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A Perfluorinated Anion Exchange Membrane with a 1,4 Dimethylpiperazinium Cation

Min-suk J. Jung, Christopher G. Arges and Vijay Ramani[a]
[a]*Center for Electrochemical Science and Engineering*
Department of Chemical and Biological Engineering
Illinois Institute of Technology
10 W, 33rd Street, Chicago, IL 60616.
E-mail: ramani@iit.edu; Fax: 312-567-8874; Phone: 312-567-3064

Supporting Information

Synthesis of AEMs

Reagents

Nafion® 111 in the sulfonyl fluoride form - E. I. Dupont, 1,4-Dimethylpiperazine (DMP) – 98% - Sigma-Aldrich, Nitrogen – purified – Praxair or Airgas, Hydrogen - purified Praxair or Airgas, Oxygen - purified Praxair or Airgas, deionized water (DI H_2O) – prepared fresh daily – with Milli-Q Water Filtration System by Millipore, 1 M Potassium Hydroxide (KOH) by diluting Potassium Hydroxide (KOH) - >90% - Sigma-Aldrich- in DI H_2O, pH Test Strip 0-14 – Ricca Chemical Company, Polysulfone (PSF) – Average MW ~ 35,000 g/mol - Sigma-Aldrich, Chloroform ($CHCl_3$) – ACS Grade - Fisher, d-Chloroform ($CDCl_3$) – D atom 99.8% - Acros Organics, d-Dimethylsulfoxide (d-DMSO) - D atom 99.9% - Cambridge Isotope Labs, Inc., N,N-Dimethylformamide (DMF) - ACS Grade - Fisher, N,N-Dimethylacetamide - ACS Grade - Fisher Platinum nominally 40% on carbon black - Alfa Aesar, Methanol (MeOH) – ACS Grade - Fisher, Sodium Carbonate (Na_2CO_3) - ACS Grade - Fisher, Paraformaldehyde – Reagent Grade - Sigma-Aldrich, Tin(IV) Chloride ($SnCl_4$) - Sigma-Aldrich, Trimethylchlorosilane - Sigma-Aldrich

All chemicals were used as received.

Nafion®-DMP$^+$ F$^-$/OH$^-$

Nafion® 111 film in the sulfonyl fluoride form was cut into strips, and the strips were immersed in DMP. The headspace of the vessel containing the film in DMP was blanketed with nitrogen and sealed. The solution with the film was stirred at 60 °C. The film was reacted with DMP for different times from 0 to 24 hours. After the reaction, the film was rinsed with DI H_2O to remove excess DMP. The film is now Nafion®-DMP$^+$ in the fluoride form (Nafion®-DMP$^+$ F$^-$). Nafion®-DMP$^+$ F$^-$ was then ion-exchanged with 1 M KOH for 24 hours at room temperature by immersing the Nafion®-DMP$^+$ F$^-$ film in 1 M KOH solution. The 1 M KOH solution was changed several times over a 24-hour period. The film is now Nafion®-DMP$^+$ in the hydroxide form (Nafion®-DMP$^+$ OH$^-$). Nafion®-DMP$^+$ OH$^-$ was immersed and rinsed with DI H_2O for several hours (at least 3 hours) to remove excess hydroxide ions. The sample was rinsed continuously until the pH of the water was between 7 to 8 to confirm removal of excess hydroxide ions.

Chloromethylated Polysulfone (CMPSF)

The synthesis of CMPSF followed a procedure similar to Avram and co-workers.[1] 5 g of PSF was dissolved in 250 mL of $CHCl_3$. After PSF was dissolved, the mixture was transferred to a 250 mL bulb flask with a stir bar equipped with a reflux condenser. 3.4 g of paraformaldehyde was added to the bulb flask and the solution was mixed while raising the temperature to 55 °C. At 55 °C, 12.4 g of trimethylchlorosilane and 0.59 g of $SnCl_4$ catalyst were added. The headspace of the bulb flask was blanketed with nitrogen and sealed. The reaction was carried out for 16 hours. CMPSF was precipitated using MeOH (5:1 volume ratio of MeOH to CMPSF solution). The solution was then filtered, collected, and dissolved in $CHCl_3$. 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 at least 12 hours.

PSF-DMP$^+$ Cl$^-$/OH$^-$

3.22 g of CMPSF was dissolved in 33 mL of DMF in a 100 mL bulb flask equipped with a magnetic stir bar. The solution was stirred at 80 °C. A 3 to 1 mole ratio of DMP to chloromethylated sites was added to the bulb flask. The bulb flask was blanketed with nitrogen and then closed. The mixture was reacted for 12 hours. 20 mL of the reaction mixture was poured on to a 4 x 6 inch glass plate in an oven set to 60 °C. After drying for 12 hours, the film was removed from the glass plate. The PSF-DMP$^+$ Cl$^-$ film was then ion-exchanged with 1 M KOH for 24 hours at room temperature by immersing the PSF-DMP$^+$ Cl$^-$ film in 1 M KOH solution. The 1 M KOH solution was changed several times over a 24 hour period. The PSF-DMP$^+$ in the hydroxide form was immersed and rinsed with DI H_2O for several hours (at least 3 hours) to remove excess hydroxide ions. The sample was rinsed continuously until the pH of the water was between 7 to 8 to confirm removal of excess hydroxide ions.

NMR Characterization

NMR measurements were carried out with a Bruker 300 MHz NMR spectrometer.

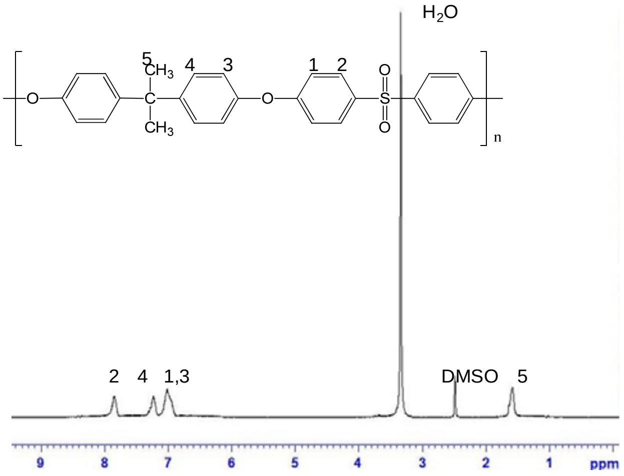

Fig 1. NMR spectra of PSF in d-DMSO.

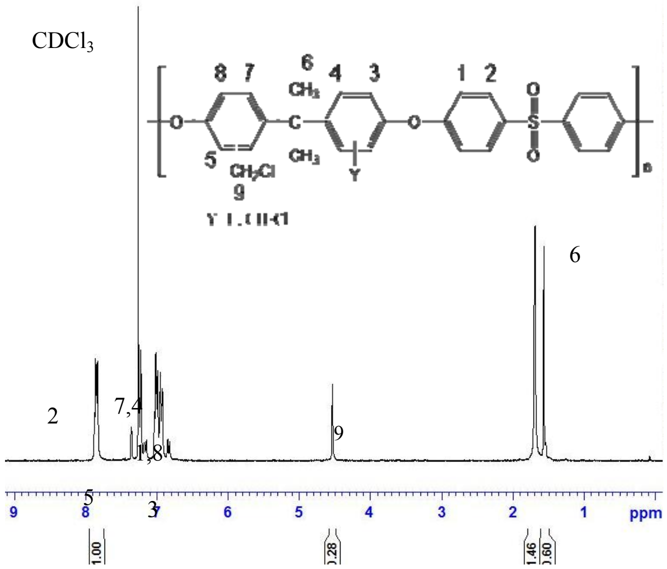

Fig 2. NMR spectra of CMPSF in $CDCl_3$.

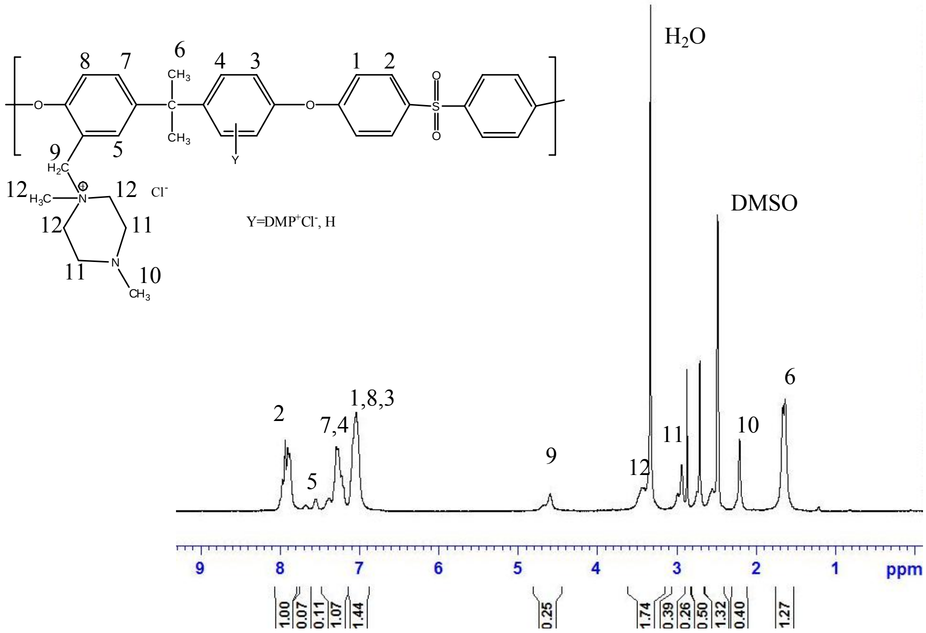

Fig 3. NMR spectra of PSF-DMP$^+$ Cl$^-$ in d-DMSO.

Calculations for NMR

Degree of Chloromethylation (DC):

$$DC = \frac{3 \cdot \text{Area}(\delta = 4.5 \text{ ppm})}{\text{Area}(\delta = 1.6 \text{ ppm})}$$

$$0.58 = \frac{3 \cdot 0.28}{1.46}$$

Conversion of chloromethylated sites to DMP$^+$

$$\% \text{ Converted } = \frac{2 \cdot \text{Area}(\delta = 2.2 \text{ ppm})}{DC \cdot \text{Area}(\delta = 1.6 \text{ ppm})}$$

$$*100\% \approx \frac{2 \cdot 0.40}{0.59 \cdot 1.27}$$

*Note: 100% conversion is approximate. The DC value of 0.59 is average for n=3. Although, one sample measured had a DC of 0.58 as shown in the example calculations of DC from Figure 2. The range of samples analyzed had DCs from 0.58 to 0.61.

Determination of Theoretical Ion-Exchange Capacity (IEC) for PSF-DMP$^+$OH$^-$

$$IEC_{Theor.}\left\{\frac{mmol}{g}\right\} = \frac{DC \cdot 1000\left\{\frac{mmol}{mol}\right\}}{MW_{AVG,Monomer}\left\{\frac{g}{mol}\right\}}$$

$$MW_{AVG,Monomer}\left\{\frac{g}{mol}\right\} = MW_{PSF} + DC \cdot (MW_{base} + MW_{counterion} - 1)$$

$$MW_{PSF} = 442\frac{g}{mol}$$

$$MW_{base} = MW_{DMP} = 114\frac{g}{mol}$$

$$DC = 0.59$$

$$MW_{counterion} = MW_{Hydroxide} = 18\frac{g}{mol}$$

$$IEC_{Theor.} \approx 1.12\frac{mmol}{g}$$

The theoretical IEC for PSF-DMP$^+$ OH$^-$ is larger than Nafion®-DMP$^+$ OH$^-$, but both are around 1 mmol/g. Although PSF-DMP$^+$ OH$^-$ has a larger theoretical IEC than Nafion®-DMP$^+$ OH$^-$, Nafion®-DMP$^+$ OH$^-$ still demonstrated better hydroxide ion conductivity.

Experimental Procedures

In-plane conductivity

In-plane conductivity measurements were carried out with a 4-point probe using electrochemical impedance spectroscopy (EIS). A 1 cm x 3 cm sample was placed in a Teflon® conductivity cell obtained from Bektech with 4 platinum wires. The conductivity cell was immersed in a temperature-controlled bath containing DI H_2O.

The procedure used for measuring hydroxide ionic conductivity required nitrogen to be bubbled through the water prior to each measurement, and during temperature changes between measurements, to minimize dissolved carbon dioxide. When performing a set of measurements across a temperature range, the sample was removed from the conductivity cell while raising the temperature of the water. The sample was immersed in DI water and stored in a sealed container to avoid carbonate/bicarbonate ion formation. The nitrogen gas was shut-off during measurement of membrane resistance. We provide data that shows that the bubbling with nitrogen minimizes the formation of carbonate ions (which in turn lead to reduced AEM conductivity). See Figure 4. It should be noted that films were ion-exchanged to hydroxide form prior to conductivity measurement. The water used for rinsing the AEM sample to remove excess hydroxide ions was also treated with nitrogen gas to remove dissolved carbon dioxide.

A Gamry potentiostat Series G 750 was used to measure the in-plane membrane resistance in the frequency range 100,000 to 0.1 Hz. A Bode plot was used to identify the pure resistance (phase angle of zero). Conductivity was measured using the following equation:

$$\sigma = \frac{L}{R \cdot t \cdot w}$$

σ = in-plane conductivity
R = in-plane membrane resistance
t = membrane thickness
w = membrane width

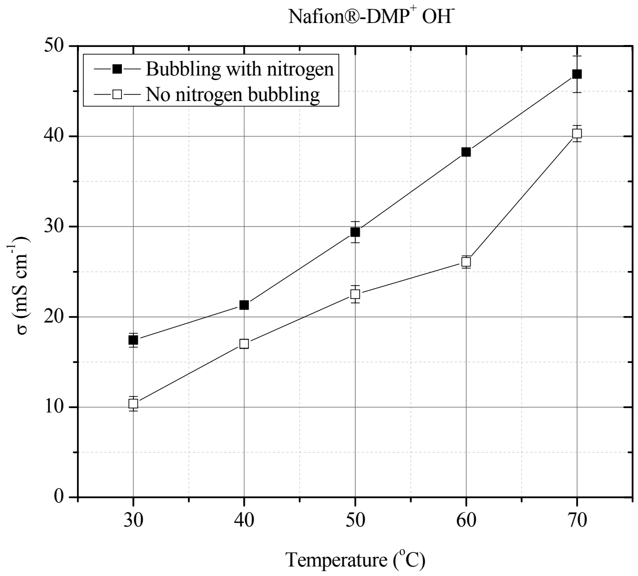

Fig 4. Comparison of in-plane conductivity of Nafion®- DMP$^+$ OH$^-$ for procedures with and without nitrogen bubbling through the DI water in the water bath. Note the drop in conductivity when Nitrogen bubbling was not used – this indicates carbonate ion formation.

Water Uptake

Ambient dry samples in the chloride or fluoride form (depending on whether it is PSF-DMP$^+$ and Nafion®- DMP$^+$) were ion-exchanged to the hydroxide form, where excess hydroxide ions were removed with DI H_2O. The samples immersed in DI H_2O were placed in a 30 °C or 60 °C temperature controlled bath for 24 hours. The samples were then removed and swabbed to remove residual water from the surface. The weights of the samples were determined. The samples were then placed in a vacuum oven for at least 12 hours to remove water. The vacuum dried samples' weights were measured. Water uptake was determined using the following equation:

$$WU = \frac{Wt_{\text{hydrated/O H}^-} - Wt_{\text{vacuum dry/OH}^-}}{Wt_{\text{vacuum dry/OH}^-}} \text{ x } 100\%$$

$Wt_{\text{hydrated/OH}^-}$ = Weight of the membrane fully hydrated in the hydroxide form
$Wt_{\text{vacuum dry/OH}^-}$ = Weight of the membrane vacuum dried in the hydroxide form

Stability Testing of Nafion®- DMP$^+$ OH$^-$

Nafion® -DMP$^+$ OH$^-$ samples were cut and immersed in 2 M KOH. The containers holding the sample in 2 M KOH were sealed and placed in a 60 °C oven. Nafion® -DMP$^+$ OH$^-$ samples were removed at specific time points and were washed thoroughly with DI water. The DI water wash should remove all cleaved DMP cation sites and excess hydroxide ions.

In-Plane Conductivity as a Function of Reaction Time

Figure 5 relates to discussion in the manuscript regarding the reaction of Nafion® in the sulfonyl fluoride form with DMP. A reaction time of 24 hours was deemed to be adequate for AEM derivatization based on the invariance in conductivity after about 8 hours, suggesting full conversion at this time.

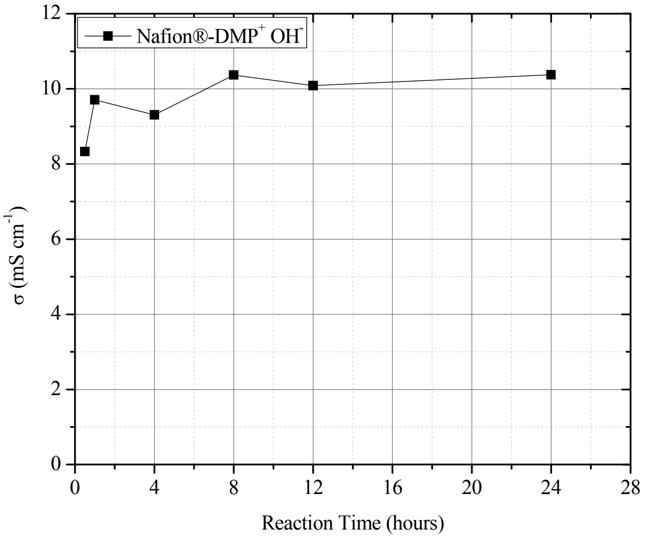

Fig 5. Nafion®-DMP$^+$ OH$^-$ conductivity as a function of reaction time.

In-Plane Conductivity and water uptake of Nafion®-DMP$^+$ CO$_3^{2-}$ versus Nafion®-DMP$^+$ OH$^-$

The ionic conductivity (Fig. 6) and water uptake (Fig. 7) of the Nafion®-DMP$^+$ AEM was also measured in the carbonate ion form and these values were contrasted with corresponding values in the hydroxide ion form of the AEM.

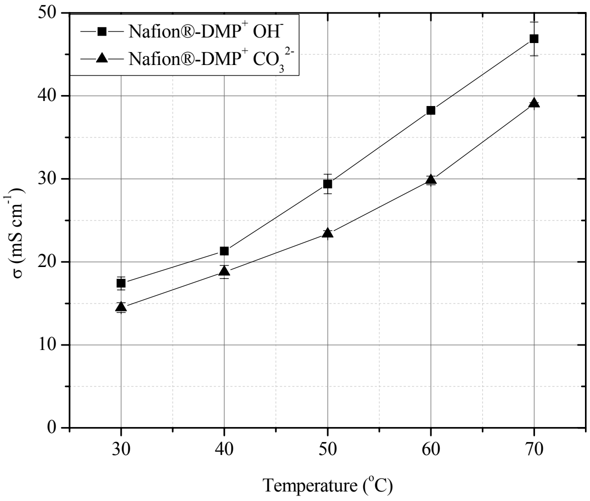

Fig 6. Ionic conductivity of Nafion®-DMP$^+$ OH$^-$ versus Nafion®-DMP$^+$ CO$_3^{2-}$.

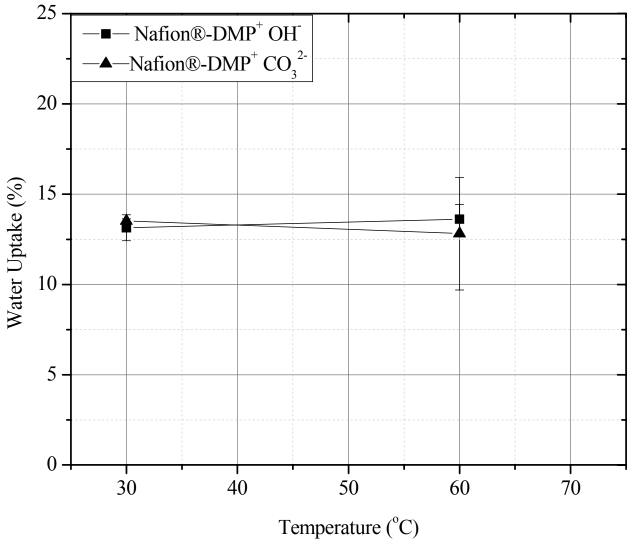

Fig 7. Water uptake of Nafion®-DMP$^+$ OH$^-$ versus Nafion®-DMP$^+$ CO$_3^{2-}$.

Nafion®-DMP$^+$ ion-exchanged to OH$^-$ using 1 M KOH demonstrated better ionic conductivity than Nafion®-DMP$^+$ ion-exchanged to CO$_3^{2-}$ using 1 M Na$_2$CO$_3$. This confirms that the procedure used for measuring ionic conductivity in the hydroxide form prevents (or minimizes) the conversion of hydroxide ions to carbonate ions. The water uptake data for Nafion®-DMP$^+$ OH$^-$ versus Nafion®-DMP$^+$ CO$_3^{2-}$ suggested that the type of counteranion does not affect water uptake much.

Fuel Cell Testing of Nafion®-DMP$^+$ OH$^-$ AEMs

Procedure for preparing membrane electrode assemblies

Gas Diffusion Electrodes (GDEs) were prepared by the painting method, using an airbrush. The microporous layer of a commercial gas diffusion layer (GDL Sigracet GDL 10BB, 420 μm, SGL Carbon Group) was covered with a thin film of Pt/C bound with a solubilized AEM ionomer. To prepare the catalyst ink, 0.128 g of ionomer (solubilized perfluorinated-DMP$^+$ OH$^-$ (see note below)) was dissolved in 7 mL of N,N-Dimethylacetamide (DMAc) to which 0.3 g of catalyst (Platinum nominally 40% on carbon black, Alfa Aesar) was added. The ink slurry was stirred overnight to break up the catalyst powder and get a homogenous dispersion. While painting the ink onto the GDL, the GDL was kept near a lamp to dry the solvent from the ink between successive applications. The Pt loading was measured gravimetrically by estimating the difference in weight before and after painting. The platinum loading was maintained at 0.50 ±0.05 mg/cm^2 for both the anode and the cathode. A membrane electrode assembly (MEA) with an active area of 5 cm^2 was assembled by placing a GDE on either sides of the Nafion®-DMP$^+$ OH$^-$ membrane and pressing at 5,000 lbs and 70 °C. The 5cm^2 MEA single cell was placed into a fuel cell hardware with single serpentine flow fields (Fuel Cell Technologies, Inc). The assembly was sealed using PTFE gaskets (12 mils thick on each side) yielding a pinch of about 10 mils. The hardware was closed by applying a torque of 15 in-lb on each of 8 bolts.

Note: Solubilized perfluorinated-DMP$^+$ OH$^-$ was prepared by reacting flakes of perfluorinated polymer containing sulfonyl-fluoride groups with DMP by immersing it in DMP at 80°C for 48 hours. The procedure was similar to the preparation of Nafion®-DMP$^+$. The derivatized flakes in the fluoride ion form were ion-exchanged to the hydroxide ion form. The hydroxide ion form of perfluorinated-DMP$^+$ OH$^-$ was soluble in DMAc. Solubilized-DMP$^+$ OH$^-$ was also processed into thin-films and shown to conduct hydroxide ions.

Procedure for fuel cell performance testing

The performance of the membrane electrode assembly was evaluated by using a Compact Fuel Cell Test Station (model 850c, Scribner Associates, Inc.) controlled using FuelCell® 3.9c software. The polarization curves were recorded at atmospheric pressure (i.e. no back pressure) using humidified (at 95%RH) hydrogen and air at 70 °C. Stoichiometric ratios of 2 with minimum flows of 0.2 L min^{-1} were employed at each side during the experiment.

Through plane conductivity of Nafion®-DMP$^+$ OH$^-$

The membrane resistance was measured by using the current-interrupt technique built into the Compact Fuel Cell Test Station. The area specific resistance was measured at 95% RH and at 70 °C. The through plane conductivity was calculated as follows

$$\sigma = \frac{t}{R}$$

σ = through plane conductivity
R = through plane membrane area specific resistance
t = membrane thickness (distance between the electrodes)

The area specific resistance was 202 mohm-cm^2. Taking into account the membrane thickness of 30μm, the through plane conductivity was calculated to be 15 mS/cm.

Note that while the through plane hydroxide conductivity was less than the in-plane hydroxide conductivity reported, this measurement was carried out at a relative humidity of 95% obtained by equilibrating the AEM using a humidified gas stream (the in-plane measurement was performed in liquid water).

Experiment to confirm attachment of DMP to Nafion®

To verify if DMP was covalently attached to Nafion®, the following experiment was performed: i.) the solubility of DMP precursor in ethanol and water was assessed (1 mL of DMP to 10 mL of solvent). DMP was soluble in both solvents, ii.) a Nafion® -DMP$^+$ F$^-$ sample was dried and its FT-IR spectrum was obtained, iii.) this Nafion® -DMP$^+$ F$^-$ film was then thoroughly washed with ethanol and water for about 12 hours with each solvent (the solvents were replaced several times over the 12 hour period), iv.) the film was vacuum dried at room temperature for 12 hours, and v.) the FT-IR spectrum of the washed AEM film was obtained. The characteristic peaks in the FT-IR spectrum representing -CH_2 and -CH_3 stretching were still present even after washing the film with solvents known to dissolve DMP. See Figure 7. This suggests that the DMP was indeed covalently bonded to the polymer. The fact that the AEM has ionic conductivity also indirectly supports that DMP is covalently bonded to Nafion®. The fluoride group on the sulfonyl-fluoride form of Nafion® is a good leaving group, while DMP is a good nucleophile. The fact that Nafion® -DMP$^+$ conducts fluoride ions indicates that one of the nitrogen atoms on the DMP ring has bonded with sulfur atom resulting in a positive charge on the nitrogen atom which makes ionic conductivity possible.

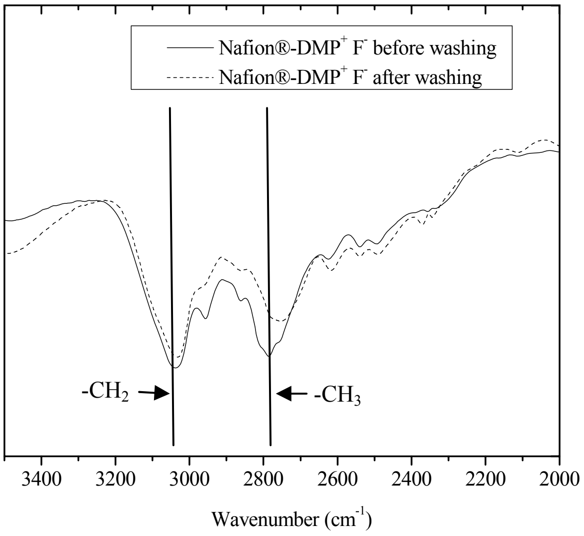

Fig 8. FT-IR spectra of Nafion®-DMP$^+$ F$^-$ before and after wash extraction

References

1.) E. Avram, E. Butuc and C. Luca, *J.M.S.-Pure Appl. Chem.*, 1997, **A34**, 1701-1714.