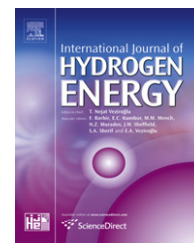


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# Characterization of an anionic-exchange membranes for direct methanol alkaline fuel cells

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## ABSTRACT

Ammonium quaternized polymers such as poly (arylene ether sulfones) are being developed and studied as candidates of ionomeric materials for application in alkaline fuel cells, due to their low cost and promisories electrochemical properties. In this work, a quaternary ammonium polymer was synthesized by chloromethylation of a commercial polysulfone followed by amination process.

Quaternized polysulfone membrane properties such as water and water-methanol uptake, electrical conductivity and Young's modulus were evaluated and compared to Nafion 117, commonly employed in direct methanol fuel cells. The anionic polysulfone membrane sorbes more water than Nafion all over the whole range of water activities, but it uptakes much less methanol as compared to Nafion. The specific conductivity of the fully hydrated polysulfone membrane equilibrated with KOH solutions at ambient temperature increases with the KOH concentration, reaching a maximum of  $0.083 \text{ S cm}^{-1}$  for 2 M KOH, slightly less conductive than Nafion 117. The elastic modulus of the polysulfone membranes immersed in water is similar to that reported for Nafion membranes under the same conditions. We concluded that quaternized polysulfone membrane are good candidates as electrolytes in alkaline direct methanol fuel cells.

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## 1. Introduction

Fuel cell technologies are at the forefront of the effort towards green and sustainable energy generation. For mobile and portable applications, the emphasis has been focused on lower temperature types ( $<80 \text{ }^\circ\text{C}$ ) including direct alcohol proton exchange membrane fuel cells (DAPEMFCs) and direct alcohol alkaline fuel cells (DAAFCS). This type of devices, for example methanol feed DMFCs, are of primary interest in the

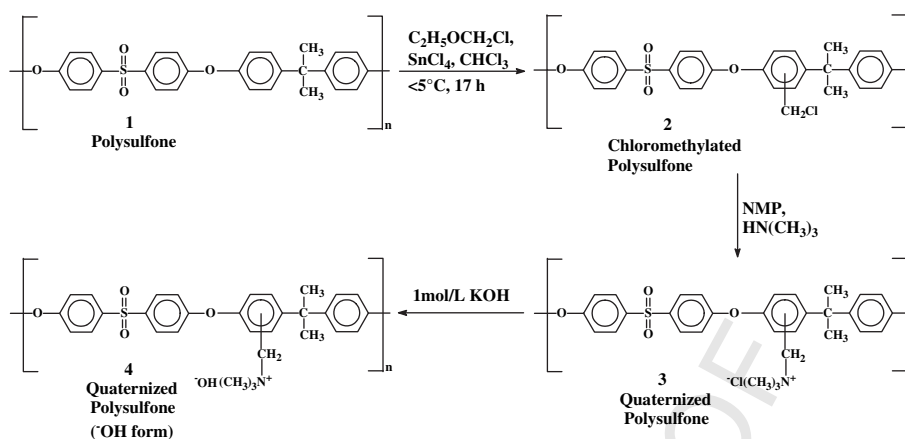
field of portable devices due to ease and speed of refuelling and large volumetric energy density of liquid methanol fuel.

Most PEMFCs are currently based on perfluorosulphonic acid polymers such as Nafion and Flemion, which have been extensively studied in fuel cell applications [1,2]. Despite their advantages of high conductivity and good mechanical and chemical properties, certain disadvantages exist that restrict their successful use in fuel cells. These drawbacks include high cost, high methanol permeability and relative low

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**Fig. 1 – Preparation of quaternary ammonium polysulfone derivatives (3,4) from commercial Udel polysulfone (1) via chloromethylated intermediates (2).**

activity when used in direct alcohol fuel cells (DAFCs) at temperatures above  $80^\circ C$  [3–5].

The main drawback of current AFCs containing a liquid electrolyte (aqueous KOH solution) is their sensitivity to carbon dioxide pollution, which drastically reduces performance [6]. A solution to this obstacle could be the replacement of the KOH solution by an anion conducting polymer electrolyte [7].

On the other hand, in DAFCs,  $OH^-$  anions are produced at the cathode and transported through the membrane to the anode where they are consumed. Due to the opposite movement of the  $OH^-$  anions through the anion exchange membrane (AEM), as compared to the transport of proton in PEM and the direction of methanol flux, an intrinsic reduction in methanol crossover is expected [8].

All these facts imply that there is an urgent need for the development of novel AEMs that can be applied in fuel cells.

Novel methods of synthesis [9] have also allowed the production of membrane materials and ionomers that could facilitate the development of AEMs equivalent to proton exchange membranes (PEMs). These polymeric membranes are expected to have lower cost and comparable electrochemical properties than PEMs. Ion-exchange membranes have been prepared using polysulfone, a high-performance engineering thermo-plastic material as base polymer due to its excellent workability and high mechanical strength [10].

Many kinds of AEMs have been developed based on quaternized polymers such as polysiloxane containing a quaternary ammonium group [11], poly(oxyethylene) methacrylates containing ammonium groups [12], quaternized polyethersulfone cardo anion exchange membranes [13], quaternized poly(phthalazinone ethersulfone ketone) [14], and radiation-grafted poly(vinylidene fluoride) (PVDF) and poly(tetrafluoroethylene-hexafluoropropylene) (FEP) [6,15].

AEMs containing a quaternary ammonium group as a cation exhibit higher thermal and chemical stability than other quaternary cations such as quaternary phosphonium or tertiary sulfonium groups [16].

The aim of this paper is to report the preparation of a new anion exchange membrane based on a quaternized polysulfone and the characterization of its mechanical properties,

water and water-methanol uptake and electrical conductivity in relation to its possible application in direct methanol alkaline fuel cells.

## 2. Experimental

All chemicals were purchased from Aldrich and used without further purification. The quaternary ammonium polymer was synthesized in two-step sequence [17,18] as depicted in Fig. 1. Polysulfone (Udel) 1 was dissolved in chloroform and then treated with chloromethyl ethyl ether in the presence of Lewis-acid catalysts ( $SnCl_4$ ) at  $ca. 5^\circ C$  for 3 h and left overnight to obtain the chloromethylated (CMPSf) intermediate derivative 2. This was followed by casting a 5 wt% solution of intermediate derivative 2 in N-methylpyrrolidone (NMP) onto a glass plate and dried at  $70^\circ C$  for 24 h. Amination with 25 wt% trimethylamine solution at  $90^\circ C$  overnight introduced quaternary ammonium groups into the membrane, giving quaternary polysulfone (QPSf) 3 with good yields. Before the membrane is used, it was immersed in concentrated KOH solution overnight, to convert the membrane from  $Cl^-$  form into  $OH^-$  form, and washed with distilled water until neutral pH. The structure and purity of the product was confirmed by  $^1H$  NMR and FTIR spectra [19].

The QPSf membranes used for electrical conductivity and elastic modulus measurements were used as prepared, while the Nafion 117 membranes were pretreated as described in the literature [20]. Thin QPSf and Nafion membranes for water and methanol uptake were prepared by casting from  $0.05\text{ g/dm}^3$  aqueous solutions of the respective polymers.

A quartz crystal microbalance (QCM) was used to measure the water and water-methanol uptake of the QPSf membranes. A thin QPSf film, in the range of 13–40 nm in thickness, was prepared by direct casting on the quartz crystal. Once the membrane become rigid was mounted on the QCM holder contained within a sealed chamber with a dry nitrogen stream, to obtain the mass of the dry film. Once the equilibrium resonance frequency has been reached, the dry nitrogen was replaced by a stream of nitrogen previously bubbled across saturated aqueous salt solutions at  $20^\circ C$ , and

the change in the resonance frequency was measured. The procedure was repeated using different saturated salt solutions, in order to measure the water uptake at controlled water activity, in the range from 0.33 to 1. Water-methanol uptake was determined by exposing the films to nitrogen saturated with methanol aqueous solution in the range of methanol concentration 0–100 wt%.

The water and methanol/water mixture uptake of Nafion films were also measured for comparison.

The mass change when dry membranes are equilibrated with water or methanol–water mixtures were calculated from the measurement of the resonant frequency shift,  $\Delta f$ , by means of the Sauerbrey's equation [21]:

$$\Delta f = \Delta m \frac{2nf_0^2}{\rho^{1/2}\mu^{1/2}A} \quad (1)$$

where  $n$  is the order of the harmonic,  $f_0$  the base frequency of the crystal,  $A$  the electrode area and  $\rho$  and  $\mu$  the density and shear modulus of the crystal, respectively.

The local elastic properties of QPSf and Nafion membranes immersed in water were measured by means of force spectroscopy using an atomic force microscopy (AFM) using a cell for liquids. The model developed by Stark et al. [22], was used to obtain Young's modulus from the linear part of the force curves, which relates the loading force and indentation depth when the AFM tip indents the membrane surface.

A commercial AFM (Veeco-DI Multimode Nanoscope IIIa) equipped with 150  $\mu\text{m}$  lateral scan range and a 5  $\mu\text{m}$  z-scanner was employed for the measurements. The elasticity measurements were done with a  $\text{Si}_3\text{N}_4$  tip with a spring constant of 0.46 N/m (Nano Devices, Veeco Metrology, Santa Barbara, California, pyramidal tip shape, cone half angle  $\alpha = 18^\circ$ , tip curvature radius  $r < 10$  nm, resonant frequency nominal: 57 kHz, measured: 47.50 kHz).

The indentation of an AFM tip fixed to a cantilever (spring constant  $k$ ) into a soft sample (Young's modulus  $E$ , Poisson's ratio  $\nu$ ) can be modeled using the Hertzian contact mechanics [23]. This theory provides a very simple but direct approach to the material elasticity for a sample with a semi-infinite thickness. The procedure to obtain the force curves has been described in detail elsewhere [24].

The electrical conductivity measurements on the QPSf and Nafion 117 membranes were carried out with a two point-probe conductivity cell designed and constructed in our laboratory, shown in Fig. 2. The two point probe conductivity cell frame was made of two Teflon blocks, with an open 'window-like structure' employed to allow determinations of conductivity of fully and partially hydrated membranes. Two wire electrodes (1 cm apart) were used to apply current and measure the voltage drop along the film. The membrane sample (3 × 3 cm) was sandwiched between the two blocks that were pressed together by four screws fastened with approximately the same torque to ensure good electrode-membrane contact.

Impedance measurements were carried out in the frequency range between 1 Hz and 1 MHz at open circuit potential with ac voltage of 5 mV by means of Frequency Response Analyzer (Autolab PGSTAT 302). The specific conductivity,  $\sigma$ , was calculated according to the following relationship:

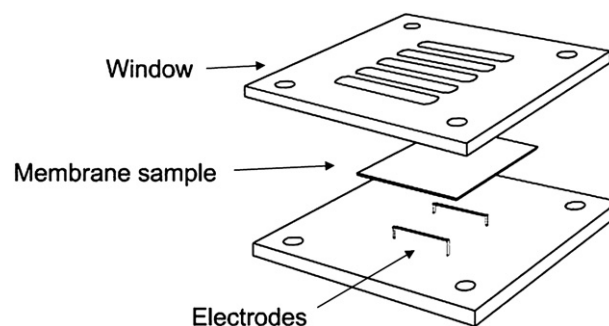


Fig. 2 – Schematic view of conductivity cell for two-point probe electrochemical impedance spectroscopy technique.

$$\sigma = \frac{l}{RA} \quad (2)$$

where  $l$  is the thickness of the membrane,  $A$  the membrane surface area exposed to the electric field, and  $R$  is the bulk resistance of the membrane sample obtained from the real axis intercept of the impedance Nyquist plot. The membrane samples were immersed in water for at least 24 h before measurements were performed.

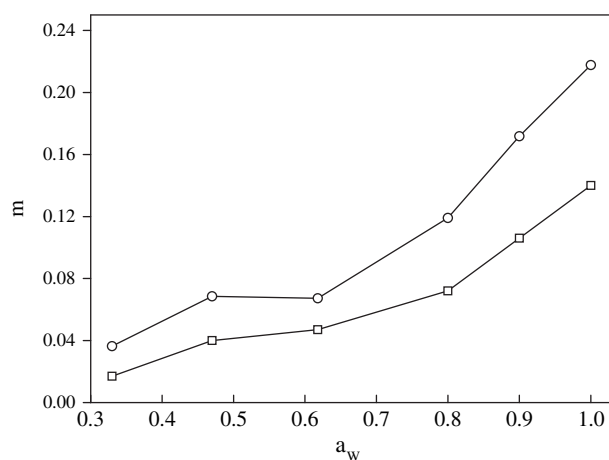
### 3. Results and discussion

#### 3.1. Water and methanol uptake

The water and methanol uptake of the QPSf membranes is of great importance, since the water content as a function of the relative humidity determines the electrical conductivity and other properties of the membrane, under different operation condition in a fuel cell. Moreover, the selective sorption of methanol and water give us some insights into the permeability of methanol through the membrane, which is a fundamental parameter for application in direct methanol AFC. For comparison, the water and methanol sorption of thin films of Nafion were also determined.

The water sorption isotherms for QPSf and Nafion membranes expose to the vapour phase at 20 °C, expressed as  $m = w_w/w_o$ , the mass (in grams) of water uptaken per gram of dry membrane, are shown in Fig. 3. It is observed that the water uptake by QPSf membranes is higher than in Nafion over the entire range of water activities considered. The effect of the membrane thickness on the water sorption in extruded and cast Nafion membranes is not clear. Some authors concluded that the sorption of water in Nafion thin membranes is similar to extruded membranes [25], while others [26,27] observed that water or organic vapors uptakes on thin perfluorosulfonic acid membranes prepared by casting are lower than those reported for thicker commercial (extruded) membranes.

We observed that thin cast Nafion membranes (28 nm thick), sorbed less water than commercial Nafion 117 membranes (178  $\mu\text{m}$  thick) [28]. However, the comparison of water and methanol uptake by thin Nafion and QPSf membranes is still valid and their measurements is much less time consuming that the sorption experiments on thicker membranes.

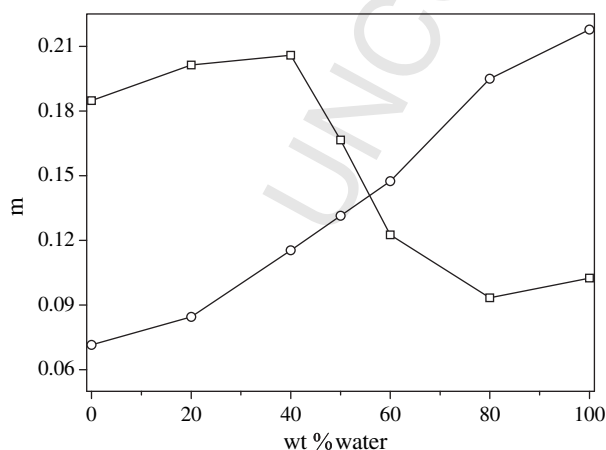


**Fig. 3 – Water sorption isotherms at 20 °C: (●) QPSf (40 nm); (■) Nafion® (28 nm).**

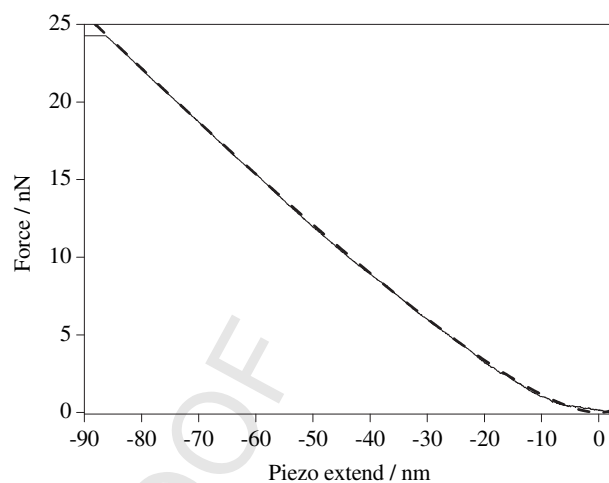
The methanol/water uptake of QPSf membranes from nitrogen equilibrated with methanol aqueous solutions at 20 °C, expressed as  $m = w_s/w_o$ , the mass (in grams) of solvent mixture uptaken per gram of dry membrane, are shown in Fig. 4 at methanol concentrations in the range 0–100 wt%.

It can be seen that the uptake of pure methanol by QPSf is almost three times lower than by Nafion, while the sorption of water by QPSf doubled that by Nafion. Therefore, the permeability of methanol in QPSf would be lower than in Nafion, provided that the diffusion coefficient of methanol in both membranes is similar. Experiments are in progress in order to confirm this claim.

The sorption behaviour of QPSf as a function of the water/methanol composition is opposite to Nafion. The total sorption of water-methanol in QPSf, expressed as mass of sorbate by mass of dry membrane, increases monotonically with the water content, and this trend is more pronounced when the uptake is measured in moles of mixture per gram of membrane. Thus, it is clear that water is preferentially sorbed over methanol by QPSf. In Nafion the total sorption increases with methanol content in the equilibrating water-methanol



**Fig. 4 – Methanol/water sorption isotherms at 20 °C: (●) QPSf (40 nm); (■) Nafion® (13 nm).**



**Fig. 5 – Indentation curves (solid line) on the QPSf membrane surface. The dashed curve was obtained by fitting the experimental data to the Stark model.**

mixture, as already found in the literature [29,30]. However, when expressed as moles of mixture per gram of dry membrane, the uptake of pure methanol and pure water are similar.

Also, the different water/methanol sorption characteristics of Nafion and QPSf could impact on the low temperature behavior of the membranes. Corti et al. [31] have demonstrated that the freezing of water in a Nafion membrane in the presence of methanol could increase up to 65%, probably as a result of the exclusion of water out of the ionic cluster regions. It is expected that this would not be the case in QPSf membranes because its sorption selectivity toward water.

### 3.2. Mechanical properties

A typical force curve in the approach direction for a 100  $\mu\text{m}$  PSf membrane is showed in Fig. 5, where it can be seen an excellent agreement with the model proposed by Stark et al. [22].

It can be noted that during the indentation does not appear neither, signals of a structural breakdowns of the sample, nor inelastic deformations, as revealed by the common slopes in the extension and retraction curves. These facts indicate that the samples have a purely elastic response to the interaction with the tip.

The results for the Young modulus of QPSf and Nafion membranes immersed in water are summarized in Table 1,

**Table 1 – Young's modulus of hydrated QPSf and Nafion membranes.**

Membrane	Young's modulus (GPa)
QPSf	$0.25 \pm 0.11$
Nafion 117	$0.29 \pm 0.08$
Nafion 117 <sup>a</sup>	0.09–0.25

<sup>a</sup> Ref. [32].



**Table 2 – Specific conductivities of QPSf and Nafion membranes.**

Membrane	$c_{\text{KOH}}$ (mol/dm <sup>3</sup> )	$\sigma$ (S cm <sup>-1</sup> )
QPSf	0 (H <sub>2</sub> O)	0.0016
	0.5	0.0192
	1.0	0.0210
	1.5	0.0675
	2.0	0.0833
	2.5	0.0533
Nafion 117	H <sub>2</sub> O	0.112

along with data reported in literature for Nafion [32]. Young's modulus obtained for Nafion immersed in water (0.29 GPa) is significantly smaller than the obtained for the dry membrane that is 1.59 GPa [24]. This behavior can be explained by the increases of the membrane elasticity upon swelling by sorption of water, as observed by Tang et al. [32] for Nafion on the basis of tensile tests.

The elastic modulus of QPSf, as compared to Nafion, would indicate that these membranes are mechanically feasible to construct MEAs for AFC.

Recently, Huang and Xiao [33] have reported mechanical properties of QPSf and benzoil guar gum blends. For pure QPSf, they reported a tensile strength of 40.7 MPa and elongation at break of 6.1%, although the Young modulus was not reported.

### 3.3. Conductivity measurements

Electrical conductivity measurements are used to corroborate if the quaternized polysulfone are suitable for fuel cell applications. Using the impedance measurements by the way of a Nyquist plot, the bulk resistance of the membrane samples,  $R$ , were obtained and specific ionic conductivities were calculated using equation (2). The results of conductivity measurements at 20 °C are summarized in Table 2. Fully hydrated Nafion 117 membrane displays higher conductivity (0.112 S cm<sup>-1</sup>) than QPSf membranes equilibrated with water, but increasing the KOH concentration increases the specific conductivity of the membrane, with the maximum of 0.0833 S cm<sup>-1</sup> at a KOH concentration around 2.0 mol/dm<sup>3</sup>. Clearly, this is a consequence of the higher ionic conductivity of the HO<sup>-</sup> ions relative to chloride ion, and the maximum conductivity would correspond to the complete replacement of chloride ions by HO<sup>-</sup> in the quaternary sites. The decrease of the conductivity at higher KOH concentrations is probably due to the displacement of the ammonium group by HO<sup>-</sup> via the nucleophilic displacement reaction, as postulated by Fang and Shen [8] for quaternized poly(phthalazinon ether sulfone ketone).

The ratio of the specific conductivity of QPSf to Nafion membranes is 0.74, at the optimum KOH concentration, which is higher than the ratio of ionic conductivities of H<sup>+</sup> to HO<sup>-</sup> in water, which is 0.57 [34]. This result would indicate that the higher water content in the QPSf membranes play a role to reduce the conductivity difference between the alkaline polysulfone and the Nafion proton conducting membranes.

## 4. Conclusions

A quaternary ammonium polymer was synthesized by chloromethylation and amination of a commercial polysulfone, and relevant membrane properties such as water and water methanol uptake, electrical conductivity and Young's modulus were evaluated and compared to Nafion 117, aiming to evaluate its applicability in direct methanol fuel cells.

The anionic quaternized polysulfone membrane sorbes more water than Nafion all over the whole range of water activities, but it uptakes much less methanol as compared to Nafion. Based on this result it is possible to predict that QPSf membranes have promising barrier properties against methanol crossover in DMFC.

The specific conductivity of the fully hydrated polysulfone membrane equilibrated with KOH solutions at ambient temperature increases with the KOH concentration, reaching a maximum of 0.083 S cm<sup>-1</sup> for 2 M KOH, slightly less conductive than Nafion 117. Taking into account the higher ionic conductivity of H<sup>+</sup> ions as compared to HO<sup>-</sup> ions in water solutions, it is concluded that the higher water uptake in QPSf helps to reduce the conductivity difference with Nafion.

The QPSf membrane exhibit excellent mechanical properties and stability for their manipulation as massive membrane, comparable to that of Nafion. Therefore, it can be concluded that QPSf membrane prepared as in this work are good candidate for MEAs preparation for DMFC.

Ionic conductivity as a function of temperature as well as alcohol permeation measurements of QPSf membrane will be addressed in a forthcoming study.

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