Assessing the Influence of Different Cation Chemistries on Ionic Conductivity and Alkaline Stability of Anion Exchange Membranes

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Supporting Information

Experimental

Synthesis

Reagents: polysulfone (PSF) – average MW ~ 35,000 g/mol – Sigma-Aldrich, chloroform ($CHCl_3$) – ACS Grade – Fisher, deuterated dimethylsulfoxide (d–DMSO) – D atom 99.9% Cambridge Isotope Labs, Inc. or Acros or Aldrich, deuterated chloroform ($CDCl_3$) – D atom 99.8% – Acros, N,N–dimethylformamide (DMF) – ACS Grade – Fisher, methanol (MeOH) – ACS Grade – Fisher, paraformaldehyde – reagent grade – Sigma-Aldrich, tin(IV) chloride ($SnCl_4$) – Sigma-Aldrich, chlorotrimethylsilane – Sigma–Aldrich, trimethylamine (TMA) in ethanol – 33 wt% - Acros Organics, trimethylphosphine (TMP) – 97% – Sigma–Aldrich, 1,4–dimethylpiperazine (DMP) – 98% – Sigma–Aldrich, nitrogen, hydrogen, oxygen, and air – purified – praxair, deionized water (DI H_2O) – prepared fresh daily (18 MΩ) – with Direct Q5 water filtration system by Millipore, 1, 2, or 6 M potassium hydroxide (KOH) solutions by dissolving KOH pellets in DI H_2O – ACS Grade – Fisher, 1 M sodium carbonate solutions by dissolving Na_2CO_3 powder in DI H_2O – ACS Grade – Fisher, platinum on carbon (Pt/C) – 40 wt% – Alfa Aesar, 1 wt% phenolphthalein indicator by dissolving phenolphthalein disodium salt in a 90:10 mixture of ethanol:DI H_2O – phenolphthalein disodium salt – 95% – Acros, 0.1 M KOH – standardized – Fisher, 0.1 M hydrochloric acid (HCl) – standardized – Fisher, 0.1 M silver nitrate ($AgNO_3$) – standardized – Fisher, 0.1 M potassium thiocyanate (KSCN) by dissolving KSCN in DI H_2O – certified ACS – Fisher, 11 wt% ferric nitrate ($Fe(NO_3)_3$) indicator – by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ in DI H_2O – ACS certified – Fisher, 1 M sodium nitrate salt ($NaNO_3$) by dissolving $NaNO_3$ in DI H_2O – Acros. All reagents were used as received.

Chloromethylated Polysulfone (CMPSF): The synthesis of CMPSF followed the Friedel-Crafts type reaction reported by Avram and co-workers.[1] An example of one batch synthesized: 20 g of PSF was dissolved in 1 L of $CHCl_3$. After PSF was dissolved, the mixture was transferred to a 2 L bulb flask with a stir bar equipped with a reflux condenser. 13.6 g of paraformaldehyde was added to the bulb flask and the solution was mixed while raising the temperature to 55 °C. At 55 °C, 60 mL of chlorotrimethylsilane and 1050 μL of $SnCl_4$ catalyst were added. The headspace of the bulb flask was blanketed with nitrogen and sealed. The reaction was carried out for various amounts of time to control the degree of functionalization (DF) of chloromethylated sites. The DF is the average number of chlormethylated sites per monomer unit. The CMPSF reaction mixture was filtered, with the filtrate being precipitated in MeOH (5:1 volume ratio of MeOH to CMPSF solution). The solution was then vacuum filtered, with the solid being collected. CMPSF was further purified by dissolving in 800 mL $CHCl_3$. The dissolved CMPSF was filtered, with the filtrate being precipitated in MeOH. The collected solid was dried in a vacuum oven at room temperature for 12 hours.

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Results and Discussion

Reaction kinetics of chlormethylated polysulfone (CMPSF)

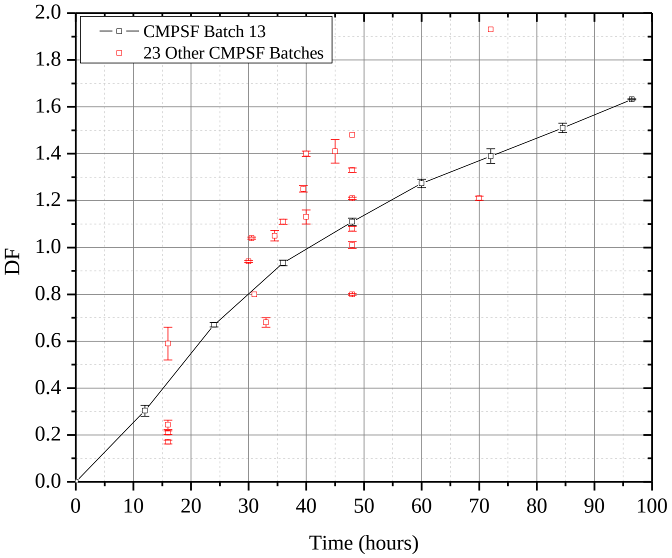


Fig. S1: The degree of functionalization (DF) for the chloromethylation of polysulfone (PSF) at different reaction times for multiple batches (red data points) and for a single batch (black data points with line).

DF - Starting CMPSF	PSF-TMA$^+$	PSF-TMP$^+$	PSF-DMP$^+$		PSF-TMA$^+$	PSF-TMP$^+$	PSF-DMP$^+$
		Chloride Form				Hydroxide Form	
0.67 ± 0.04	0.98 ± 0.00	1.14 ± 0.02	0.92 ± 0.01	Conversion	0.95 ± 0.01	0.37 ± 0.01	0.98 ± 0.08
	1.27 ± 0.00	1.46 ± 0.06	1.12 ± 0.01	Theor. IEC (mmol g^{-1})	1.27 ± 0.01	0.49 ± 0.02	1.23 ± 0.10
0.94 ± 0.01	1.04	n/a	n/a	Conversion	1.10	n/a	n/a
	1.80	n/a	n/a	Theor. IEC (mmol g^{-1})	1.97	n/a	n/a
1.01 ± 0.03	n/a	n/a	0.81 ± 0.01	Conversion	n/a	n/a	0.88 ± 0.04
	n/a	n/a	1.31 ± 0.01	Theor. IEC (mmol g^{-1})	n/a	n/a	1.51 ± 0.07
1.04 ± 0.01	0.96 ± 0.01	1.11 ± 0.04	n/a	Conversion	0.98 ± 0.03	n/a	n/a
	1.79 ± 0.05	2.03 ± 0.08	n/a	Theor. IEC (mmol g^{-1})	1.91 ± 0.05	n/a	n/a
1.11 ± 0.02	1.09 ± 0.01	1.07 ± 0.01	0.94 ± 0.03	Conversion	1.16 ± 0.02	n/a	0.98 ± 0.03
	2.16 ± 0.05	2.05 ± 0.02	1.64 ± 0.09	Theor. IEC (mmol g^{-1})	2.39 ± 0.04	n/a	1.81 ± 0.05
1.19 ± 0.01	1.00 ± 0.01	1.06 ± 0.01	0.88 ± 0.01	Conversion	1.05 ± 0.01	n/a	0.97 ± 0.02
	2.10 ± 0.06	2.14 ± 0.03	1.62 ± 0.05	Theor. IEC (mmol g^{-1})	2.27 ± 0.02	n/a	1.87 ± 0.05

Table S1: Summary of original theoretical ion-exchange capacity (IEC) values and conversion of chloromethylated sites to cation sites.

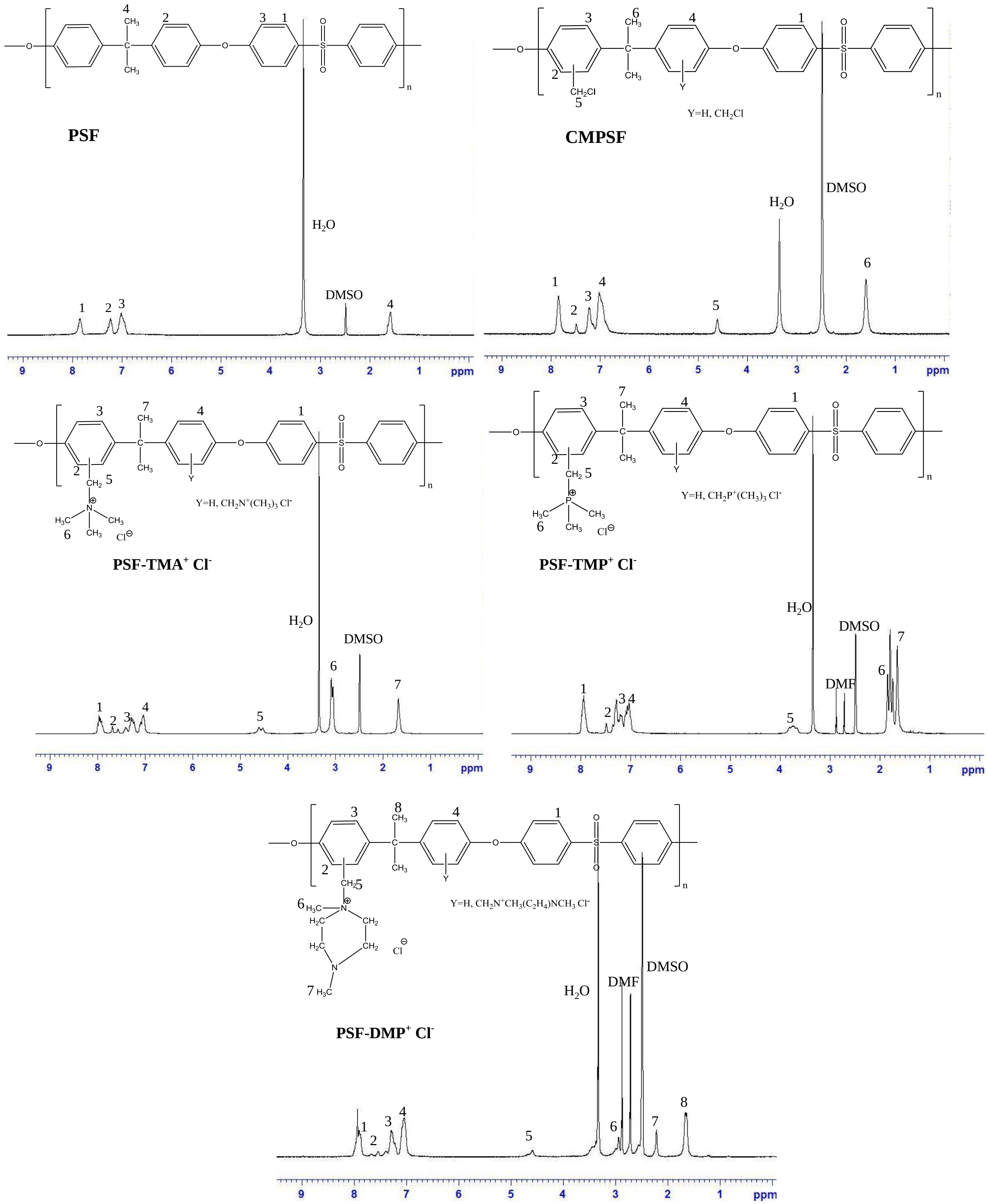


Fig. S2: ^{1}H NMR spectra of PSF, PSF functionalized with chloromethylated sites (CMPSF), and PSF with TMA$^+$, TMP$^+$, and DMP$^+$ cations in the chloride form.

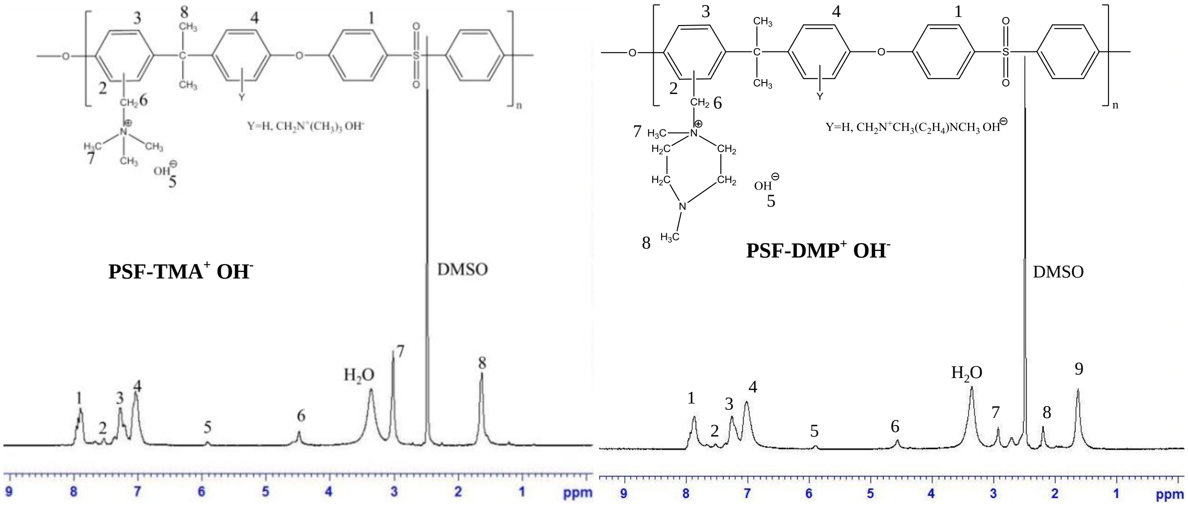


Fig. S3: ^{1}H NMR spectra of PSF with trimethylammonium cations (PSF-TMA$^+$) and PSF with 1,4-dimethylpiperazinium cations (PSF-DMP$^+$) in the hydroxide form.

Fig. S4: Thin film anion exchange membranes ranging from 40 to 80 μm in thickness.

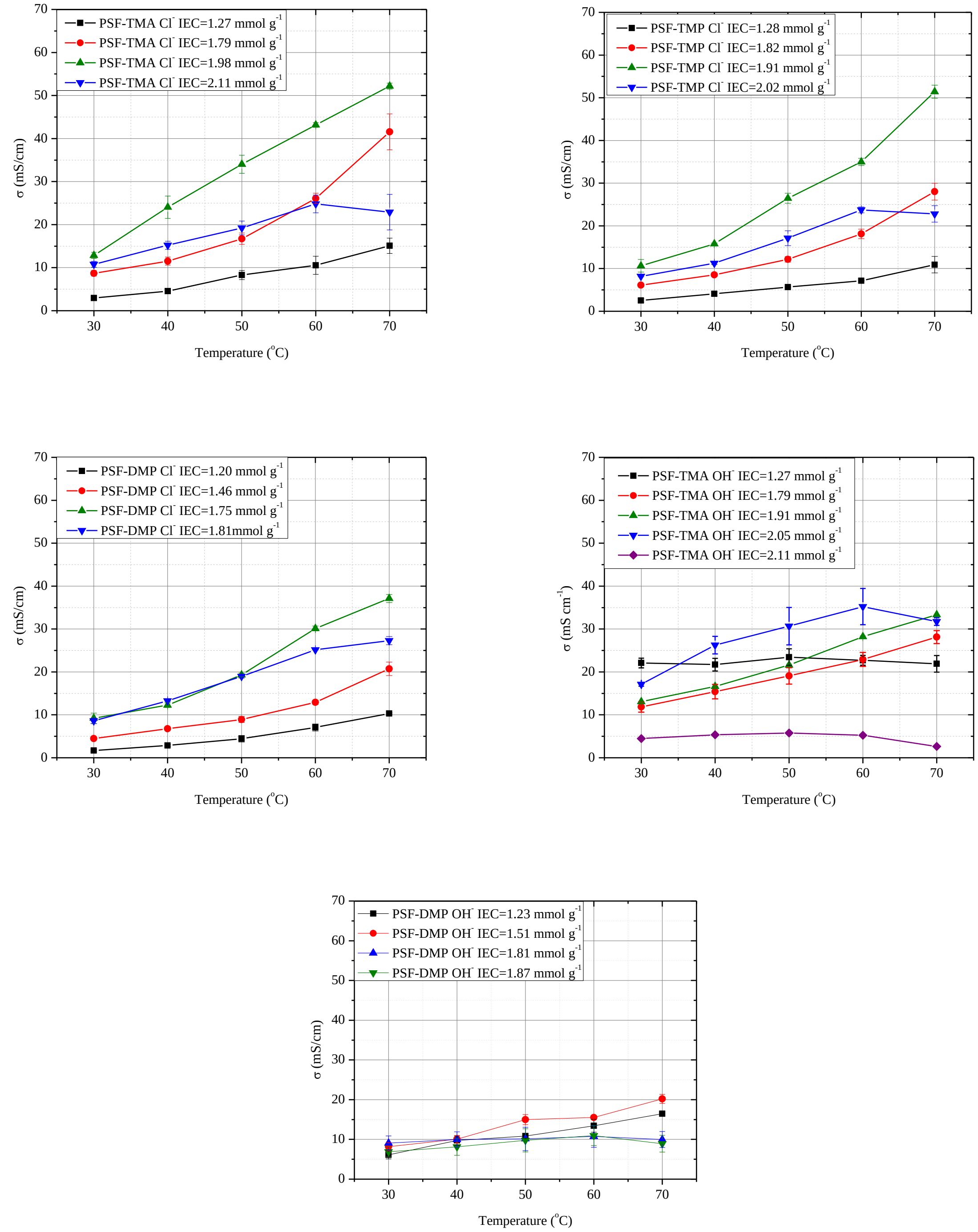


Fig. S5: Ionic conductivities of anion exchange membranes (AEMs) in DI H_2O in chloride or hydroxide form as function of temperature at various IECs. Note: IECs are theoretical IEC values.

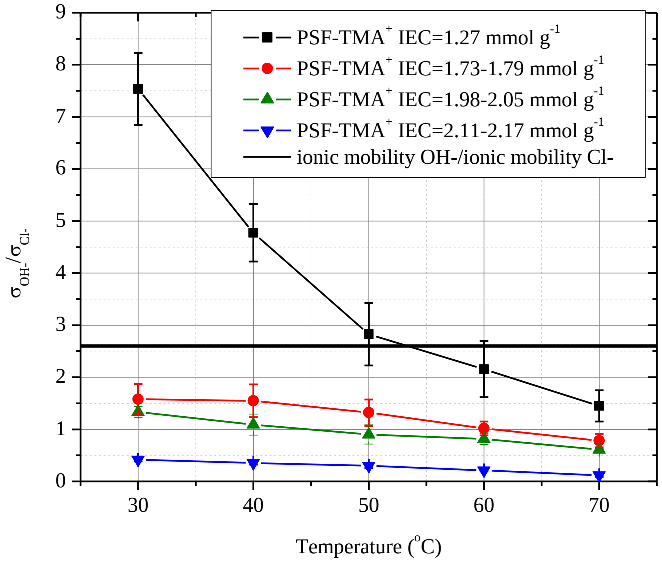


Fig. S6: Ratio of hydroxide ion conductivity to chloride ion conductivity vs. temperature for PSF-TMA$^+$ for different IECs. Note: IECs are theoretical IEC values.

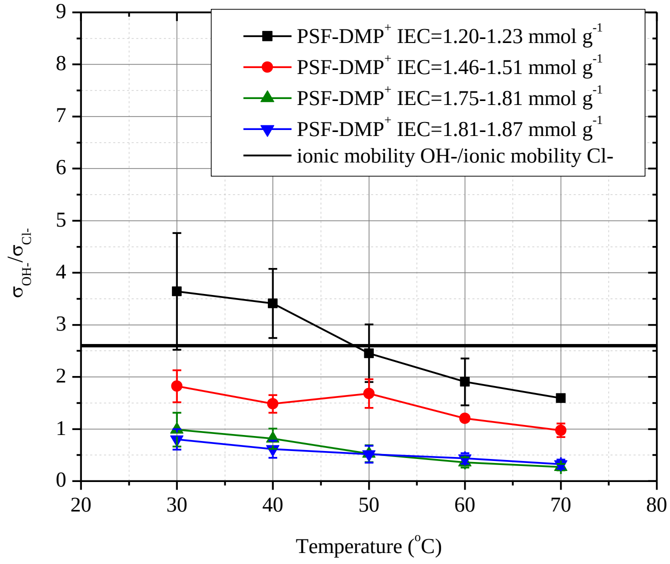


Fig. S7: Ratio of hydroxide ion conductivity to chloride ion conductivity vs. temperature for PSF-DMP$^+$ for different IECs. Note: IECs are theoretical IEC values.

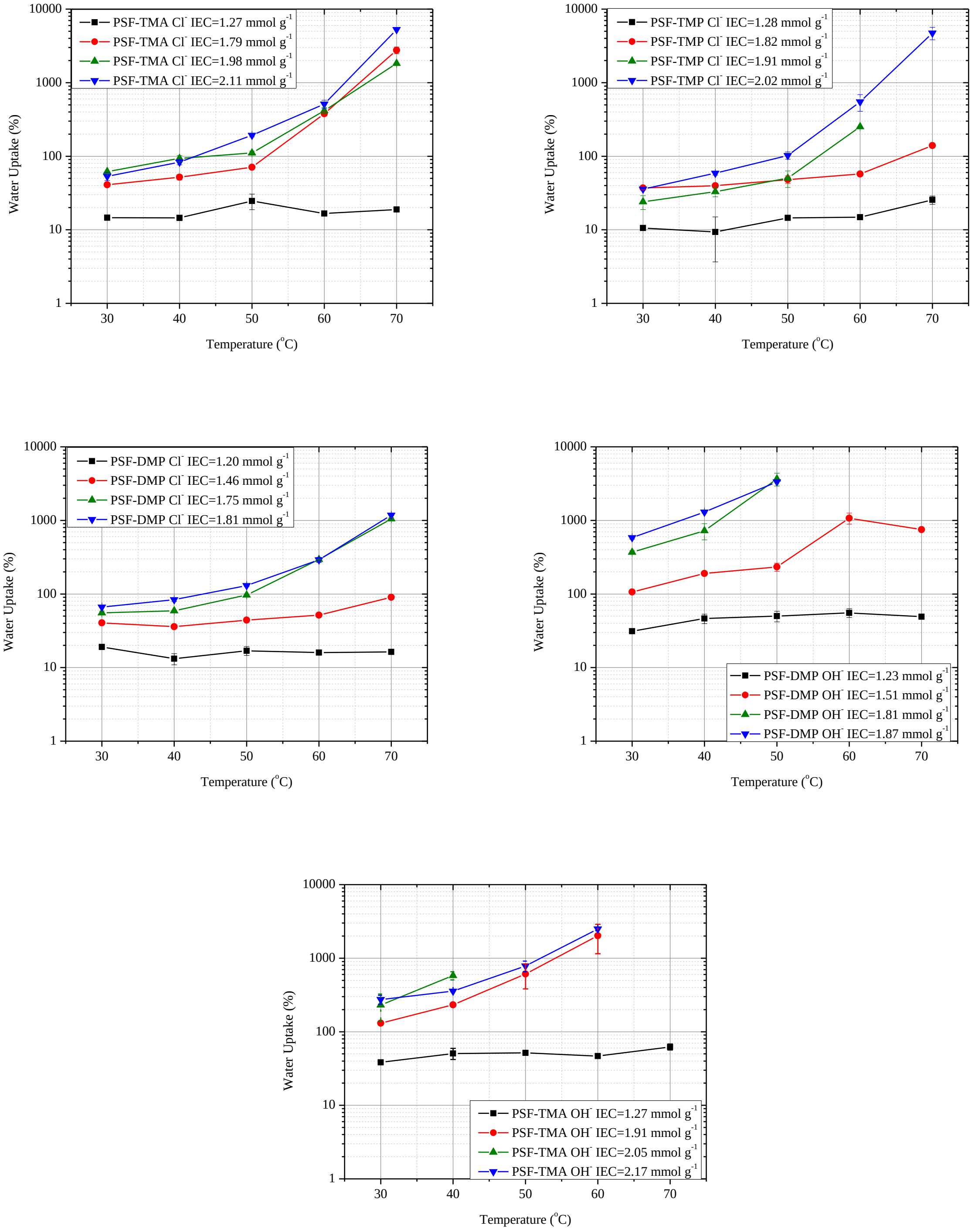


Fig. S8: Liquid phase water uptake of AEMs in chloride or hydroxide form as function of temperature at various IECs. Note: IECs are theoretical IEC values.

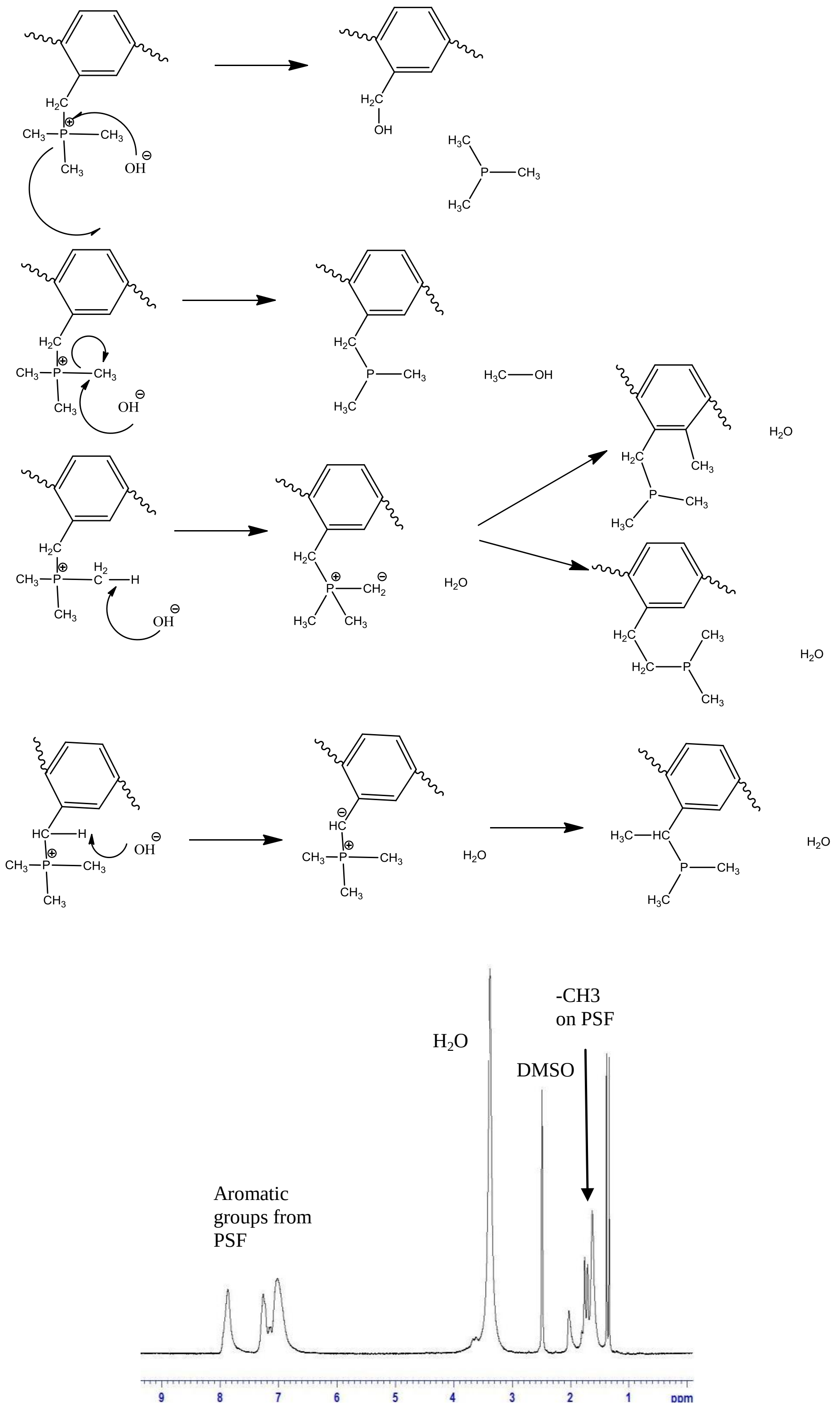


Fig. S9: Proposed degradation mechanisms of PSF–TMP$^+$ and ^{1}H NMR of PSF–TMP$^+$ OH$^-$.

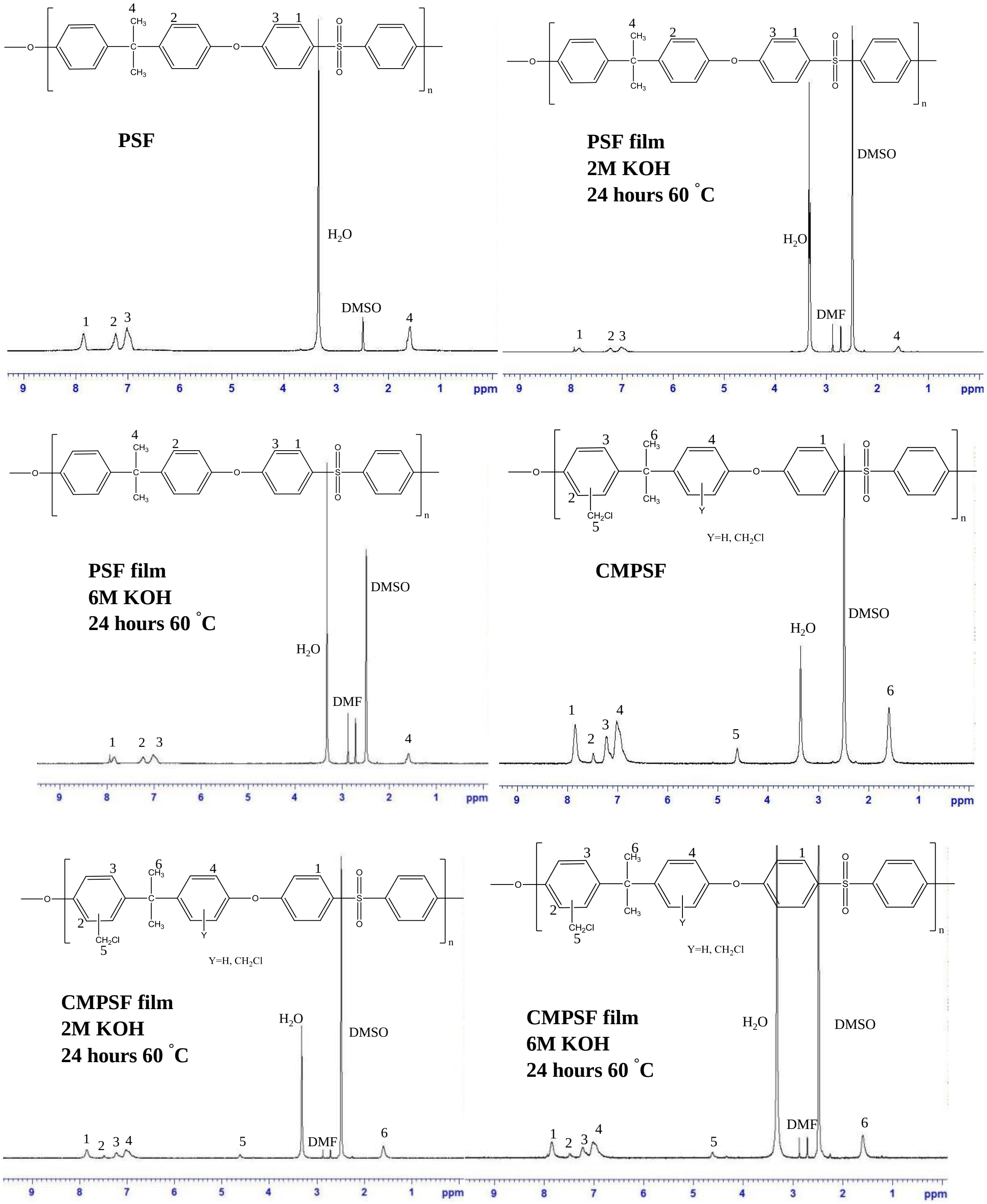


Fig. S10: ^{1}H NMR spectra of PSF and CMPSF materials and PSF and CMPSF films exposed to different concentrations of aqueous potassium hydroxide solutions at 60 °C for 24 hours. PSF and CMPSF materials did not show changes in their ^{1}H NMR spectra after exposure to aqueous potassium hydroxide solutions.

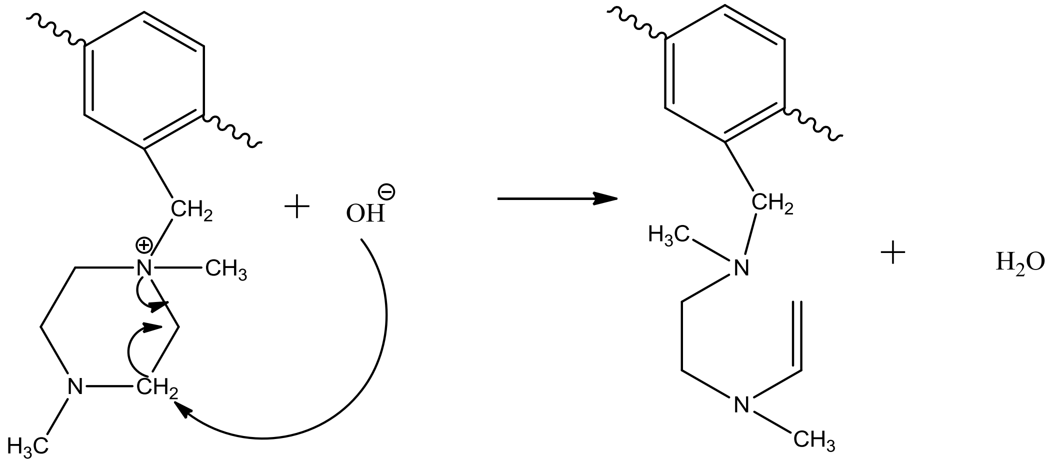


Fig. S11: Proposed Hoffman elimination degradation mechanism of DMP$^+$ cation attached to PSF in the presence of the hydroxide ion.

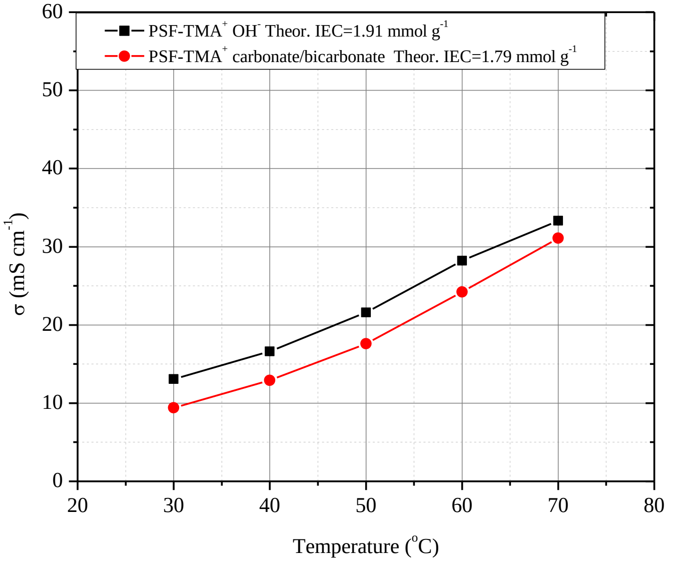
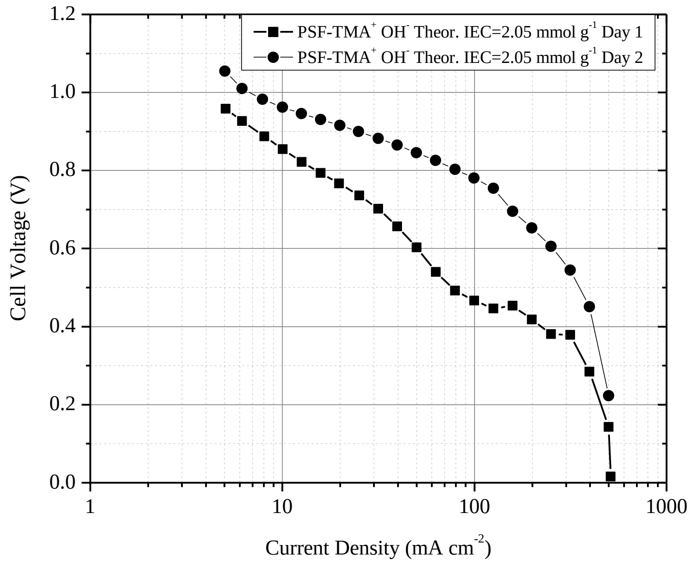


Fig. S12: Ionic conductivity plot of PSF-TMA$^+$ (from the same starting CMPSF DF=1.04 ±0.01) comparing different hydroxide and carbonate anions. The lower ion conductivity of PSF-TMA$^+$ carbonate/bicarbonate is attributed to the lower ionic mobility of the carbonate/bicarbonate anion. Note: PSF-TMA$^+$ carbonate/bicarbonate ^{1}H NMR spectra showed a conversion of 0.98.



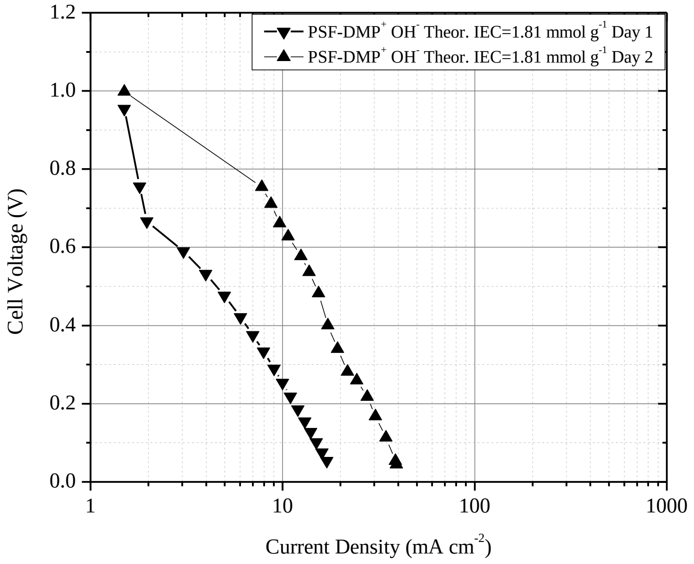


Fig. S13: Fuel cell performance data of different PSF AEMs tested initially and subsequently a day later. Better fuel cell performance data was attained on the second day due to the conditioning of the cell to replace carbonate ions with hydroxide ions.

References

1.) E. Avram, E. Butuc and C. Luca, *J.M.S.-Pure Appl. Chem.*, 1997, **A34**, 1704.