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Original Article

Modified polyvinyl chloride membrane grafted with an ultra-thin polystyrene film: structure and electrochemical properties



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ABSTRACT

The work explores the synthesis and the properties of a novel composite membrane system based on modified polystyrene (PS) grafted onto a polyvinyl chloride (PVC) membrane. PVC membranes were prepared by solution-casting followed by exposure to an atmospheric pressure dielectric barrier discharge (DBD) with O₂ to obtain an activated surface for grafting PS to it. Moreover, the thus prepared membranes were chemically modified furthermore by amination with polyethyleneimine or sulfonation with 4 M sulfuric acid. The membrane surface characteristics such as wettability, structure and morphology were investigated using water contact angle measurements, attenuated total reflection Fourier transform infrared spectroscopy and scanning electron microscopy experiments. The thermogravimetric stability and electrolytic responses of the membranes were studied utilizing TGA, ion exchange capacity (IEC), and solvent uptake. A significant result of plasma and chemical modification was to produce a membrane material with low permeability. Thus, the methanol permeability of the sulfonated membranes measured for 12 h was measured to $2.34 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ compared to $177.00 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of Nafion 117® which is considered as a benchmark. This result indicates that the prepared sulfonated samples are an innovative and effective material for decreasing the methanol crossover in fuel cells to a great extent. This makes the PVC-g-St membranes are promising and attractive as new materials for polyelectrolyte membrane for fuel cells.

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1. Introduction

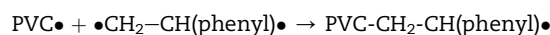
There is no doubt that the increasing growth in human population around the world call for an increased and significant high consumption of energy. This is a great challenge to the human society in order to preserve the natural sustainable energy [1]. With the serious environmental impact resulting from the traditional use of conventional energy sources such as fossil fuels, researchers have made great efforts to develop clean, environment friendly alternative energy sources [2]. In comparison to many other types of green energy sources, fuel cells have many advantages. Their components are simple, the design is distinctive, and they have a highly efficient energy conversion with a clean environment protection. Polymer electrolyte membrane-based fuel cells (PEMFCs) consisting mainly of an anode, a cathode and a polyelectrolyte membrane (PEM) [3]. The most important part in fuel cell is the proton exchange electrolyte membrane which is responsible for the transfer of the electrons from the cathode to the anode. The fuel cell performance is due to several requirements including high hydraulic oxidation stability in the actual fuel environment, a good mechanical stability in the dry and acidic state, a low electronic conductivity, an inefficient supply of gas or liquids and a high proton paralysis. Perfluorosulfonic acid (PFSA) is the most commercially used material for PEMs (Flemion®, Acipex® and Nafion®) [4]. These membranes have a high proton conductivity at moderate operating temperatures in a large range of relative humidity and a good physical as well as chemical stability [5]. But there are also drawbacks that have limited the application of Nafion®, including its high permeability for fuel and therefore, high costs, as well as their environmental incompatibility with other materials. However, efforts have been made to develop alternative low-cost membranes as potential PEMs. In the most strategies a number of modified sulfonated aromatic polymers such as polyarylene ethers (PAE) or aromatic polymers based on functionalized aromatic hydrocarbons are suggested [6]. It is known that the efficiency of fuel cells is affected by several factors including pressure, the relative humidity of the gas flow, temperature and others. In order to improve the fuel cell performance must be understood. Several research institutes working in these areas have addressed the influence of operations conditions on the fuel cell performance and also simulations were proposed to study the efficiency of fuel cells [7].

Poly (vinyl chloride) (PVC), is one of the most widely produced thermoplastic resins. Therefore, it has been widely employed in industry due to its low price, chemical resistance, good mechanical properties and excellent dielectric properties. Thus, it was selected for the current study [4,8–10]. Although, PVC based membranes exhibited a big potential to be utilized as the membrane material in fuel cells, also investigations relating to PVC based HT-PEMs have been reported to our best knowledge [11].

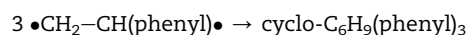
Plasma technologies can be promising approach for the developments of PEM [12]. The application of plasma technology applied to PEMs is mainly based on plasma polymerization [13]. The modification of PEMs with plasma immobilization technology is an innovative way to change the

surface of the polymer membranes, where the polymer surface is modified on a thickness of several tens of nanometers [14,15]. Changing of interfaces can have a significant effect for instance on the fuel permeation of PEMs. Exposure to inert gas plasmas, such as argon or nitrogen, is also used for surfaces modification of polymer [16]. Changing of plasma conditions during plasma treatment has also an effect of modification [17]. Generally, discharge specifications like power, time, pressure, flow rate, etc. has much influence on surface modification [18]. However, plasma treatment at low pressure (vacuum) is well suited for controlling the functionality of the treated polymer because it is well investigated since about 60 years and is proved to be successful. Unfortunately, use of plasma at low pressure is more expensive than such at atmospheric pressure. Therefore, plasma treatment at atmospheric pressure is increasingly used because saving of vacuum system and it could be carried out continuously in contrast to low-pressure processes [19].

Here, plasma-grafting and plasma polymer deposition of styrene onto PVC substrates is the goal of this work. The mechanism of polystyrene formation by plasma techniques is probably based on plasma-induced radical polyreactions [20]. Plasma exposure activates the substrate surface and initiates simultaneously the formation of styrene radicals which can graft to radical sites at the PVC surface and start a graft polymerization form a well-adherent homopolymer. It is assumed that the π -bond in the vinyl monomer is opened on plasma exposure [21]. However, such mechanism produces biradicals. In case of grafting by radical–radical recombination:

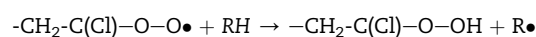
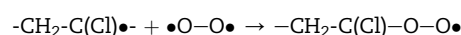
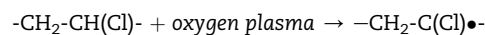


The remaining radical at the tertiary carbon atom can start a regular chain growth polymerization from substrate, similar to those started with commercial initiators, which produce monoradicals. Whereas homopolymerization via biradicals is immediately interrupted at the formation of cyclohexane rings by radical–radical recombination:

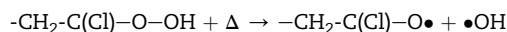


This effect is well known from macromolecular chemistry and is called as C_6 limit. Such cyclohexane derivate is soluble and can be removed by washing easily.

Here, an indirect grafting from was applied. The PVC membrane was exposed to the atmospheric oxygen plasma to transfer generated C radical sites into peroxides and afterwards to hydroperoxides by H abstraction from PVC:



The hydroperoxide decomposes at heating or at irradiation to monoradicals which can initiate a regular chain growth graft polymerization from PVC:



This thermally induced decay of hydroperoxides can start a graft reaction as well as a homo-polymerization.

The current work focuses on grafting of styrene onto the surface of a PVC membrane to obtain novel and effective composite materials as polyelectrolyte membranes. The hydrophilic character of the membrane is important and fundamental for fuel cells to improve the characteristics of the membranes. To improve further the characteristics of plasma-grafted membranes, chemical modification with polyethyleneimine was tested followed by a sulfonation process via exposure to diluted H_2SO_4 . The thermal stability of the modified membranes was evaluated by thermogravimetric analysis. In addition, water, methanol and ethanol uptakes were measured for the grafted membranes. The obtained materials outperform the properties of commercial Nafion 117® membranes.

2. Experimental part

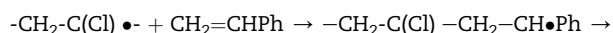
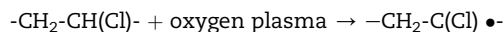
2.1. Materials

Styrene 99% and polyethyleneimine were purchased from Accros Chemicals co. PVC was obtained from Sabic co. It degrades at temperatures above 250 °C. H_2SO_4 , and THF (99.5%) were received from Fisher chemicals co. All chemicals were used without further purification.

2.2. Membrane preparation

2.2.1. Preparation of PVC-g-St membranes

The casted polyvinylchloride film was exposed to atmospheric O_2 plasma and then grafted by styrene (PVC-g-St) in two-step processes. First, PVC films were prepared by dissolving 3% PVC w/v in THF under stirring and then casted on glass plates using a spreader knife. The film was dried afterwards for 24 h at 60 °C. The thickness of films was in the range from 40 to 80 μm . Secondly, the PVC film was activated by O_2 plasma and then directly immersed in 15 mL of the styrene monomer for 1 h to avoid the consuming of all generated radicals or ions on the surface of PVC substrate.



The substrate polymer is surely dissociated to oligomers with many radicals and functional groups. These reactive centers guarantee best interactions between substrate and coating (covalent bond). However, the involved oligomers have not more the mechanical strength as the virgin polymer. Therefore, it is a compromise between enough reactive centers for interactions (bonds) and preservation of mechanical strength [22–24]. It should be noted that the deposited layer is a mixture of grafted polystyrene or styrene oligomers and adsorbed polystyrene.

The thickness of the grafted ultra-thin polystyrene layer onto the PVC membrane was estimated to be ~ 2.5 nm. A

density of 1 g cm^{-3} was assumed to calculate the film thickness of the grafted layer, because the densities of ultra-thin layers are difficult to measure. Therefore, the absolute values of the thicknesses can have errors, but this potential error is the same for all discussed cases. Therefore, relative changes might be discussed.

2.2.2. Amination processes

The prepared and modified PVC-g-St membranes were rinsed in a solution of 10% of polyethyleneimine in hot water (40 °C) for different time (6, 12, 18 and 24 h) and then washed with distilled water for 30 min. Finally, the sample was dried again at 60 °C. Polyethyleneimine (PEI) interacts with remained acidic anchoring points of oxygen plasma treatment and forms ionic bonds or interactions and is physically adsorbed. Another possibility is the covalent bonding of PEI by substitution of chlorine from the PVC substrate.

2.2.3. Sulfonation processes

The aminated PVC-g-St membrane was dipped in 4 M sulfuric acid at room temperature for different times (6, 12, 18 and 24 h) and then, the membrane was washed with distilled water until a pH value of ~ 7–7.5 was obtained. Afterwards the membrane was dried in an oven at 60 °C [9].

2.3. Plasma reactor

The discharge cell of the planar dielectric-barrier discharge (DBD) system contains two circular stainless-steel electrodes of 15 cm in diameter, separated by a Pyrex glass sheet through an O ring. The gap between the electrodes was about 1 mm. For more details see elsewhere [25]. One electrode was connected to a high voltage AC transformer which generates a 50 Hz sinusoidal voltage (0–12 kV, 15 mA) used as a power supply for maintaining the discharge. The other electrode was grounded.

The membrane samples were inserted into the discharge gap between the two electrodes. Plasma treatment of the PVC membrane was applied at a constant discharge power of 4 W. A 100 MHz two channel digital storage oscilloscope (Type HM1508) was used to record the course of current and waveform of the applied voltage during plasma treatment. The consumed power was estimated by replacing the 100 Ω resistor by a 10 nF capacitor to measure the charges accumulated in the discharge cell. For more detail see ref. [25].

2.4. Instrumental characterizations

2.4.1. Contact angle

A contact angle meter VCA 2500 XE equipped with a CCD camera and analysis software (AST Products, Billerica, MA) was used to measure the contact angle of a static water droplet with the prepared membrane surface as an indication for their hydrophilicity.

2.4.2. Fourier transforms infrared spectroscopy (FTIR)

The membranes were also investigated using a Fourier transform infrared spectrometer (Shimadzu FTIR-8400s, Japan) working in the attenuated total reflectance (ATR) mode. The data were measured in the wave number range

from 4000 to 400 cm^{-1} accumulated with 64 scans with a resolution of 4 cm^{-1} .

2.4.3. Secondary Electron Microscopy

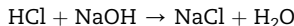
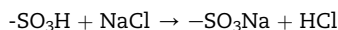
The morphological features and microstructure of the polymeric membranes were studied by Secondary Electron Microscopy (SEM) using a JEOL JSM-6360LA device (Japan). The acceleration voltage was set to 20 kV. The samples were glued on stainless steel stubs with a double-sided tape. A 10–20 nm thick gold layer was sputtered onto the samples. The magnification was in the range of 500 to 20,000.

2.4.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was applied to study the thermal stability of the membranes by measuring their weight loss with increasing the temperature applying a heating rate of 10 K/min in nitrogen atmosphere. For that purpose, the thermogravimetric analyzer Shimadzu TGA-50 was used in the temperature range from room temperature to 800 °C.

2.4.5. Ion exchange capacity (IEC)

The IEC is directly related to the number of hydrophilic functional groups in the polymer membranes. It is generally measured by a volumetric method. A membrane sample in the H^+ counter ion form was immersed in 20 mL of a 2 M NaCl solution at room temperature for 12 h.



The amount of HCl released from the membrane was titrated with a standard 0.1 N NaOH solution in presence of phenolphthalein as an indicator. IEC in milliequivalents of functional groups per gram of the dry sample was calculated by Eq. (1) [3].

$$\text{IEC} = \frac{\text{Titre value (in ml)} \times \text{Normality of NaOH}}{\text{Weight of dry polymer membrane (in g)}} \text{meq/g} \quad (1)$$

2.4.6. Water, methanol and ethanol uptakes

The water, methanol and ethanol uptake of the modified PVC membrane was estimated as weight ratio of the swollen PVC-g-St composite membrane (W_{wet}) to the weight of the dry membrane (W_{dry}). For this purpose, the membrane samples were cut into 2 × 2 cm pieces and then vacuum-dried for 12 h to measure W_{dry} . The dried membranes were also either dipped in deionized water, methanol or ethanol at room temperature and W_{wet} was measured in dependence on time. The water uptake of membranes is given as in the Eq. (2):

$$\text{uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100. \quad (2)$$

2.4.7. Calculation of the methanol permeability

The methanol permeability (P) was investigated for the membranes which have good IEC data. The permeability is evaluated by plotting the methanol concentration C_B in the (water) compartment versus time as Eq. (3):

$$C_B(t) = (A P / V_B L) \cdot C_A \cdot (t - t_0) \quad (3)$$

where C_A is the methanol concentration in the feed. A and L are the area and thickness of membranes, respectively. Therefore, the Eq. (3) can be modified to Eq. (4).

$$P = \alpha (V_B L) / (A C_A) \quad (4)$$

where α is the slope of the plot C_B versus time. For more details see reference [3].

2.4.8. Calculation of the membrane efficiency

Proton conductivity and methanol impermeability of the membranes are the most important parameters to estimate their applicability in direct methanol fuel cells (DMFCs). However, the membrane performance can be characterized by Eq. (5) [3]:

$$\Phi = \sigma / P \quad (5)$$

where Φ is the efficiency factor that estimates the overall membrane operation as ratio of the conductivity (σ) and the permeability. Nevertheless, here the IEC was used as an indicator for conductivity. Therefore, the efficiency of the membranes is characterized by employing the ratio of the IEC and the methanol permeability:

$$\Phi = \text{IEC} / P \quad (6)$$

3. Results and discussion

3.1. Wettability measurements

The hydrophilicity of PVC surfaces was investigated before and after modification on exposure to the oxygen DBD plasma, before and after grafting with PS in terms of static water contact angle (WCA). The WCA of pristine PVC was found to be 54° and was reduced to 10° ± 1° after the atmospheric O_2 plasma treatment. It is obviously that the oxygen plasma treatment has significantly increased the number of polar oxygen-containing functional groups at the surface.

However, washing of the sample with THF re-increases the contact angle close to the original value of the unmodified PVC. Therefore, it must be concluded, that the oxygen plasma

Table 1 – Contact angle of modified PVC compared to the untreated samples; g = Grafting, A = amination (Polyethyleneimine) for 18 h, S=Sulfonating for aminated compound for 18 h too.

Samples	Contact angles [°]
PVC	54 ± 3
PVC- O_2	10 ± 1
PS	70 ± 1.7
PVC-g-St	40 ± 2.3
A (PVC-g-St)	38 ± 0.9
S(PVC-g-St)	33 ± 1.2

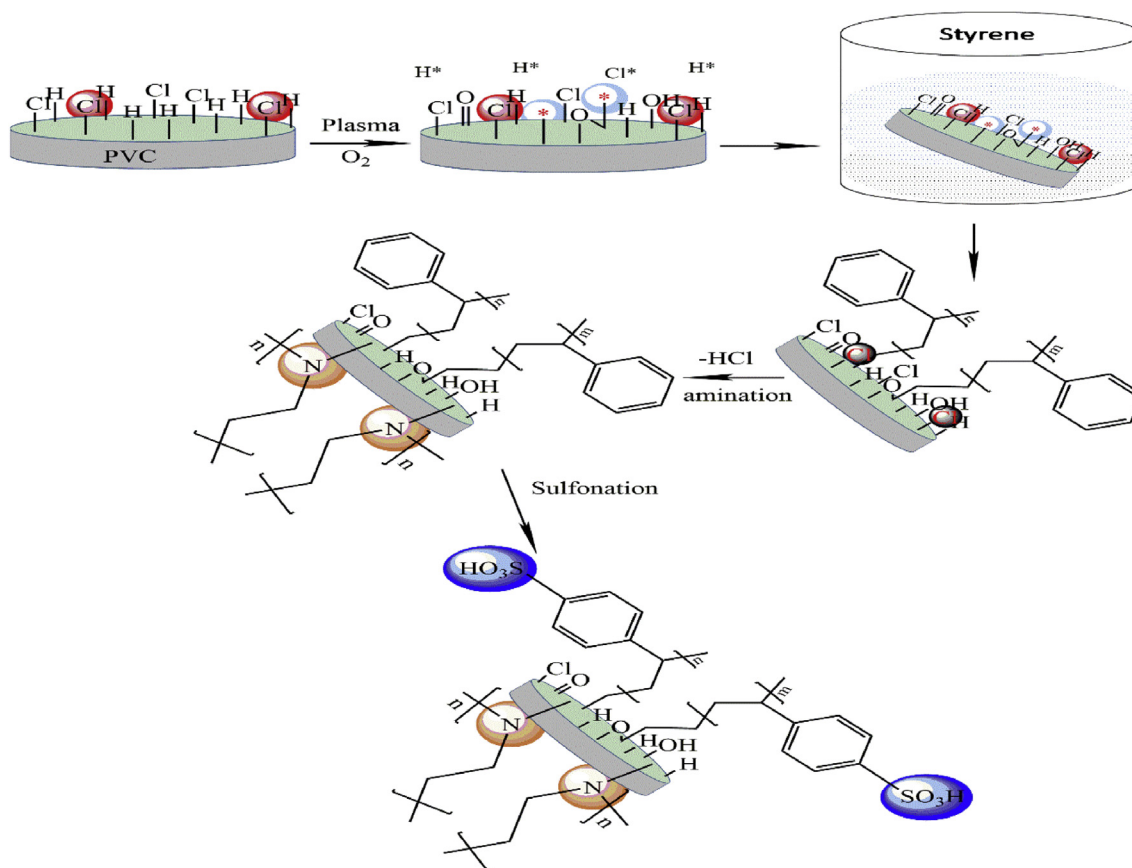


Fig. 1 – Chemical modification of PVC films by plasma O₂ treatment followed by amination and sulfonation processes. The generated radicals or ions at the PVC backbones was presented as star.

exposure alone has produced a polar surface layer of low-molecular weight oxidized material (LMWOM) which can be easily removed by washing, thus, oxygen plasma alone is

insufficient to modify PVC membranes for PEM applications. The contact angle (θ) of the modified PVC membrane after grafting with PS was measured, too.

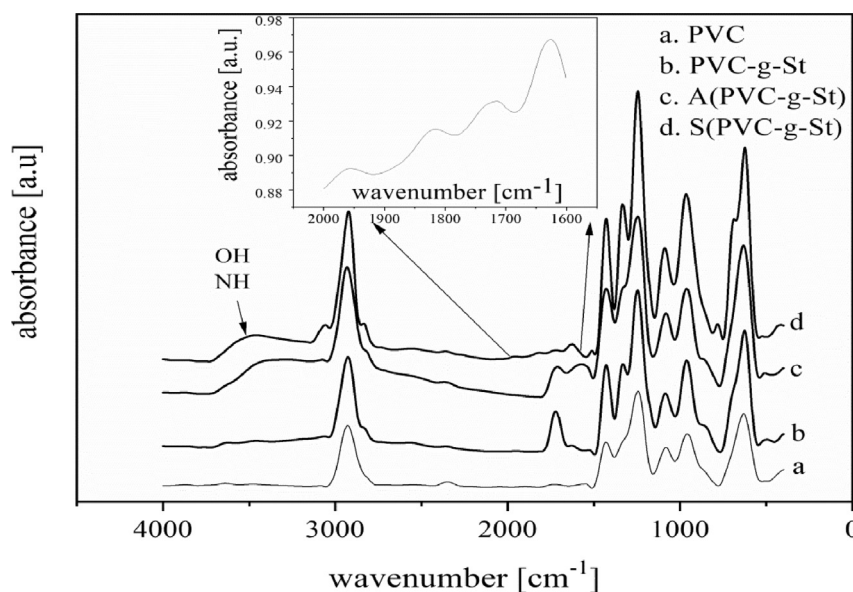


Fig. 2 – ATR- FTIR spectra of pure PVC in comparison to that of PVC-g- St, A (PVC-g-St) and S (PVC-g-St). A = aminated for 18 h and S = sulfonated for 18 h. The inset shows the spectra in the wave number range from 2000 to 1600 cm⁻¹ in S (PVC-g-St) sample.

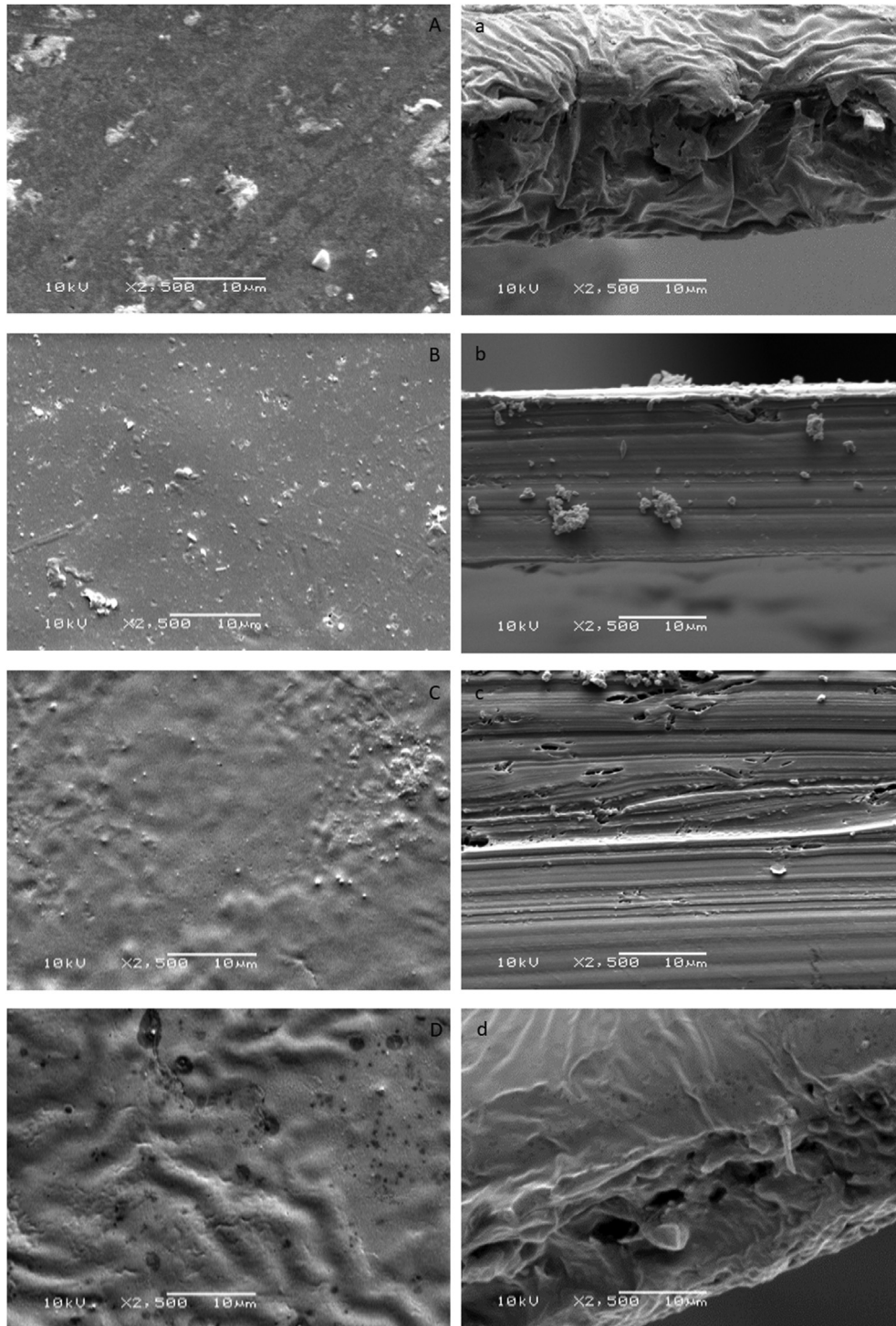


Fig. 3 – SEM images of treated and untreated PVC membranes. A, B, C and D refer to the surface of pure PVC, PVC-g-St, A (PVC-g-St) and S(PVC-g-St), respectively, where a, b, c and d are the corresponding cross section.

In [Table 1](#), the values of Θ are depicted for all prepared samples. The WCA Θ was reduced to 40° and $\sim 30^\circ$ for the PVC-g-St, the aminated sample (PVC-g-St-Am) and the additionally sulfonated sample after the amination process (PVC-g-St-Am-SO), respectively. The hydrophilicity corresponds to the O, N

and SO_3 containing groups detected in the FTIR spectra (see below) which reduce the contact angle and increase the surface wettability. Grafting of PVC films with styrene (St) as “grafting from process” results surprisingly in a lower WCA value than that for a dense polystyrene layer (see [Table 1](#)).

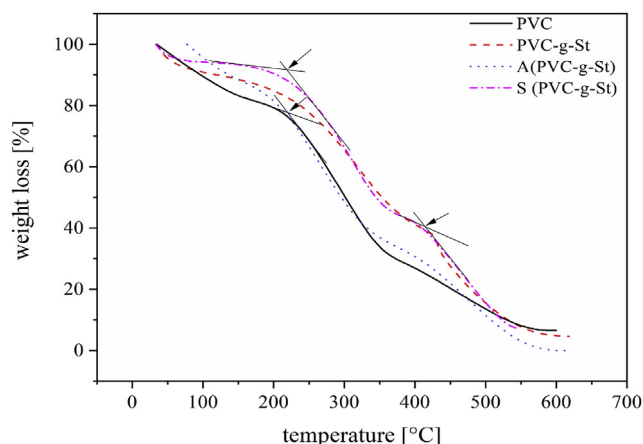


Fig. 4 – TGA thermograms for pure PVC, PVC-g-St, A (PVC-g-St) aminated for 18 h, and S (PVC-g-St) sulfonated for 18 h membranes.

Thus, it can be concluded considering also the calculated low thickness and thus not completely closed St layer that some of the polar oxygen groups introduced by the oxygen plasma onto the surface of PVC are still active at the surface. The amination by polyethyleneimine and its subsequent sulfonation lower the WCA only slightly. This was expected because the amination alone is not an efficient adsorptive process at the partially St coated membrane surface. However, the reduction of the WCA values after amination plus sulfonation processes is an indication for the introduction of new functional groups such as = N-, and -SO₃H at the surface of the PVC-g-St membrane (Fig. 1).

The hydrophilic character of the membrane surface after oxygen plasma exposure needed for application as PEM has unfortunately a drawback. However, in the light for an application as PEM, this drawback turns into an advantage. The membrane must be only partially hydrophilic to avoid the dissolution of the membrane layer in the fuel such as methanol or ethanol etc.

The chemical grafting of styrene (“grafting from”) is initiated by the reaction of molecular oxygen with plasma-generated radical sites forming peroxy groups as shown already in the section Introduction ($\equiv\text{C}\cdot + \cdot\text{O}-\text{O}\cdot \rightarrow \equiv\text{C}-\text{O}-\text{O}\cdot$), their conversion hydroperoxides ($\equiv\text{C}-\text{O}-\text{O}\cdot + \text{H}-\text{R} \rightarrow \equiv\text{C}-\text{O}-\text{OH} + \cdot\text{R}$) suited for starting a chain-growth polymerization (by their thermally or radiation-induced decay into radicals ($\equiv\text{C}-\text{O}-\text{OH} + \Delta \rightarrow \equiv\text{C}-\text{O}\cdot + \cdot\text{OH}$)). The alkoxy radicals then can initiate the grafting reaction of the styrene ($\text{CH}_2=\text{CHAr}$) monomer ($\equiv\text{C}-\text{O}\cdot + n \text{CH}_2=\text{CHAr} \rightarrow \equiv\text{C}-\text{O}-[\text{CH}_2-\text{CHAr}]_n\cdot$). The OH radicals start a homopolymerization [26,27].

Additionally, polyethyleneimine interacts with acidic anchoring points remaining from the oxygen plasma treatment forming ionic bonds, picks up a proton. The thus formed ammonium site can interact with anionic sites at the substrate surface. Another possibility is the covalent bonding of PEI by substitution of chlorine from the PVC substrate (Fig. 1).

3.2. Chemical composition of the modified membrane

FTIR spectroscopy was used to characterize the chemical composition of membranes in a near-surface layer of 1–2 μm. The FTIR spectra of the PVC membrane as well as those

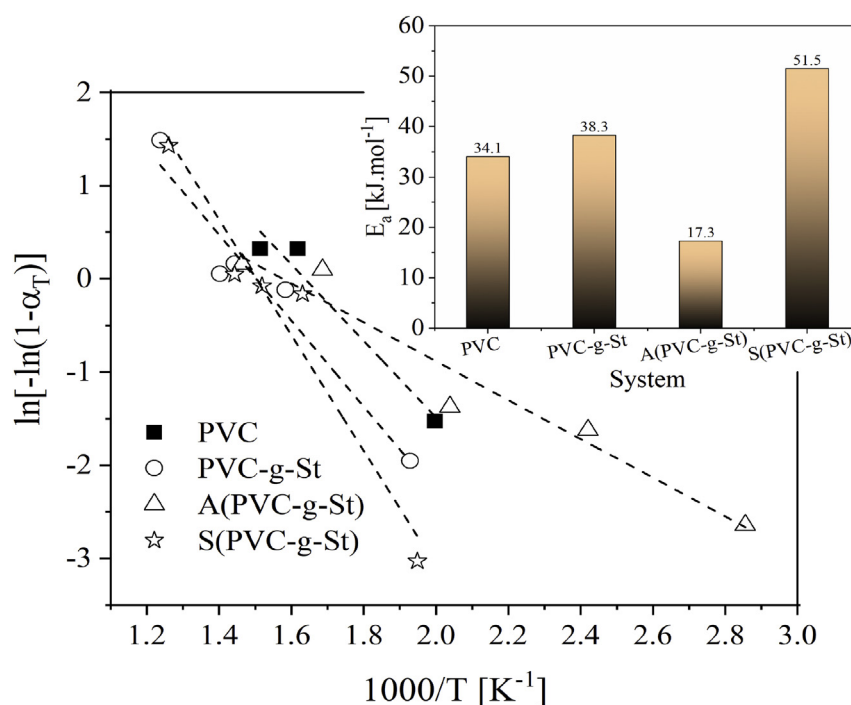


Fig. 5 – $\ln[-\ln(1-\alpha_T)]$ vs $(1000/T)$ for pure PVC, PVC-g-St, A (PVC-g-St) aminated for 18 h, and S (PVC-g-St) sulfonated for 18 h membranes. The inset gives the calculated activation energy.

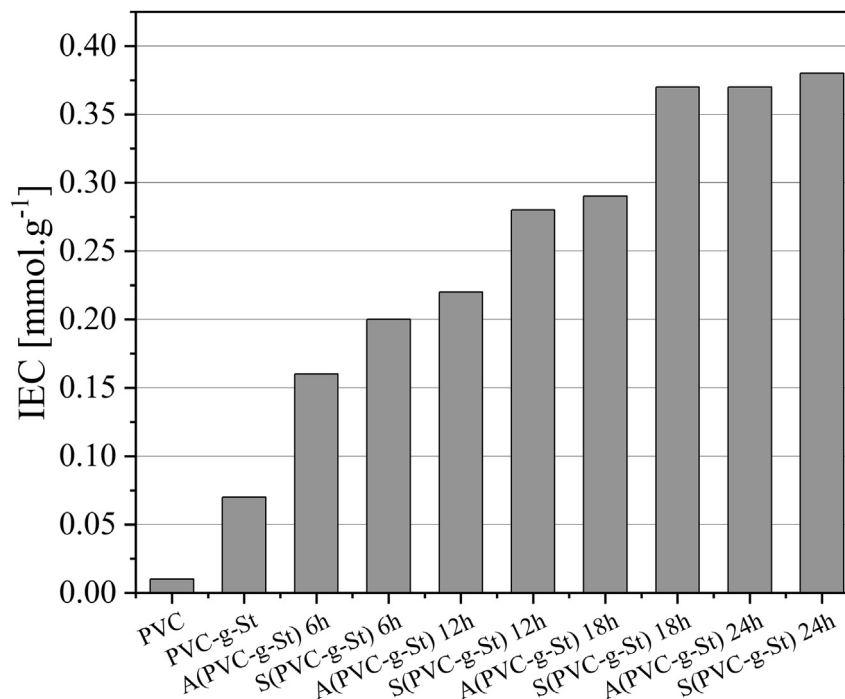


Fig. 6 – IEC data for the pure PVC, PVC-g-St, A (PVC-g-St), and S(PVC-g-St) membranes for different times of the amination and sulfonation processes.

grafted, modified by amination and then additionally by sulfonation are presented in Fig. 2. The spectra of grafted films are different from that of the blank PVC film (Fig. 2a). The spectrum of PVC grafted with styrene displays fingerprints of PS confirming that an ultra-thin PS film was successfully deposited onto the surface of the PVC film (Fig. 2b). The broad band at the wavenumber range from 3200 cm⁻¹ to 3400 cm⁻¹

indicates OH and NH groups resulting from the O₂ plasma treatment and the amination process (Fig. 2b and c) [28].

The additional band at 3063 cm⁻¹ observed for the PS-grafted film is assigned to the C–H vibrations of its aromatic ring [29], where the peaks at 1527 and 1629 cm⁻¹ refer to the C=C bonds of the aromatic ring (Fig. 2b and c). The peak at 1720 cm⁻¹ indicates the presence of C=O groups which could

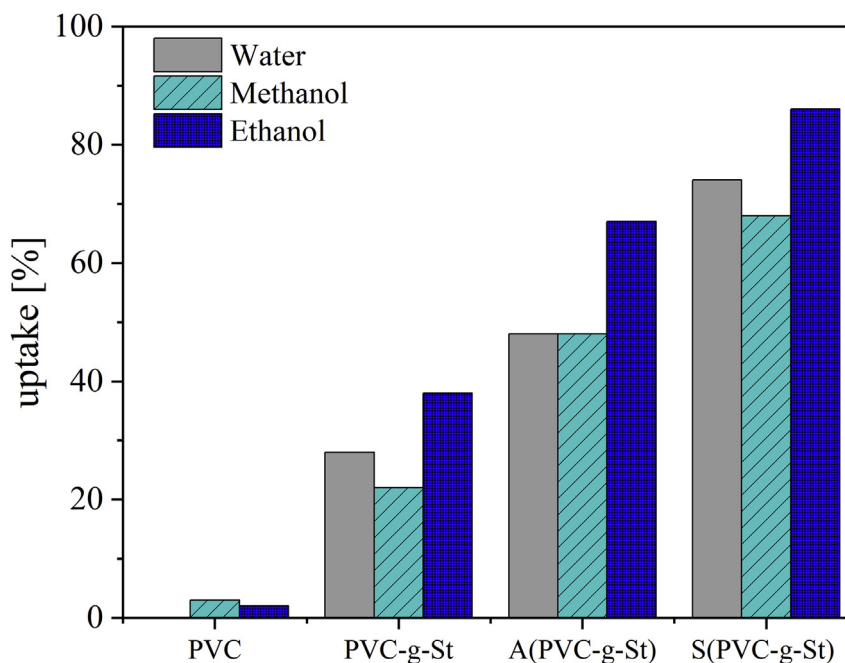


Fig. 7 – Water, methanol and ethanol uptake of PVC, PVC-g-St, A (PVC-g-St) and S(PVC-g-St).

formed by the O₂ plasma treatment as discussed above (Fig. 2b and c) [30].

The IR spectra supported the change in the chemical composition of the PVC membrane modified by exposure to the O₂ plasma and confirm that a thin layer of PS was grafted. Additionally, the broad band from 2500 cm⁻¹ to 3700 cm⁻¹ in the spectra of modified PVC indicate the existence of considerable quantities of polar OH after exposure to the oxygen plasma. This broad band becomes more pronounced after amination as expressed by the band at $\nu_{N-H} \approx 3300$ cm⁻¹ (Fig. 2c). Moreover, a band at 1330 cm⁻¹ may be associated to C–N–C groups [31] and the band observed at 686 cm⁻¹ corresponds to the SO₃H groups (Fig. 2d) [32]. The four bands found in the wave number range from 2000 to 1600 cm⁻¹ are characteristic for the mono-substitution of aromatic rings as occurring in PS (the inset of Fig. 2).

3.3. Topography of the membranes

Fig. 3 displays the surface morphology of the pure PVC film compared to that of (PVC-g-St), aminated A (PVC-g-St) and sulfonated S(PVC-g-St). For the PVC and the membranes grafted with PS no phase separation is observed.

The changes in morphology are due to the modification process of the PVC membrane surface by subsequent amination followed by the sulfonation process. Obviously, the closed structure of PVC changes to an open porous morphology due to the grafting. The smooth surface morphology of the PVC-g-St membrane after amination and sulfonation (Fig. 3) is due to the good compatibility between the two polymer components (i.e. PVC and PS). Moreover, the inter hydrogen bonds between O···H on PVC surface and N···H in polyethylenimine play an important role for such smooth surfaces feature.

3.4. Thermal stability of the membranes (thermogravimetric analysis (TGA))

The weight loss in % as a function of temperature is presented for the different membranes in Fig. 4. It is obvious that the weight loss for all treated membranes is lower than that of blank PVC indicating that a membrane with high thermal stability was obtained. For all membranes, a small transition around 100 °C is observed, which corresponds to the loss of absorbed water. The weight loss around 250 °C indicates the thermal degradation of the sulfonic groups and the weight loss around 450 °C is assigned to the degradation of the main chains. The remaining mass at high temperatures corresponds to the carbonation of hydrocarbons and to the extra carbons which were inserted from the imine material in the modification process.

The influence of grafting and modification on the thermal decomposition rate of PVC membrane was investigated by the Broido model [33,34]. This model is a useful tool for calculating the activation energy (E_a) for thermal degradation based on the residual mass following Eq. (7):

$$\ln [-\ln (1 - \alpha_t)] = -E_a/RT + \text{const.} \quad (7)$$

where T is temperature, E_a is the activation energy, R is the general gas constant and α_t is the fractional weight loss

corresponding to a stage of the decomposition. For calculating α_t Eq. (8) was used.

$$\alpha_t = (W_0 - W_t) / (W_0 - W_\infty) \quad (8)$$

where W_0 is the initial sample weight, W_t is the sample weight at temperature of stage (t) and W_∞ is the weight at the end of the reaction. By plotting $\ln [-\ln (1 - \alpha_t)]$ versus $(1000/T)$ a straight line was obtained (see Fig. 5) and E_a is estimated. The calculated values were presented in the inset of Fig. 5.

It is obvious that the highest activation energy was measured for the sulfonated sample while that for the aminated one was lower than that for pure PVC and PVC grafted with PS. This enhancement in activation energy for the sulfonated membrane is an indication of a higher thermal stability of the layer grafted to the surface of PVC membranes.

3.5. Ion exchange capacity

Fig. 6 depicts the IEC data for the different modified PVC membranes immersed in the NaCl solution. The IEC values of blank PVC are low as expected because of the low level of ionized functional groups present in the membrane. However, the IEC values were increased by the amination process and the sulfonated samples gave the best results with an optimum time of 18 h for sulfonation. Nevertheless, in practical cases, the proton conductivity of a PEM depends on various parameters, such as water uptake, ion exchange capacity (IEC), swelling ratio, proton conductivity, and fuel permeability all related to the microstructure of the membrane. As well known, the presence of both hydrophobic (mainly carbon-chains) and hydrophilic functionalities (-SO₃H) on the same polymeric chain leads to the formation of nano-domains, which are responsible for the proton conductivity of the hydrated PEM. The IEC values increase with increasing time of amination followed by sulfonation and are arranged as 6 < 12 < 18 = 24 h.

3.6. Water, methanol and ethanol uptake

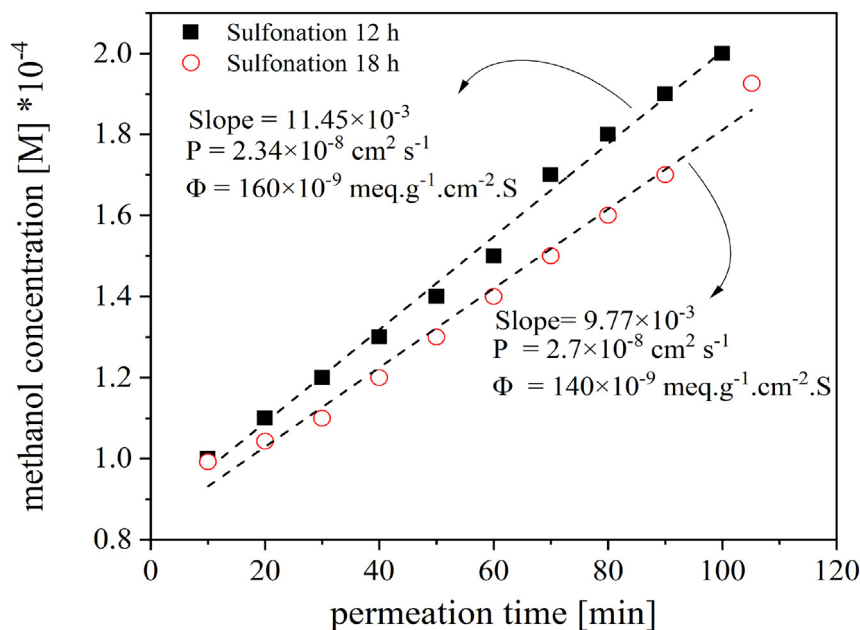
The wettability of PEMs is needed for proton transfer [35]. The uptake measurements were carried out at room temperature in deionized water, methanol and ethanol. The uptake in % of the modified PVC membranes is compared to that of pure PVC (see Fig. 7). It is worth noting that the PVC film modified by O₂ plasma and then grafted with PS strongly affects the uptake of the membranes due to the introduced functional groups as discussed above (Fig. 1). The resulting uptake refers to the fact that the aminated and sulfonated samples act as electrolyte membranes. The water uptake increased by the deposition of PS onto PVC membrane and was further enhanced by amination. This increase becomes even more pronounced after the sulfonation process. Additionally, the increase of the uptake in case of ethanol is higher than that of methanol and water. This result means that such membranes could be used as an electrolyte membrane in direct ethanol fuel cells.

According to Table 2, it is concluded that the work presented here results in materials that can have strong advantages for fuel cells applications compared to other

Table 2 – Comparison between present work and previous research.

Name of membrane	CA []	Water uptake%	IEC (meq g ⁻¹)	Ref.
PP-PEM ₁ = ST-TMSA AT 20W	–	82	1.12	[35]
PPPEM ₂ = ST-TMSA AT 50W	–	73	0.86	
PP-PEM = ST-TMSA AT 80W	–	52	0.53	
D (PS-PAA-DVB) D0 with Pt	–	15.0673	0.1242	[36]
D (PS-PAA-DVB) D0 without Pt	–	15.2210	0.1436	
D (PS-PAA-DVB) D55 with Pt	–	64.3408	0.4150	
D (PS-PAA-DVB) D55 without Pt	–	64.9186	0.4231	
D (PS-PAA-DVB) D110 with Pt	–	104.4259	0.5434	
D (PS-PAA-DVB) D110 without Pt	–	105.1197	0.5524	
T (PS-PAA-TMPTMA) T0 with Pt	–	14.2666	0.0654	
T (PS-PAA-TMPTMA) T0 without Pt	–	14.9514	0.0783	
T (PS-PAA-TMPTMA) T55 with Pt	–	81.4613	0.6219	
T (PS-PAA-TMPTMA) T55 without Pt	–	83.5415	0.6525	
T (PS-PAA-TMPTMA) T110 with Pt	–	137.0323	0.8844	
T (PS-PAA-TMPTMA) T110 without Pt	–	139.8289	0.9030	
SPAEK/PSSAMA-5	102	17.12 ± 0.87	1.924	[37]
SPAEK/PSSAMA-10	94	20.56 ± 0.65	2.054	
SPAEK/PSSAMA-15	84	23.16 ± 0.97	2.365	
SPAEK/PSSAMA-20	81	29.45 ± 0.72	2.569	
SPAEK/PSSAMA-25	75	24.12 ± 0.95	1.630	
SSEBS	–	164 ± 7	1.825	[38]
SSEBS-SiO ₂ 7.5%	–	185 ± 8	1.622	
SSEBS-S-SiO ₂ 2.5%	–	175 ± 10	1.990	
SSEBS-S-SiO ₂ 5%	–	187 ± 9	2.55	
SSEBS-S-SiO ₂ 7.5%	–	210 ± 8	3.015	
SSEBS-S-SiO ₂ 10%	–	200 ± 11	2.821	
PVC-g-St	40	30	0.075	current work
A (PVC-g-St)	38	50	0.294	
S(PVC-g-St)	33	77	0.381	

where St = styrene, TMSA = Trifluoromethane sulfonic acid, PEM₁, PEM₂ and PEM₃ refers to 20, 50 and 80 w, respectively [35]. SPAEK = sulfonated poly (arylene ether ketone), PSSAMA = polystyrene sulfonic acid-co-maleic acid, 5, 10, 15, 20,25 mass% of crosslinker [37]. SSEBS = sulfonated polystyrene ethylene butylene polystyrene, SiO₂ (2.5, 5, 7.5, 10 wt%) [38], D(PS-PAA- DVB) & T(PS-PAA- TMPTMA) (0, 55, 110) indicates to DMSO in % [36].

**Fig. 8 – Variation of the methanol concentration vs. permeation time for the sulfonated membranes for 12 and 18h.**

approaches. Here, cheap basic materials, continuous atmospheric pressure treatment, a solvent free grafting process and low energy consumption (only 3 W) during plasma processing were used. Compared to the low input promising results were obtained such as high IEC, solvent uptake, and hydrophilicity.

3.7. Permeability of methanol and membrane efficiency

Electrolyte membranes with a low permeability of the electrolyte and a high conductivity are required for application in fuel cells. The methanol permeability of the sulfonated membranes for 12 and 18 h was determined in a diffusion cell in which the membrane was fixed between two tanks filled with 2 M aqueous methanol and de-ionized water. Fig. 8 reveals the change of the methanol concentration versus the permeation time. A linear dependence was obtained. The permeability for the sample sulfonated for 18 h and 12 h are 2.7×10^{-8} and $2.34 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively compared to $1.77 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [39] for Nafion 117® indicate that the sulfonated samples were effective for decreasing the methanol crossover by ca. two orders of magnitude in comparison to Nafion117® under the same conditions and in the same cell [4].

As mentioned in the experimental part for calculation of membrane efficiencies, the ratio of IEC to the methanol permeability was used as an indicator for the performance of membranes for DMFC following eq. (6). The efficiency factors for the sulfonated membranes for 12 and 18 h were estimated (Fig. 8). It was found that the maximum efficiency was achieved for the sample which was sulfonated for 12 h indicating that this material is attractive for application in DMFCs.

4. Conclusion

PVC membranes were prepared and grafted with an ultra-thin polystyrene film after exposure to a dielectric barrier discharge at atmospheric pressure in O₂ gas. A hydrophilic surface of modified PVC was obtained approved by water CA and FTIR measurements. The properties of the membrane have been improved, such as thermal stability as evidenced by TGA measurements. The solvent uptake of membranes increases step by step with grafting of PS, amination and sulfonation, highest in the case of ethanol. Moreover, the efficiency factors for the sulfonated membranes were calculated and the maximum value was achieved with 12 h sulfonation ($160 \times 10^{-9} \text{ meq g}^{-1} \text{ cm}^{-2} \text{ S}$). This makes the PVC-g-St membranes as a promising and attractive new material for polyelectrolyte membranes maybe for applications in fuel cells.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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