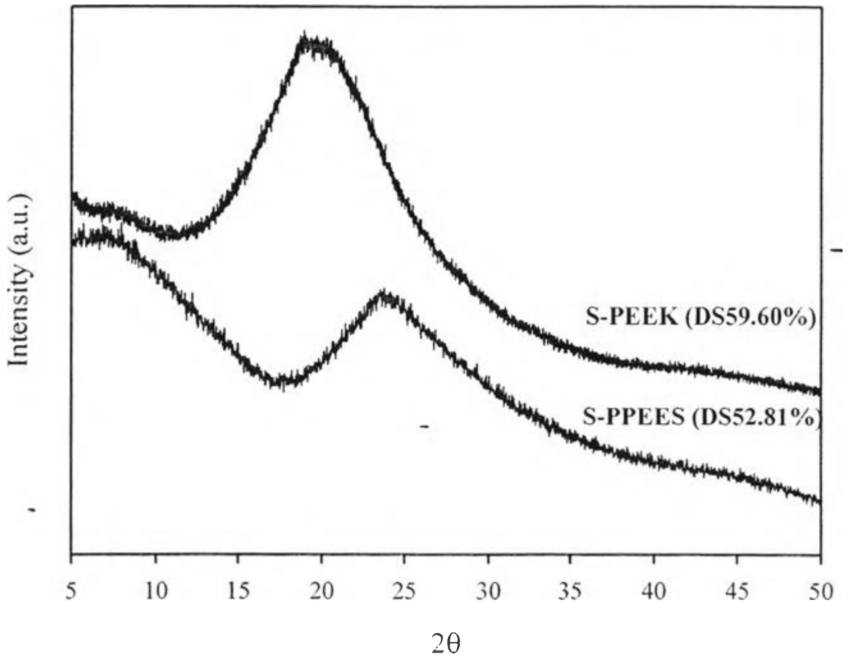

Figure K3 XRD pattern of sulfonated poly(ether ether ketone) and sulfonated poly(phenylene ether ether sulfone).

Figure K3 shows broad amorphous scattering of XRD patterns of S-PEEK and S-PPEES. However, the XRD pattern of S-PPEES is broader than S-PEEK which indicates that the S-PPEES is a more amorphous structure than S-PEEK due to steric hindrance. The chain packing of S-PPEES is lower than S-PEEK because S-PPEES is composed of the sulfone group (O=S=O) which provides more steric hindrance than the ketone group (C=O) of S-PEEK, resulting in a more amorphous structure [Baschek et al., 1999].

Appendix L Nuclear Magnetic Resonance (NMR)

The structures of sulfonated PEEK and PPEES were determined by a NMR spectrometer (Bruker Biospin Avance 500 MHz NMR spectrometer) using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent. For each analysis, 3 wt% polymer solution was prepared in DMSO and the experiment was conducted at room temperature.

L1 Sulfonated poly(ether ether ketone)

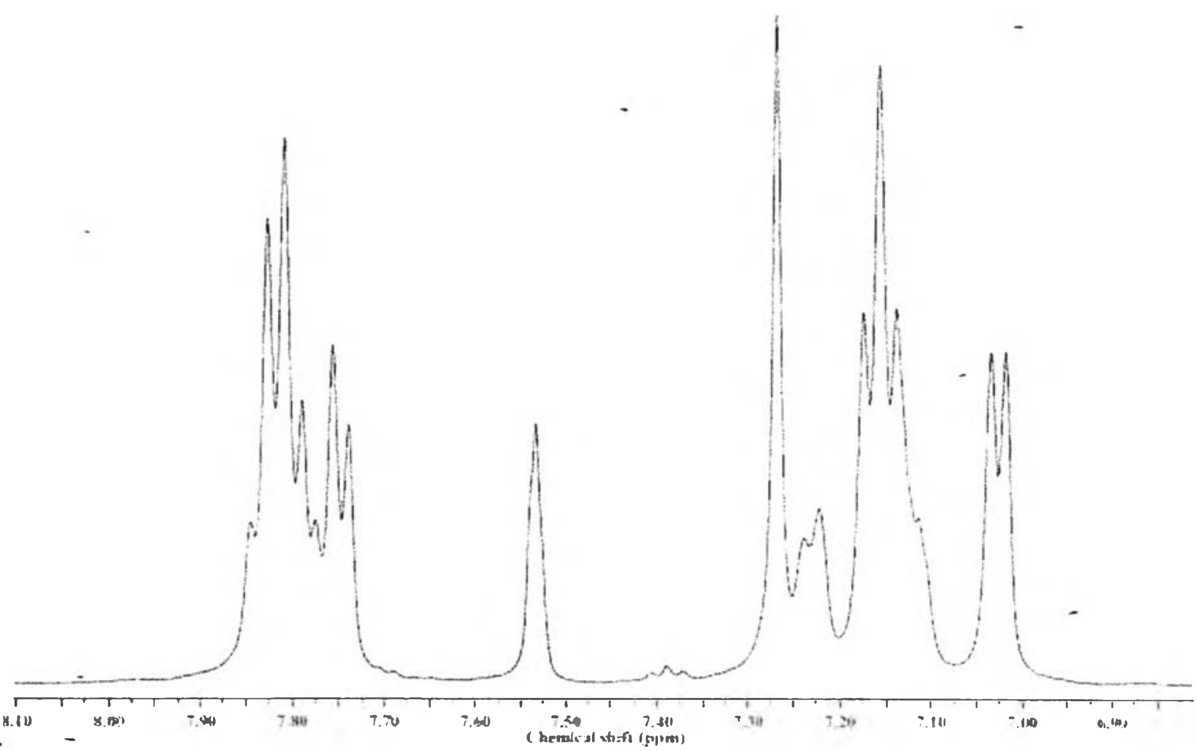

Figure L1 NMR spectrum of poly sulfonated poly(ether ether ketone).

L2 Sulfonated poly(phenylene ether ether sulfone)

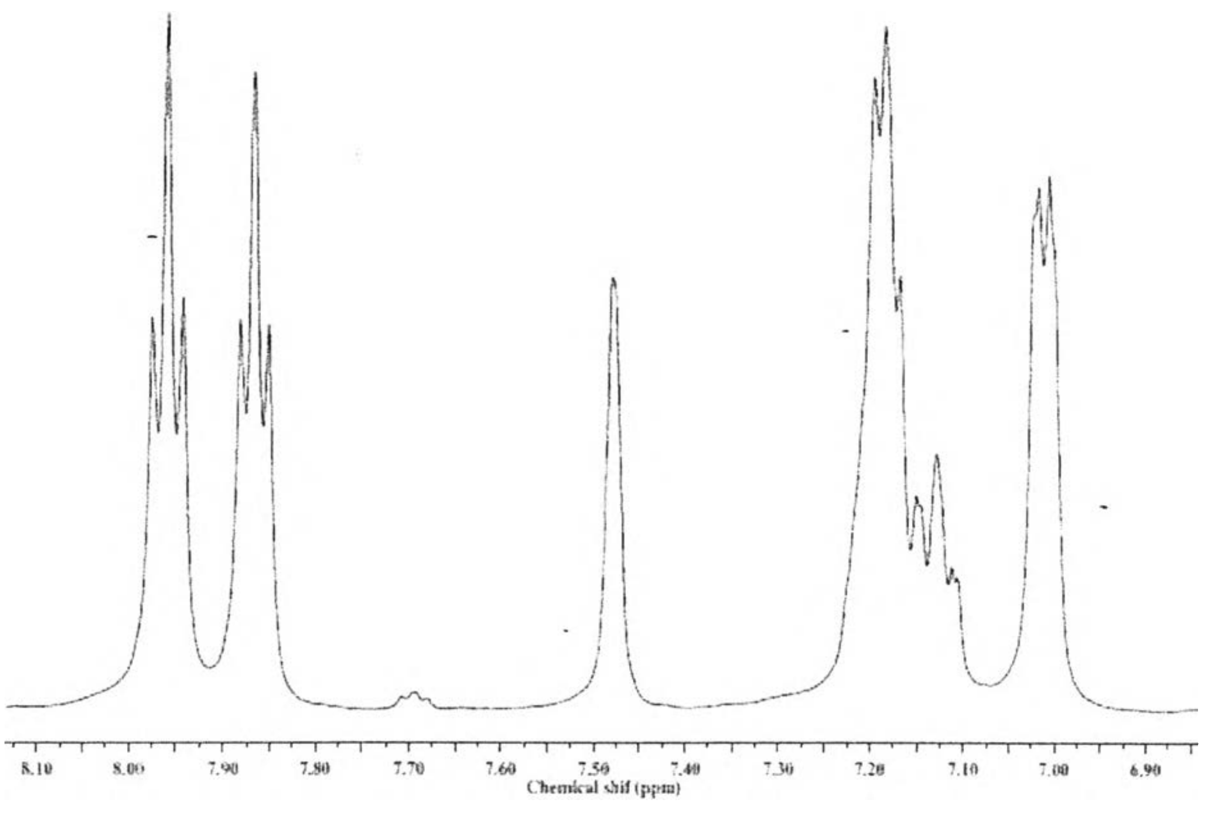

Figure L2 NMR spectrum of sulfonated poly(phenylene ether ether sulfone).

Sulfonation of PEEK and PPEES are an electrophilic substitution reaction, in which the SO_3H groups are introduced into the hydroquinone segment of the polymer chains by the ether linkage and the sulfone linkage of PEEK and PPEES, respectively. The presence of the SO_3H group on S-PEEK and S-PPEES causes a down-field shift of the hydrogen (H_E) to 7.55 ppm and 7.45 ppm for S-PEEK and S-PPEES, respectively. The doublets at 7.15 and 7.25 can be assigned to the hydrogen (H_C and H_D) on hydroquinone ring (Yee *et al.*, 2013; Unveren *et al.*, 2010).

CURRICULUM VITAE

Name: Mr. Somchai Watpathomsub

Date of Birth: July 11, 1989

Nationality: Thai

University Education:

2008–2011 Bachelor Degree of Petrochemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhonpathom, Thailand

Publications:

1. Buasri, A.; Chaiyut, N.; Loryuenyong, V.; Phakdeepataraphan, E.; Watpathomsub, S.; and Kunakemakorn, V. (2013). Utilization of Biodiesel Wastes as a Bioresource for the Preparation of Activated Carbon, International Journal of Applied Physics and Mathematics, 3(3), 173-177.

Proceedings:

1. Watpathomsub, S.; Sirivat, A.; and Jitkarnka, S. (2014, April 22) Modified Poly(ether ether ketone) and Poly(phenylene ether ether sulfone) as Proton Exchange Membrane for Vanadium Redox Flow Battery. Proceedings of the The 5th Research Symposium on Petrochemical and Materials Technology and the 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

Presentations:

1. Watpathomsub, S.; Sirivat, A.; and Jitkarnka, S. (2014, April 22) Modified Poly(ether ether ketone) and Poly(phenylene ether ether sulfone) as Proton Exchange Membrane for Vanadium Redox Flow Battery. Proceedings of the The 5th Research Symposium on Petrochemical and Materials Technology and the 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.