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Comparative study of the cation permeability of protonic, anionic and ampholytic membranes

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Abstract

The vanadium ion permeability of various ion-conducting polymer membranes was determined using a home-made apparatus. The study includes proton-conducting sulfonated poly(ether ether ketone) (SPEEK) with various cross-linking degrees, anion-conducting membranes, such as polysulfone with quaternary ammonium groups (PSU-QA) and sulfaminated PEEK (SA-PEEK), and amphoteric membranes based on PEEK containing both sulfonic and sulfonamide groups (SAM-PEEK) that can conduct both cations and anions. The polymer structure was investigated by NMR spectroscopy. The permeability of SPEEK decreases with the cross-linking degree and can be up to two orders below the permeability of a Nafion 117 reference membrane ($1.4 \cdot 10^{-6}$ cm²/min). The cation permeability of SA-PEEK attains values as low as $5.0 \cdot 10^{-10}$ cm²/min, whereas amphoteric SAM-PEEK has a cation permeability of $7.0 \cdot 10^{-10}$ cm²/min. A factor or merit is introduced, defined as the ratio of ion conductivity and ion permeability ; the highest value, corresponding to the best compromise of high ion conductivity and low permeability of electrochemically active ions, is found for highly cross-linked SPEEK, SA-PEEK and SAM-PEEK membranes. The influence of the polymer backbone (PEEK or PSU), the degree of cross-linking, determined by NMR spectroscopy, and the grafted ionic groups (sulfonic acid, sulfammonium, and quaternary ammonium) on the cation permeability is discussed.

Keywords: Ionomers, cross-linking, Nafion, sulfonic acid, quaternary ammonium, sulfammonium, NMR spectroscopy

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Introduction

Ion exchange membranes have many applications in various fields, including inverse osmosis, electrodialysis, and electrochemical energy technologies, such as fuel cells and redox flow batteries¹⁻⁶. In most of these applications, the separator membrane must impede the cross-mixing of ionic solutions. For example, an ion exchange membrane is employed in different electrochemical devices to separate the positive and negative half-cells and to prevent the permeation of the electrochemically active species (e. g. vanadium ions in all-vanadium redox flow batteries) while presenting the required ionic conductivity by non-electrochemically active ions⁷. The membrane separator is a key material for commercialization of electrochemical energy technologies, because it determines the performance and its cost can be a main part of the whole system.

Important properties that a high performance ion exchange membrane should therefore present are^{7,8} i) high ion conductivity, required to minimize the Ohmic loss and to increase the voltage efficiency in batteries, ii) high ion selectivity: the separator must be permeable to the charge balancing ions of the supporting electrolyte (e.g. protons, hydrogensulfate ions or others), but must prevent permeation of the electrochemically active ions, which leads to self-discharge in the case of the redox flow battery and reduces the Coulombic efficiency, and iii) mechanical stability, which is another requisite for an optimal performance of the membrane separator.

Many large scale electrochemical devices use expensive perfluorinated membranes (e.g. Nafion) as separator, given their excellent chemical stability and relatively high ionic conductivity⁸. However, it is well known that Nafion presents a relatively large cation permeability, a limited mechanical stability and a high price. Efforts have therefore been made to develop less expensive membranes with lower permeability and better mechanical properties⁹⁻¹².

Alternative non-fluorinated cation exchange membranes have been developed¹³⁻¹⁵. The family of sulfonated aromatic polymers (SAP^{7,9,16,17}) is of particular interest, because it is well known that, in fuel cell devices, the gas permeability of SAP is below that of perfluorinated ionomers^{18,19}, due to more tortuous and less connected hydrated channels; the gas permeability can be further reduced by the presence of cross-link bonds²⁰. The behavior of SAP with respect to the cation permeability and the effect of cross-linking is explored in this work.

In principle, anion exchange membranes (AEM) can prevent cation permeation owing to the Donnan exclusion effect, reducing significantly the cation cross-over. The Donnan exclusion is due to the presence of ionic groups grafted on the polymer backbone that repulse ions with similar charge. For example, positively charged ammonium groups in anion exchange ionomers oppose cation permeation.

Ampholytic (amphoteric) ion exchange membranes (AIEM) have both cation and anion exchange groups, and might thus combine a relatively low cation and anion permeability^{21,22}.

We present in the following the vanadium permeability, the ionic conductivity and mechanical properties of various ion exchange membranes, including protonic (with various degree of cross-linking), anionic, and amphoteric ionomers and discuss the relationship with the type of grafted ionic groups (sulfonic acid, sulfammonium, quaternary ammonium) and the type of polymer backbone, such as poly(ether ether ketone) (PEEK) or polysulfone (PSU). Both aromatic polymers have a large strength and stiffness due to the rigid phenyl rings in the macromolecule. PEEK presents a slightly higher stiffness than PSU^{23,24}, due to the quaternary carbon in the PSU structure that increases the backbone flexibility. PSU results more permeable to hydrogen (788.4 vs 108.6 cm² min⁻¹)^{25,26} and oxygen (82.8 vs 6.6 cm² min⁻¹)^{25,27} gas.

The ionomer structure was characterized by NMR spectroscopy, which is also used for the determination of the cross-link density.

Vanadium was chosen as a model cation, because VO²⁺ ions can be easily observed by UV spectroscopy. Furthermore, vanadium is the active species in the All Vanadium Redox Flow Battery, one of the most promising large scale electrochemical storage systems.

Experimental

Nafion 117 (equivalent weight, EW=1100 g/mol) was supplied by Sigma-Aldrich. Poly(ether ether ketone) (PEEK, 450P, MW = 38300 g/mol) and polysulfone (PSU, MW = 55500 g/mol) were supplied by Victrex and Solvay, respectively. Other reagents were used as received from Sigma Aldrich.

Membrane synthesis

The repeat units of sulfonated poly(ether ether ketone) (SPEEK), polysulfone with quaternary ammonium (PSU-QA), sulfaminated poly(ether ether ketone) (SA-PEEK), and sulfonated and sulfaminated poly(ether ether ketone) (SAM-PEEK) are shown in Scheme 1. The synthesis procedures were reported elsewhere and are briefly presented as follows.

SPEEK^{28,29}

SPEEK with ion exchange capacity (IEC° = 2.50 eq/Kg, degree of sulfonation, DS = 0.9) was prepared by reaction of PEEK with concentrated sulfuric acid at 50 °C for 96 h. Membranes were cast using a home-made doctor-blade type apparatus using dimethylsulfoxide (DMSO) as casting solvent, and dried in the oven for 24 h at 120 °C. After cooling to room temperature, the

resulting membranes were peeled off and thermally treated at 180 °C for 3, 10, and 24 h. The mechanism of cross-linking was studied and described in references^{30,31}.

The IEC was measured by acid-base titration²⁸. The degree of cross-linking (DXL) of samples can be calculated according to the equation:

$$DXL(\%) = \frac{IEC^{\circ} - IEC_{fin}}{IEC^{\circ}} \cdot 100 \quad (1)$$

The IEC after cross-linking (IEC_{fin}) was 2.30, 1.95, and 1.62 eq/Kg corresponding to a DXL of 8, 22 and 35 % respectively.

The membrane thickness was 60 μm for entries 2, 3 and 4 (Table 1), and 55 μm for entry 5.

PSU-QA³²

Quaternary ammonium polysulfones were prepared by amination reactions starting from chloromethylated-PSU (CM-PSU) with two degrees of chloromethylation (DCM = 0.8 and 1.1). *PSU-TMA (trimethylamine)*. CM-PSU (1 meq) and a solution of trimethylamine in ethanol (2 meq) were dissolved in DMSO under N_2 at RT. The solution was kept for 3 days at 70 °C, and then heated under vacuum. The IEC values determined by titration were 0.8 and 1.6 eq/Kg starting from DCM 0.8 and 1.1 respectively.

PSU-DABCO (1,4-diazabicyclo[2.2.2]octane). A similar procedure was followed for the synthesis of the DABCO derivative using a ratio between chloromethyl groups and DABCO of 1:1.5. After dissolution of the two precursors, the solution was kept under stirring for 4 days at 70 °C, and then heated under high vacuum. The IEC were determined by titration and were 1.1 and 1.3 eq/Kg starting from DCM 0.8 and 1.1 respectively.

Membranes were cast in a Petri dish, using DMSO as casting solvent, at 100 °C for 24 h. The membrane thickness is reported in Table 1. Before the measurements, the membranes were immersed 24 h at 25 °C into 1 M solution of NaHSO_4 and thoroughly washed several times in deionized water.

SA-PEEK³³

The reaction of PEEK with chlorosulfonic acid for 5 h at 50 °C gave chlorosulfonated PEEK with a chlorosulfonation degree of 0.9 and a degree of cross-linking of 0.1 determined by ^1H NMR spectroscopy. The chlorosulfonated polymer and dimethyl- or diethylamine in equivalent ratio 1:3 were kept at 50 °C for one day. The product, precipitated by adding methanol, was dried overnight at 80 °C.

The SA-PEEK membranes were cast at 120 °C for 24 h, using N-methylpyrrolidone (NMP) as

casting solvent. The membrane thickness was 25 μm for both samples (entries 8 and 9). In the final step, the cast membranes were immersed into 2M solutions of H_2SO_4 during 24 h. The sulfamation degree (DSA) after reaction was 0.9 as determined by ^1H NMR spectroscopy. The IEC values, calculated according to the formula reported in Ref [28], were for dimethylamine IEC = 2.34 eq/kg (entry 10) and for diethylamine IEC = 2.20 eq/kg (entry 8 and 9).

SAM-PEEK³⁴

The reaction of SPEEK with DS = 0.87 (IEC = 2.43 eq/Kg) with thionyl chloride and an excess of dimethylformamide (DMF) gave a complete conversion in the chlorosulfonated polymer (CS-PEEK). CS-PEEK (1 meq) reacted with a half amount of dimethylamine (0.5 meq) in THF at RT under N_2 atmosphere. The solution was kept at 50 $^\circ\text{C}$ for 20 h and then precipitated in methanol. The precipitate was treated with a saturated solution of NaHCO_3 in order to hydrolyze the remaining SO_2Cl groups. The final polymer, SAM-PEEK, was cast in DMSO onto a Petri dish and then dried in the oven for 24 h at 80 $^\circ\text{C}$. The membrane thickness was 25 μm (entry 10). In the final step, the cast membranes were immersed into 2 M solutions of H_2SO_4 during 24 h. The IEC of SAM-PEEK, giving the amount of acidic groups, was determined by potentiometric acid-base titration of the polymer. The measured IEC, corresponding to sulfonic acid groups, was 1.49 eq/Kg. Considering that the initial IEC of SPEEK was 2.43 eq/Kg the amount of sulfonamide groups was 0.94 eq/Kg. This value was confirmed by NMR spectroscopy³⁴.

NMR spectroscopy

^1H NMR spectra were recorded with a Bruker Avance 300 spectrometer operating at 300.13 MHz. Chemical shifts (ppm) are referenced to tetramethylsilane (TMS). DMSO- d_6 was used as solvent.

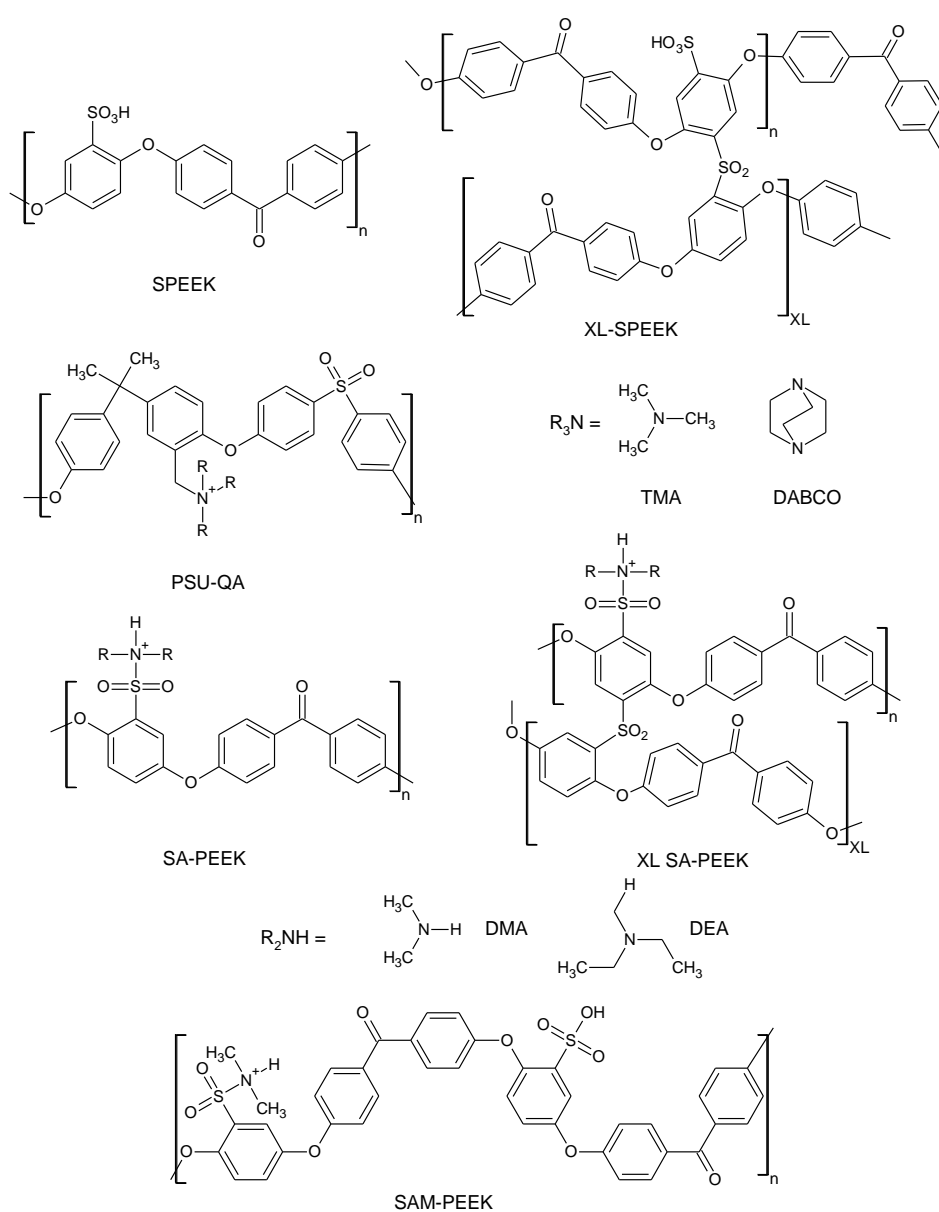
Water uptake measurements

The water uptake WU was measured by full immersion of membrane samples in deionized water at 25 $^\circ\text{C}$: polymer samples were weighed before and after immersion times of 24 h. The dry mass was obtained after keeping the sample 72 h over P_2O_5 . The water uptake WU can be calculated from the ionomer mass in wet (m_{wet}) and dry (m_{dry}) conditions, according to:

$$WU = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (2)$$

Mechanical measurements

Tensile stress-strain tests were performed using an ADAMEL Lhomargy DY30 traction machine at 25 °C at a constant crosshead speed of 5 mm/min. Particular attention was given to the macroscopic homogeneity of membranes made by casting and only apparently homogeneous membranes were used for mechanical tests. The membrane samples had 5 mm width and 25 mm length. The border of the membranes, where composition may be inhomogeneous, was eliminated by cutting carefully the specimens. The selected tensile curves corresponded only to tests with a final rupture in the central part of the specimens. The other cases of rupture, e.g., near or under grips, were systematically eliminated. Prior to measurements, the polymer samples were stabilized at 25 °C and humidity (50±10) % RH. The measurement time was below 5 min.



Scheme 1. Repeat units of investigated polymers.

Permeability measurements

The vanadium ion permeability was measured according to the standard procedure¹⁴ in a home-made, hermetically closed, membrane-separated diffusion cell with two identical chambers made of Teflon. The reference chamber was filled with a 3 M H₂SO₄ solution containing 1.5 mol/L of VO₂, while the other chamber was filled with a 3 M H₂SO₄ solution containing 1.5 mol/L of MgSO₄, in order to balance the osmotic pressure. The vanadium concentration was chosen to avoid vanadium precipitation, while being acceptable for stationary applications³⁵. Inside the two half-cells, two magnetic rods ensured continuous agitation on a stirrer plate thus avoiding any concentration gradient inside the two solutions. The amount of permeated vanadium was detected by UV-visible spectroscopy using a Varian Cary 300 Scan UV-visible spectrophotometer. Figure 1 shows the UV spectra for various VO²⁺ concentrations and the calibration curve obtained at a wavelength of 760 nm, according to the Lambert-Beer law.

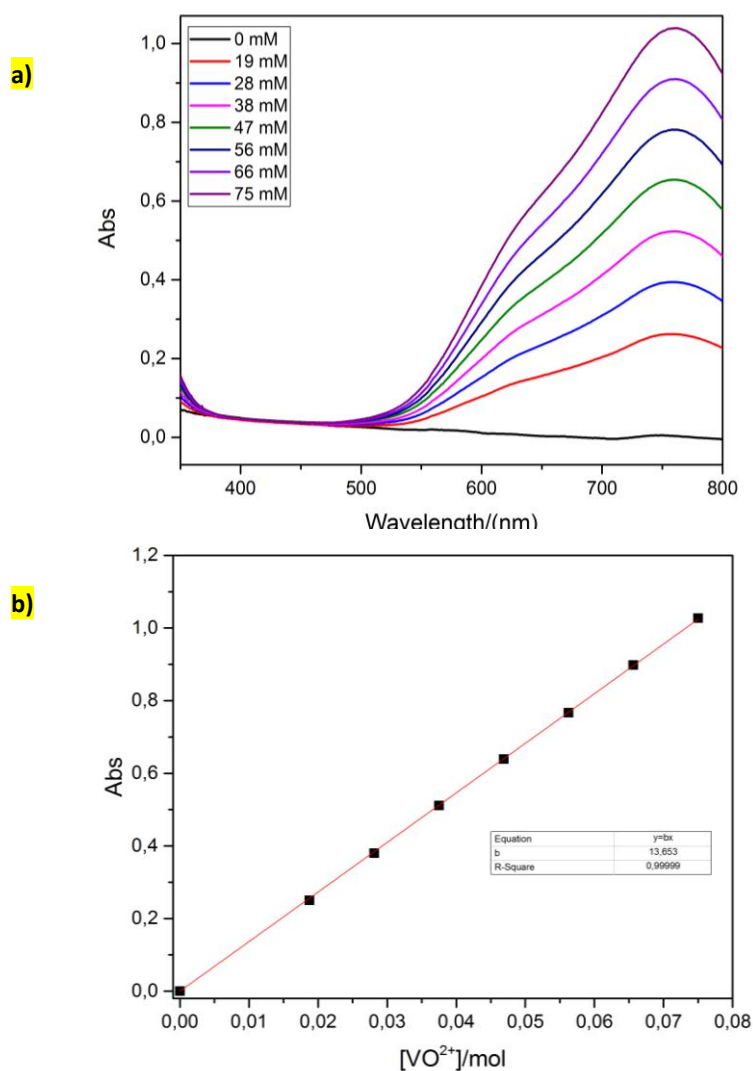


Figure 1. a) UV spectra of VO²⁺ solutions at various molar concentrations and b) calibration curve.

The permeability P can be calculated from the rate of concentration change dC/dt according to the equation (3), where d and A are respectively the membrane thickness and exposed area ($A = 0.64 \text{ cm}^2$):

$$\frac{dC}{dt} = \frac{PA}{Vd} (C_R - C(t)) \quad (3)$$

V is the volume of the reference cell. C_R and $C(t)$ are the vanadium concentrations in the reference cell and in the measurement cell at time t , respectively.

Ionic conductivity measurements

The ionic conductivity was measured by impedance spectroscopy (EG&G model 6310 and Parstat 4000) in a Swagelok cell with stainless steel electrodes (area $A = 0.26 \text{ cm}^2$), closed with reproducible force, after carefully washing the membranes in deionized water to remove any remaining salts from the synthesis procedures. The AC voltage amplitude was 20 mV and the frequency range 1-10⁶ Hz. All measurements were made at 25 °C in fully humidified conditions. The through-plane membrane resistance R was determined from the high frequency intersection of the impedance arc with the real axis in a Nyquist impedance plot. The ionic conductivity σ can be calculated from the membrane thickness d and the electrode area A using the equation:

$$\sigma = \frac{d}{R \cdot A} \quad (4)$$

Results and discussion

Proton-conducting partially cross-linked SPEEK membranes

The vanadium permeation through SPEEK membranes with various degrees of cross-linking is reported in Figure 2 together with control experiments on Nafion 117. The permeability of Nafion is in good agreement with literature data¹⁴. One can clearly observe the reduced permeability of sulfonated aromatic polymer membranes versus the perfluorinated ionomer (Table 1), confirming the well-known advantage of SAP^{17, 36-38}. The smaller permeability of SPEEK can be attributed to the lower nanophase separation of SAP, due to the lower hydrophobicity of the aromatic polymer domains and the lower acidity of the sulfonic groups vs. the superacidic perfluorinated sulfonic acid^{19, 39-41}. This leads to smaller ionic clusters and more tortuous hydrated channels with more dead-ends⁴¹.

A further significant decrease of permeability can be obtained by cross-linking SAP⁴², e.g. by a thermal procedure reported recently^{20, 31} (Figure 2). This procedure reduces the average channel size, because the length of covalent sulfone bonds is only about 0.26 nm³⁰.

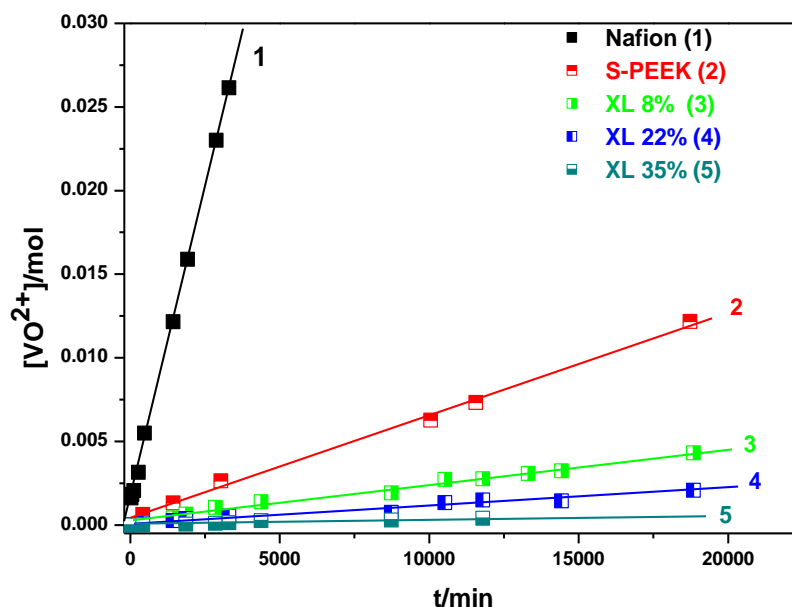


Figure 2. Vanadium permeation in SPEEK membranes with various degrees of cross-linking and comparison with Nafion 117. In brackets the entry code in Table 1.

The amount of cross-linking can be determined from NMR spectra (Figure 3), provided that the ionomer remains soluble in the solvent used for NMR, which is not the case at high degrees of cross-linking.

Figure 3a shows the NMR spectrum of SPEEK. The area of signal C, corresponding to the hydrogen in *ortho* to the sulfonic acid group, gives the degree of sulfonation. The group of signals A (4 hydrogens) that remains unchanged during the reaction is taken as reference. In the spectrum of XL-SPEEK (Figure 3b), the presence of a new signal (D) is assigned to the proton in *ortho* to the sulfone moiety that shifts the resonance downfields^{43, 44} demonstrating the occurrence of cross-linking. The degree of reticulation was evaluated by the intensities of resonances A and D and was 8% in perfect agreement with titration data (Table 1, code 2).

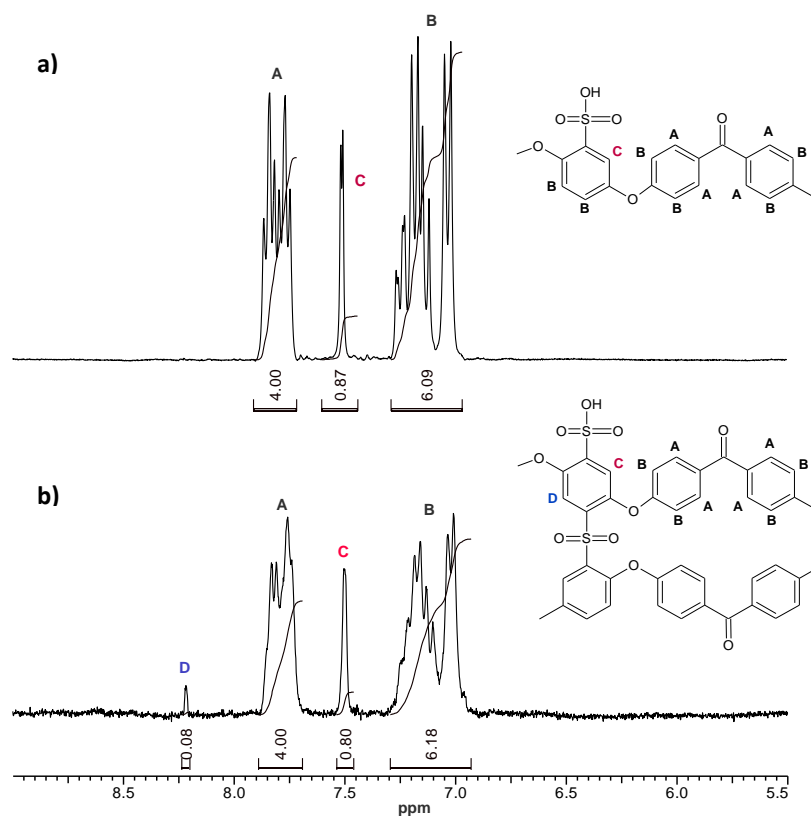


Figure 3. ^1H NMR spectra of a) SPEEK DS = 0.9 (Table 1, code 2) and b) XL-SPEEK DS = 0.8, DXL = 8% (Table 1, code 3) in DMSO-d_6 .

The mechanical properties of SPEEK with various cross-linking degree are reported in Table 1. The Young modulus is related to the Van der Waals forces between the macromolecules, while tensile strength is associated with strong bonds, like covalent or ionic.

The enhancement of mechanical properties by reticulation is known for a long time⁴⁵⁻⁴⁷: in our case the increase of Young modulus is linked to the reduced water uptake, because the high dielectric constant of water reduces the Van der Waals interactions between the macromolecular chains.

The enhancement of tensile strength with reticulation is consistent with the formation of new covalent bonds between the macromolecules⁴⁸.

The cation permeability is related to the average size of the hydrated nanometric channels that decreases with the amount of reticulation. In fact, there is a good exponential correlation between the tensile strength and the cation permeability (Figure 4). A strong reduction of the permeability

of reactive gases, oxygen and hydrogen, in cross-linked SPEEK has been reported previously^{18, 48}.

The ion conductivity is also reduced as shown in Table 1, given that some sulfonic acid groups are lost by the cross-linking process. One should however mention that we developed strategies to optimize the ion conductivity, based on large hydration at high temperature that only cross-linked membranes can support (“memory effect”⁴⁹).

This antagonistic behavior can be described by introducing a factor of merit F , defined as the ratio of ion conductivity σ and ion permeability P :

$$F = \frac{\sigma}{P} \quad (5)$$

Table 1 shows that the best compromise between high ion conductivity and low electrochemically active ion permeability is obtained for a cross-linking time of 24 h.

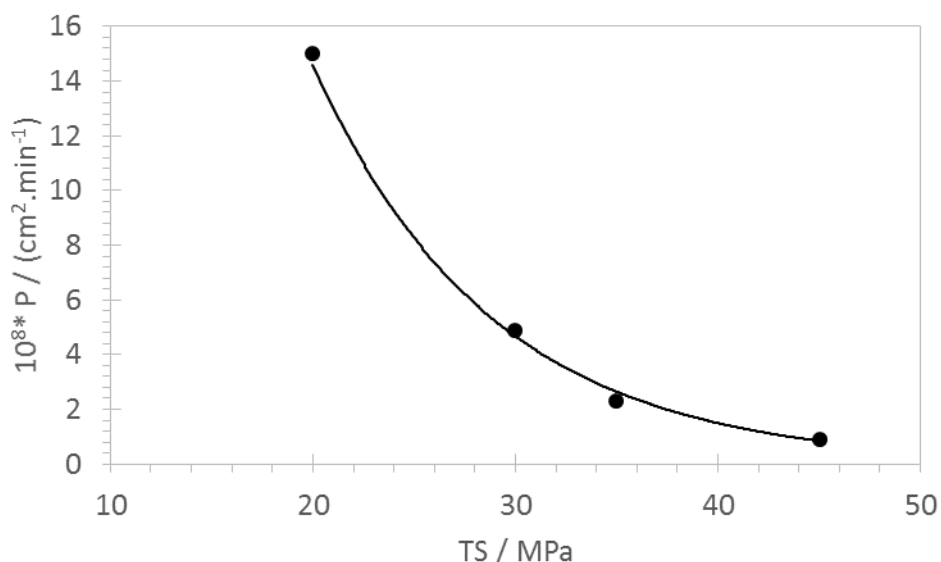


Figure 4. Cation permeability P as function of the tensile strength TS of partially cross-linked SPEEK membranes.

Anion-conducting membranes: PSU-QA and SA-PEEK

A further reduction of cation permeability is difficult to achieve with cation-conducting membranes, but can be reached by changing the type of grafted groups on the ionomer backbone.

A typical ¹H NMR spectrum of PSU-QA is reported in Figure 5.

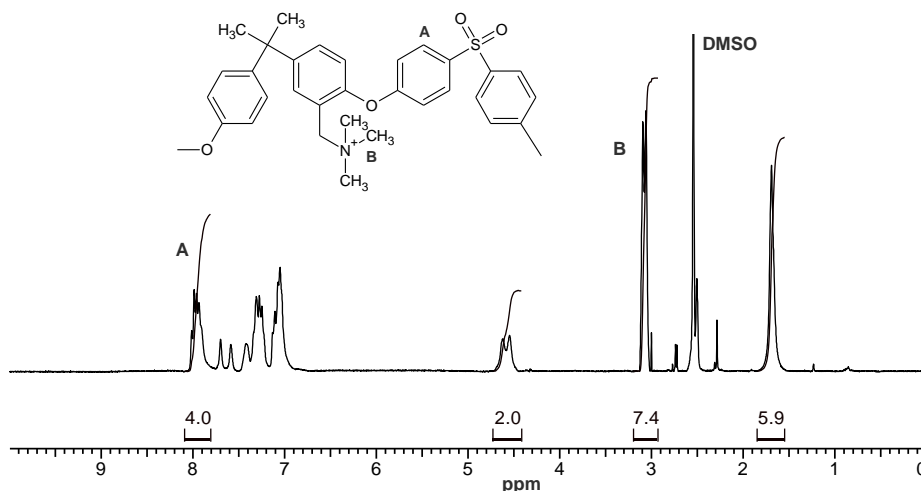


Figure 5. ^1H NMR spectrum of PSU-TMA (Table 1, code 6) membrane (IEC = 1.59 eq/kg) in DMSO-d_6 .

The aromatic peaks appear between 6.9 – 8 ppm. The group of signals A corresponds to the hydrogens in *ortho* to sulfone moieties that remain unchanged during the reaction. The signal of the $\text{N}(\text{CH}_3)_3$ group (B) appears at 3.1 ppm, while the peaks due to the CH_2N group are centred at 4.6 ppm. The ratio between the areas of protons at 7.9 ppm (A) and 3.1 ppm (B) gives the degree of amination. When B = 9 H the DAM is 1; in this case the ratio between A and B is 0.82, in very good agreement with the titration data.

Figure 6 shows cation permeation data for anion-conducting membranes prepared with quaternary ammonium groups (TMA and DABCO) grafted on polysulfone backbones. The permeability was measured for two series of samples with different IEC values. The thickness of the studied membranes is reported in Figure 6. The calculated permeability values were 0.5 and $2.0 \cdot 10^{-8} \text{ cm}^2 \text{ min}^{-1}$ for TMA samples (0.8 and 1.6 eq/Kg, respectively), 3.3 and $47.0 \cdot 10^{-8} \text{ cm}^2 \text{ min}^{-1}$ for DABCO samples (1.1 and 1.3 eq/kg respectively). The cation permeability is lower for TMA, especially with low IEC. Apparently, these data are in contrast with the Donnan exclusion effect that should be more important with a larger number of ion exchange groups; probably the much enhanced water uptake with large IEC³² leads to larger channel sizes and increased cation permeation. The cation permeability is higher for DABCO, although it contains two nitrogen atoms which could lead to an internal cross-linking of two macromolecules, as discussed in the

literature⁵⁰. However, the synthesis was performed with equivalent amounts of DABCO and chloromethylated PSU in order to avoid cross-linking³². One can estimate that the large size of the bulky DABCO molecule increases the average channel size, enhancing the cation permeation. In a previous work, the fluoride ion diffusion coefficient in PSU-TMA and PSU-DABCO was measured by NMR spectroscopy⁵¹. The diffusion coefficient can be used to estimate the ratio porosity ε /tortuosity τ ⁵² of the membrane by the following scaling equation:

$$D = \frac{\varepsilon}{\tau} D^{\circ} \quad (6)$$

In this equation, D is the diffusion coefficient measured in the ionomer and D° the diffusion coefficient measured in a reference aqueous solution⁵³. This procedure gave a lower ratio (0.10) for PSU-TMA than for PSU-DABCO (0.18)⁵¹, which was attributed to the larger size of bulky DABCO that increases porosity. This factor should enhance the cation permeability in PSU-DABCO in agreement with the data.

The relatively large permeability observed for all PSU-QA samples, in comparison with SPEEK membranes showed previously, can be related to the higher permeation values of PSU in comparison with PEEK²³⁻²⁶, although in SPEEK the Donnan effect is absent.

The data of ion conductivity, water uptake, and mechanical properties are reported in Table 1 for samples with IEC 1.6 and 1.3 eq/kg (entry 6 and 7). The conductivity is due to HSO_4^- ions (see experimental).

Obviously the water uptake and ion conductivity are lower than with hydroxide ions³², in accordance with the lower hydration and lower mobility of hydrogensulfate ions, and the Young modulus is larger. These results confirm the relationship between water uptake, ion conduction and stiffness discussed for SPEEK. The mechanical properties are comparable to un-crosslinked SPEEK, but definitely below cross-linked ionomers (XL SPEEK and SA-PEEK). The factors of merit are unfavorable, showing that PSU-QA is not a very good system for low permeation separators.

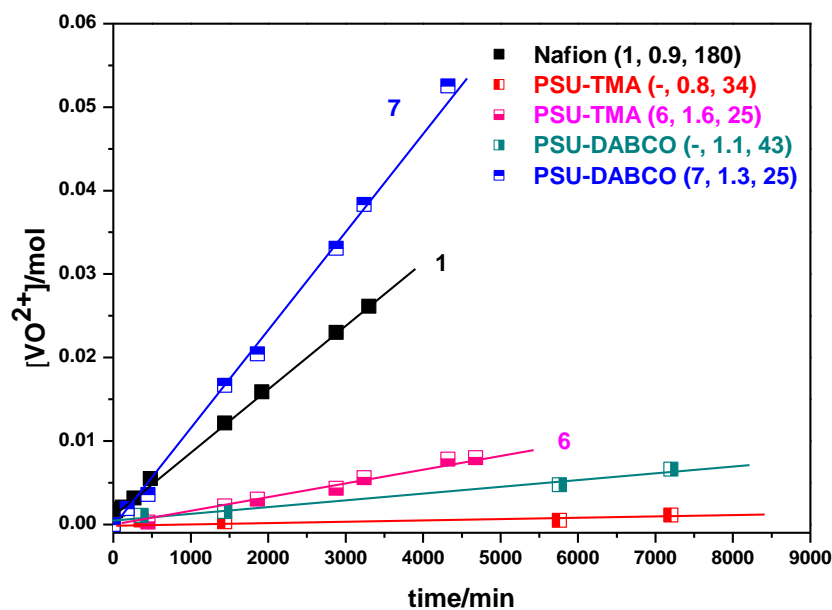


Figure 6. Vanadium permeation in PSU membranes quaternized with TMA or DABCO with various degrees of amination and comparison with Nafion 117. In brackets the entry code in Table 1 (if present), IEC (eq/kg), and the membrane thickness (μm).

For a more direct comparison with protonic PEEK membranes, we studied the cation permeability of AEM with sulfonamide groups grafted on PEEK.

The protonation of the sulfonamide group leads to a sulfammonium group, which is stable also in absence of excess acid, as shown previously³³. Furthermore, a small degree of cross-linking (DXL = 0.1) is introduced by the sulfonation procedure with chlorosulfonic acid³³, as shown by the NMR spectrum (Figure 7). Evidently, this structure leads to a very efficient reduction of cation permeation by the Donnan exclusion and the permeability values are very low (Table 1).

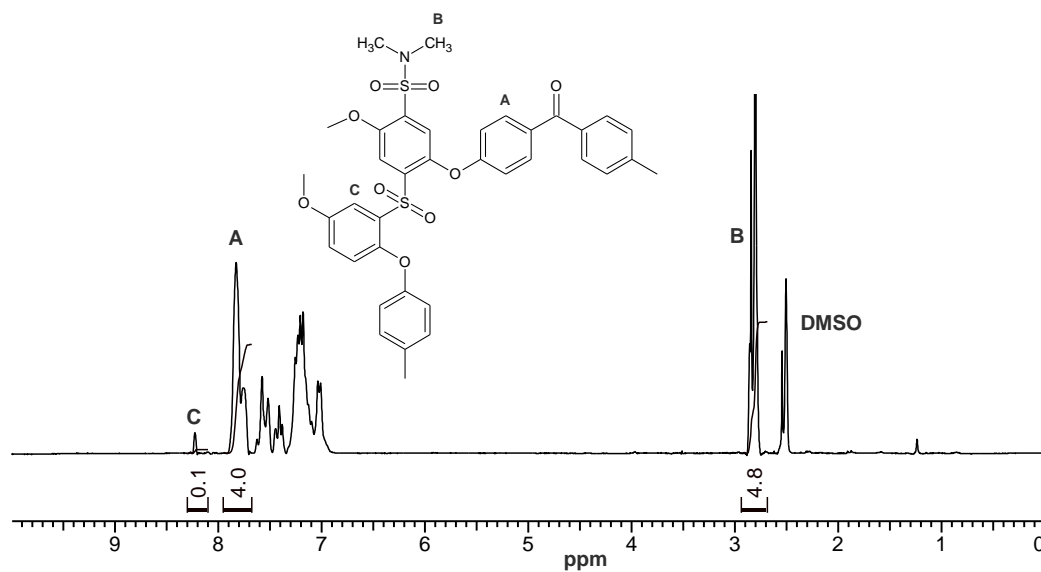


Figure 7. ^1H NMR spectrum of SA-PEEK (Table 1, code 8) in DMSO-d_6 .

The signal C in Figure 7 is characteristic of the presence of cross-linking and is due to the hydrogen in *ortho* to sulfone groups. The ratio with the signal A at 7.8 ppm, due to hydrogens in *ortho* to ketone groups (4 H), gives a degree of cross-linking of 10%. The signals B at 2.8 ppm correspond to methyl groups (6 H) linked to nitrogen. The relative intensity of signals A:B is 4.0:4.8, equivalent to a degree of sulfamination of 0.8 matching a complete amination reaction. The asymmetry of protons in *ortho* to the $-\text{SO}_2\text{N}(\text{CH}_3)_2$ groups resulted enhanced by the substitution of a chlorine atom in the chlorosulfonate derivative with bulky methyl groups in the sulfonamide derivative.

The cross-linking probably reduces the average channel size like in the case of SPEEK and explains the ultra-low vanadium permeability and also a relatively low water uptake. The reticulation of membranes is a very efficient method for reducing the cation permeability. The smallest permeability is reached with diethylamine, although the molecular volume is somewhat larger than that of dimethylamine; the basicity of diethylamine is slightly higher so that a stronger bond in acidic solution is achieved.

The conductivity in Table 1 is due to hydrogenosulfate ions, because the membrane was functionalized in H_2SO_4 (see experimental); conductivities due to other anions are reported in reference ⁵⁴. The factor of merit and the mechanical properties, Young modulus and tensile strength, are optimal among the investigated membranes (Table 1).

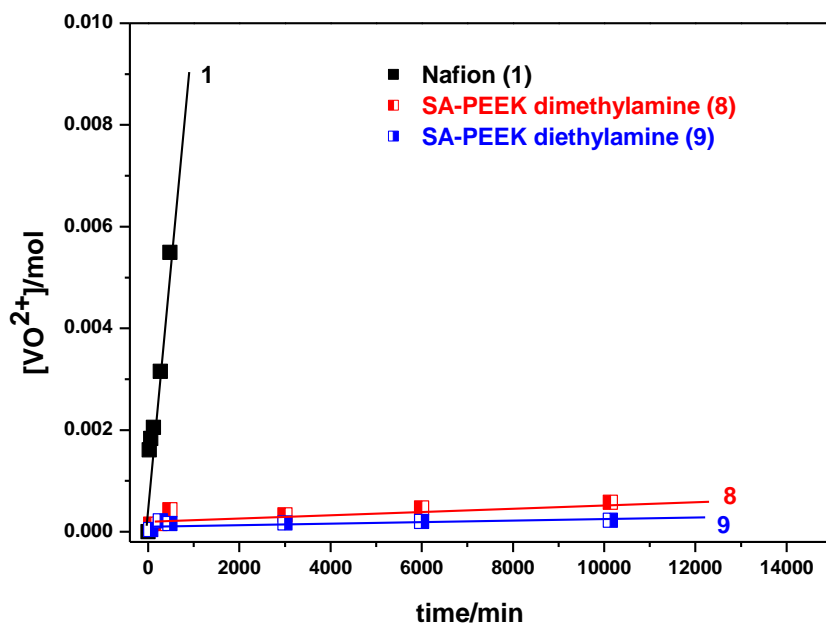


Figure 8. Vanadium permeation in SA-PEEK membranes with dimethylamine or diethylamine and comparison with Nafion 117. In brackets the entry code in Table 1.

Ampholytic membranes: SAM-PEEK

Ampholytic ionomers contain ionic groups with simultaneously mobile cations and anions and in our case a slight excess of sulfonic groups vs. sulfonamide groups³⁴. Ampholytic membranes should therefore present a relatively low permeation rate for both cations and anions. In acidic conditions, encountered in our permeation experiments, both groups are ionized and the mobile ions are H_3O^+ and HSO_4^- . The ionic conductivity reported in Table 1 contains contributions by both ions, but remains relatively low.

In this case, the membrane was however not cross-linked, due to the different synthesis procedure by reaction of SPEEK with thionyl chloride instead of direct chlorosulfonation³⁴. For this reason, the mechanical properties (Young modulus and tensile strength) are below those of cross-linked SA-PEEK membranes (Table 1).

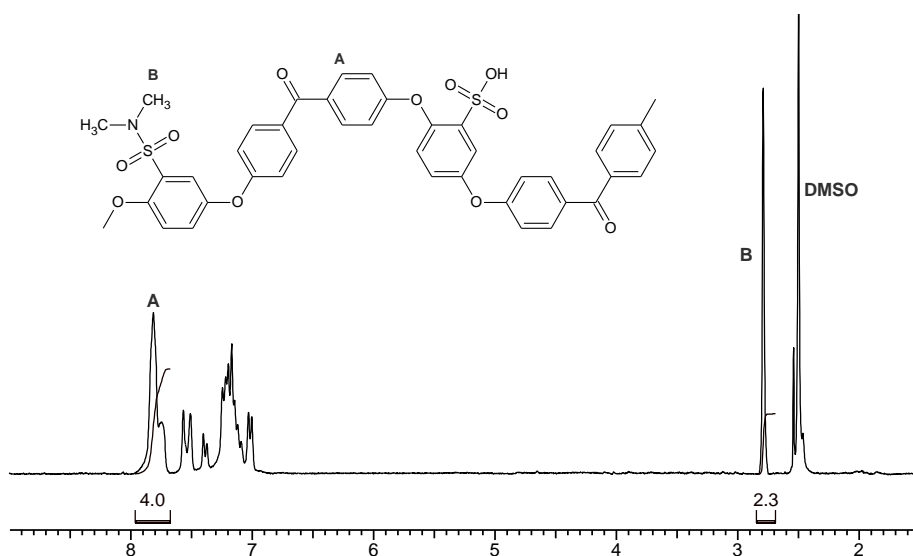


Figure 9. ^1H NMR spectrum of SAM-PEEK (Table 1, code 10) in DMSO-d_6 .

The ^1H NMR spectrum of SAM-PEEK (Figure 9) shows the signal of the methyl groups attached to nitrogen at 2.8 ppm (B). The amount of amination is calculated from the integration of hydrogens of methyl groups (6H) and the aromatic hydrogens in *ortho* to the ketone group (A, 7.8 ppm, 4H) that are unchanged during the reaction. A complete transformation into sulfonamide groups would give a ratio of 4:5.2, considering the initial DS of SPEEK. The obtained ratio of 4.0 : 2.3 indicates a conversion of 45 %, corresponding to a degree of amination of 0.39 or an IEC of 0.98 meq/g in good agreement with the value determined by titration (0.94 meq/g).

The curve in Figure 10 shows a very low permeation rate and the cation permeability reported in Table 1 is the second lowest, confirming the lower permeation of ionomers based on PEEK, but slightly higher than SA-PEEK, probably because the membrane is not cross-linked. The factor of merit is the second best (Table 1, code 10).

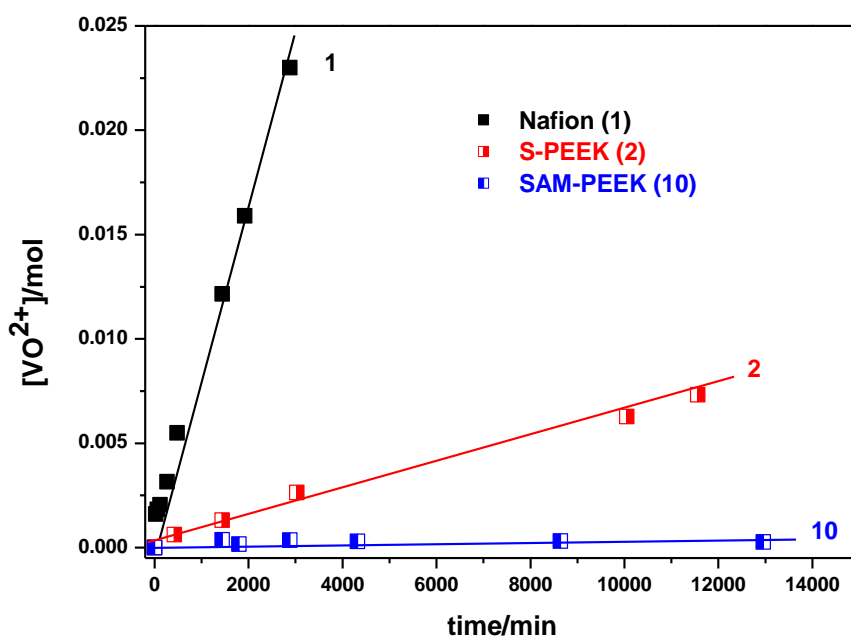


Figure 10. Vanadium permeation in SAM-PEEK membranes and comparison with SPEEK and Nafion 117. In brackets the entry code in Table 1.

Conclusion

In this work, we studied the cation permeability, ion conductivity, water uptake and mechanical properties of various types of ion exchange membranes (IEM). The structure was investigated by NMR spectroscopy. The comparison of IEM with protonic, anionic or mixed proton/anion conductivity shows that the issue of ion crossover can be managed by choice of the membrane type.

A figure of merit factor (ratio ion conductivity / permeability) is introduced to express the membrane performance. The ionic conductivity is of critical importance. The permeability measurements in acidic solution show an ultra-low vanadium permeability and excellent factor of merit for highly cross-linked SPEEK membranes, anion-conducting membranes with grafted sulfonammonium groups and amphoteric membranes with both sulfonic acid and sulfammonium groups. Apart the Donnan exclusion of cations in anionic and ampholytic membranes, the effect of some cross-linking is very significant, probably by a reduction of the average size of the nanometric ion-conducting channels.

Furthermore, the data show that membranes based on PEEK are better performing than those based on PSU, like PSU-QA, suggesting an important effect of the polymer backbone in addition to the kind of grafted ionic group.

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Table 1. Ion exchange capacity IEC, thickness, water uptake WU, ionic conductivity, vanadium ion permeability, figure of merit and mechanical properties (Young modulus E and Tensile Strength TS) of various protonic, anionic and amphoteric ion exchange membranes at 25 °C.

Code	Membrane	IEC / meq g ⁻¹	WU / (± 1) %	Thickness (± 2)/ μm	Ionic conductivity/ mS cm ⁻¹	VO ²⁺ permeability/ 10 ⁻⁸ cm ² min ⁻¹	Figure of merit / mS min cm ⁻³	E and TS/ MPa
1	Nafion 117	0.9	21	180	36 ± 2	140	0.26	270 12
2	SPEEK	2.5	160	60	16 ± 1	15	1.07	850 20
3	SPEEK XL=8%	2.3	48	60	15 ± 1	4.9	3.06	1160 30
4	SPEEK XL=22%	1.9	17	60	14 ± 1	2.3	6.09	1300 35
5	SPEEK XL=35%	1.6	8	55	13 ± 1	0.9	14.44	1450 45
6	PSU-TMA	1.6	36	25	1.0 ± 0.1	2	0.5	1180 33
7	PSU-DABCO	1.3	25	25	1.1 ± 0.1	47	0.02	1250 46
8	SA-PEEK (Dimethyl- amine)	2.3	29	25	2.6 ± 0.9	0.1	26	1460 53
9	SA-PEEK (Diethyl- amine)	2.2	27	25	3.3 ± 0.6	0.05	66	1550 51
10	SAM-PEEK	2.4	24	25	3.0 ± 0.7	0.07	42.8	1270 37

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