

# Polymer Electrolyte Membranes Based on Blends of Sulfonated Polysulfone and PEO-Grafted Polyethersulfone for Low Temperature Water Electrolysis

Valadoula Deimede,<sup>1</sup> Diamadoula Labou,<sup>2</sup> Stylianos G. Neophytides<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Patras, 26500 Patras, Greece

<sup>2</sup>Foundation of Research and Technology-Hellas, Institute of Chemical Engineering Sciences (FORTH/ICE-HT), 26504 Patras, Greece

Correspondence to: V. Deimede (E-mail: deimede@upatras.gr)

**ABSTRACT:** Polymer electrolyte membranes based on blends consisting of polyethylene oxide (PEO) grafted polyether sulfone (PES-g-PEO) and sulfonated polysulfone (SPSF(Na)) are prepared and their electrochemical and mechanical properties are investigated with respect to water electrolysis operation. The prepared blends are amorphous; they exhibit high glass transition temperatures and high thermal stability, thus ensuring the dimensional stability under electrolysis cell operation. Because of the presence of the water soluble constituent PES-g-PEO, the prepared blend membranes show very high water uptakes, reaching up to 370 wt %. Membrane electrode assemblies are fabricated and evaluated in single cells demonstrating that proton conductivity depends on the PEO-g-PES content as well as the PEO molecular weight. Namely, the increased concentration of PES-g-PEO leads to increased number of charge carriers, thus result in enhanced ionic conductivity. The use of longer PEO units (MW 5000), due to their improved chain mobility, facilitates the fast proton conduction as well. The maximum proton conductivity value is achieved ( $1.4 \times 10^{-2}$  S cm<sup>-1</sup>, 80°C) for the blend with the higher PEO-g-PES content (20 wt %) and the higher PEO molecular weight (5000). Under electrolysis cell operation, the above-mentioned membrane with the lower ohmic resistance shows the best performance, although it is still poor mainly due to the use of Pt as anode. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39922.

**KEYWORDS:** blends; polymer electrolytes; water electrolysis

Received 6 June 2013; accepted 2 September 2013

DOI: 10.1002/app.39922

## INTRODUCTION

Water electrolysis is a potential method of storing energy from renewable power sources into hydrogen.<sup>1</sup> The combination of water electrolyzers and fuel cells could provide an ideal green and efficient mode for future energy utilization systems.<sup>2</sup> In recent years, water electrolyzers using the proton exchange membranes (PEM) have been of increasing interest.<sup>3–7</sup> Water electrolysis based upon PEM was developed for submarine<sup>8</sup> and space programs<sup>9</sup> where the first PEM water electrolyzers (PEMWE) were applied by General Electric as early as the 1960s. The advantages of PEMWE over alkaline electrolyzers include lower parasitic energy loss and higher ecological purity hydrogen output.<sup>10</sup> Although Nafion membranes are the benchmark electrolytes for PEMWE, they are scarcely applied in large scale hydrogen production<sup>11</sup> due to their high cost and conductivity loss at temperatures higher than 80°C.<sup>12–14</sup> Many noteworthy steps<sup>15–17</sup> have been made over the past decade for the development of a broad range of cost-effective polymers such as sulfonated aromatic polymers, for example,

polyether ether ketones, polysulfones (PSF), polyimides, polybenzimidazoles, and polyoxadiazoles as alternatives to conventional perfluorosulfonic acid types. However, to the best of our knowledge, only a few reports in the open literature address the development of new polymer electrolytes for use in low PEM water electrolysis.<sup>18,19</sup> It should be kept in mind that polymer electrolytes should meet characteristics such as high mechanical strength, high water absorption, good chemical and electrochemical stability, high conductivity, and good thermal stability, as all are required for long-term operation in PEM electrolyzers.<sup>20</sup> Sulfonated polysulfone (SPSF) has been used as polymer electrolyte in PEMFCs<sup>21</sup> due to its exceptional mechanical properties as well as its excellent chemical and electrochemical stability related to the presence of the rigid backbone. However, as high sulfonation degrees are required for high proton conductivity, the preparation of highly SPSFs resulted in membranes with poor mechanical integrity due to their extensive swelling (or solubility) in water. To solve this problem, different approaches have been proposed, that is,

blending of SPSF with other polymers,<sup>22,23</sup> preparation of composite membranes based on SPSF/TiO<sub>2</sub><sup>24</sup> or SPSF/SiO<sub>2</sub><sup>25</sup> where inorganic fillers were introduced to improve the mechanical stability as well as to preserve a suitable hydration level of the membrane in the fuel cell environment. Our approach for the preparation of mechanical robust polymer electrolytes with high ionic conductivity involves blending of polysulfones with moderate sulfonation degrees and water soluble aromatic polyethersulfones containing poly(ethylene oxide) (PEO) chains (PES-g-PEO). The mechanical strength of the blend membranes is provided by the SPSF of moderate sulfonation degrees, while the high water uptake and consequently the high proton conductivity is facilitated by the use of the PEO-based component. The grafting of hydrophilic PEO groups onto an aromatic polyether backbone is expected to facilitate water absorption as PEO is a water soluble polymer. Conversely, PEO exhibits poor mechanical strength as well as low ambient conductivity which is mainly coupled with its semi-crystalline character.<sup>26,27</sup> A well-known synthetic strategy to suppress crystallinity of PEO-based systems and thus improve ionic conductivity is blending<sup>28,29</sup> in which PEO acts as the conductive phase and the other component serves as the mechanical support. SPSF in sodium salt form (SPSF(Na)) as well as polyethersulfones containing PEO side groups of different side chain length have been prepared and blended for use as electrolytes in PEMFCs by our group in previous works.<sup>30,31</sup>

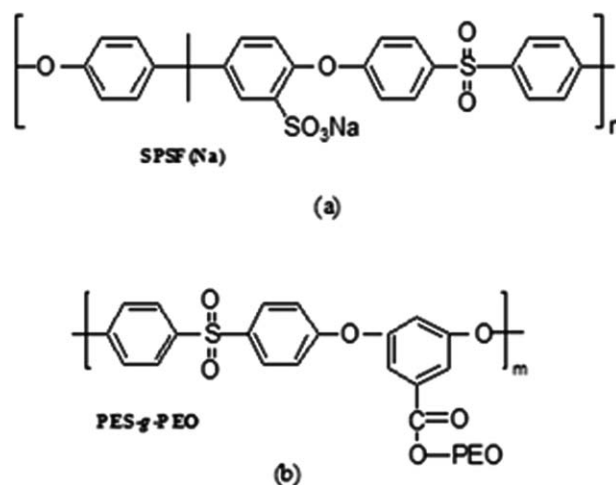
In this work, polymer electrolyte membranes were prepared by blending SPSF with polyethersulfone containing PEO side chains of different length and evaluated their thermomechanical stability, crystallinity as well as their electrochemical performance. The aforementioned blends combine the high glass transition temperatures with the thermal stability and amorphicity along with the high water absorption ability. Membrane-electrode-assemblies (MEAs) have been fabricated and tested in water electrolysis unit cells. More specifically, the influence of the molecular weight and weight fraction of PES-g-PEO on the conductivity of the blend membranes and consequently to the electrolytic performance has been studied. High ionic conductivity values in the range of  $10^{-2}$  S cm<sup>-1</sup> at 80°C were obtained.

## EXPERIMENTAL

### Polymer Blend Preparation

SPSF in the sodium salt form (SPSF(Na)) with a degree of sulfonation 45% was prepared according to a previously described procedure.<sup>30</sup> The sulfonation degree was determined by using <sup>1</sup>H-NMR spectroscopy. PES-g-PEO<sub>x</sub> polymers, where  $x = 2000$  and  $5000$  is the molecular weight ( $M_n$ ) of PEO, were synthesized according to the method described elsewhere.<sup>31</sup>

Blends were prepared by dissolving SPSF(Na)<sub>45</sub> and PES-g-PEO<sub>x</sub> in DMF (5%, w/v) at different weight ratios (90/10, 80/20, and 70/30). The obtained solution was poured onto a glass plate at 85°C for 20 h. Homogeneous, transparent membranes with good mechanical properties and thickness equal

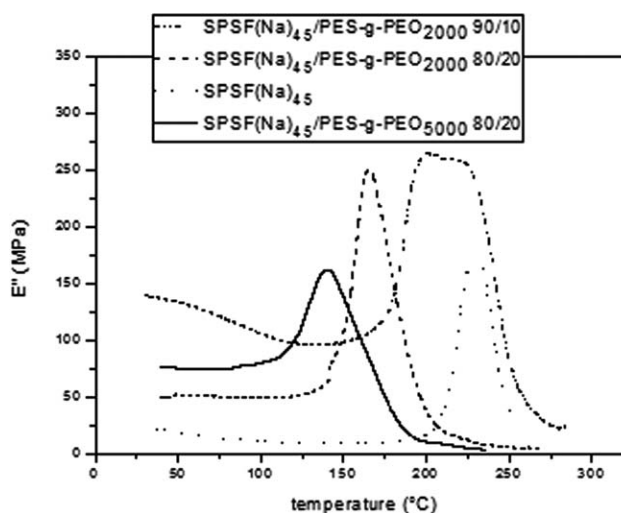


**Scheme 1.** Chemical structures of SPSF in sodium salt form (SPSF(Na)) (a) and poly(ethylene oxide)-graft-polyethersulfone homopolymer (PES-g-PEO) (b).<sup>31</sup>

to 80  $\mu$ m were obtained. To remove any excess of the solvent, the membranes were dried under vacuum at 90°C for 3 days. The chemical structures of the prepared blends are given in Scheme 1.

### Electrodes Preparation and MEA Fabrication

Electrodes were prepared by mixing the catalyst powder (28 wt % Pt/C, E-Tek) with PES-g-PEO<sub>x</sub> binder in a ratio of 1:1 in isopropanol and the prepared ink was applied on a gas diffusion layer (GDL). GDL was prepared using carbon cloth (E-Tek, De Nora Group N. A.), on which was sprayed a slurry made of carbon powder (Shawinigan Acetylene Black) and PTFE suspension (Aldrich), followed by sintering at 340°C under static air. The Pt loading varied between 1 and 2 mg cm<sup>-2</sup>. MEAs were fabricated by placing the electrodes on both sides of the water doped membrane and assembled in the single cell. The assembling force used was 3 N m.



**Figure 1.** Temperature dependence of the loss ( $E'$ ) moduli of blends SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub>, SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> and pure SPSF.

### Experimental Techniques

Dynamic mechanical analysis (DMA) measurements were conducted using a solid-analyser RSA II, Rheometrics Scientific, at 10 Hz.

Thermogravimetric analysis (TGA) was performed on a TA Instruments thermogravimetric analyzer model Q50. The samples were heated at  $10^{\circ}\text{C min}^{-1}$  to  $800^{\circ}\text{C}$  under an argon atmosphere.

The crystallinity grade of the prepared membranes was investigated through X-ray diffraction technique using a Bruker D8 Advance diffractometer. The diffraction data were collected at a constant rate of  $0.02^{\circ}\text{ min}^{-1}$  in the  $2\theta$  range from  $10^{\circ}$  to  $40^{\circ}$  with CuK $\alpha$  radiation.

The surface and the cross-sectional morphology of the membranes were studied by Scanning electron microscopy (SEM) using a LEO Supra 35VP microscope. The specimens for the cross-section study were prepared by fracturing the membranes in liquid nitrogen.

The water uptake behavior of the prepared blend membranes was studied using the following procedure. The membranes were dried under vacuum at  $90^{\circ}\text{C}$  for 3 days, weighted, and then immersed in distilled water for 24 h at determined temperatures. Surface attached water was quickly removed with tissue paper and the weight of the wet membrane determined. The water uptake of the membranes was determined by the following relation:

$$\text{Water uptake (\%)} = \frac{W - W_0}{W_0} \times 100,$$

where  $W$  and  $W_0$  are the weights of the wet and dried blend membrane, respectively.

The electrochemical characterization of the membrane electrode assembly (MEA) was evaluated in a self-constructed cell with an effective area of  $4.8\text{ cm}^2$ . Humidification of the membrane was attained by a pair of independently heated humidifiers positioned on both sides of the cell. The intense hydrated conditions, leading to liquid water existing in the cell, were achieved by setting the humidifiers up to  $100^{\circ}\text{C}$  while cell's temperature was at least  $20^{\circ}\text{C}$  lower. The ionic conductivity was determined by electrochemical impedance spectroscopy at open circuit under helium hydrated atmosphere. The electrochemical study was performed via polarization measurements using a computer controlled Potentiostat/Galvanostat (EG&G Princeton Applied Research 263A) while a frequency response analyzer (EG&G 1025) was used for the estimation of the electrolyte's resistance of the system via ac impedance technique. The impedance data were collected in the frequency range of 10 MHz to 10 mHz with a voltage amplitude of 10 mV.

The specific ionic conductivity value  $\sigma$  was calculated through the following expression

$$\sigma = \frac{l}{RS},$$

where  $l$  is the membrane thickness equal to  $80\text{ }\mu\text{m}$ ,  $R$  is the ionic resistance measured by impedance spectroscopy, and  $S$  is the effective geometrical area equal to  $4.8\text{ cm}^2$ .

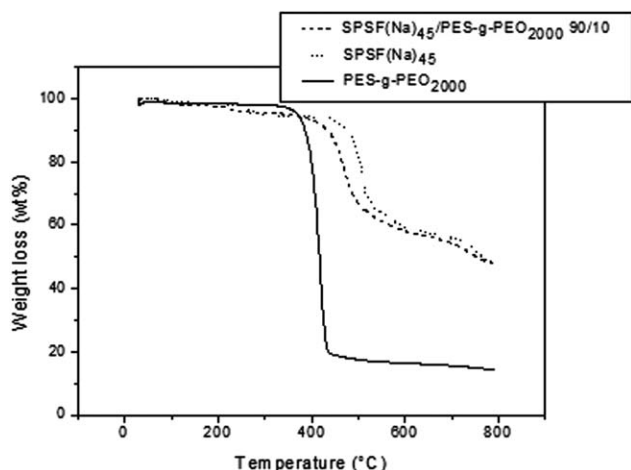
### RESULTS AND DISCUSSION

Many efforts have been devoted to prepare solid polymer electrolytes with increased ionic conductivity and dimensional stability as well as suppressed crystallinity at ambient conditions. Water absorption and retention are key properties of a polymer electrolyte used at low temperatures as they greatly affect conductivity and thus cell performance. Therefore, polymer blend membranes comprised of sulfonated polysulfone<sup>30</sup> and water soluble polyethersulfones bearing PEO side chains of different length<sup>31</sup> (PEO content varies between 89.4 and 95.5 wt %) have been prepared targeting toward the water uptake improvement and thus to conductivity and cell performance enhancement while maintaining their excellent mechanical strength. Additionally, blending is an effective method to suppress the crystallinity of a PEO-based blend component, thus resulting in increased ionic conductivity.

DMA experiments were performed to investigate the miscibility behavior of these blends based on the single glass transition temperature ( $T_g$ ) criterion. The temperature dependence of the loss moduli ( $E''$ ) curves of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> blends with  $x = 2000$  and  $5000$  (PEO molecular weight) as well as pure SPSF are shown in Figure 1. As it is observed, for SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> blends with  $x = 2000$ , the corresponding blend with composition 90/10 shows two overlapping peaks at  $200$  and  $221^{\circ}\text{C}$ , implying partial miscibility of the system. It should be noted that pure SPSF has one sharp peak at  $230^{\circ}\text{C}$  corresponding to its glass transition temperature. In particular, the higher temperature peak is associated with the  $T_g$  of a SPSF rich phase, whereas the lower temperature peak can be assigned to the  $T_g$  of a phase with higher PES-g-PEO content.

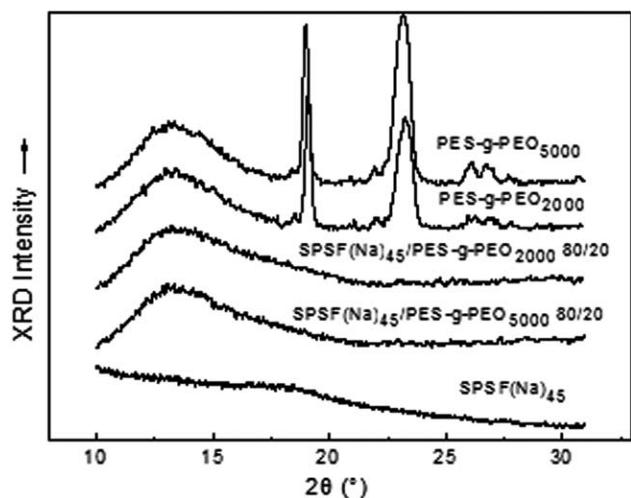
On the contrary, when the PEO-g-PES content is increased to 20 wt %, the corresponding blend shows a single  $T_g$  at  $165^{\circ}\text{C}$ , between the  $T_g$ s of the pure polymers ( $T_g$  of pure PES-g-PEO cannot be measured by DMA technique since it does not form any free-standing film), indicating miscibility between blend components. The same behavior, meaning the presence of a single  $T_g$ , which is shifted to lower temperatures, is observed for blend with even higher PES-g-PEO content (30 wt %, not shown here). It is well known that interactions between acid and base polymers promote miscibility.<sup>30,32,33</sup> Namely, the acidic groups (sulfonate) of SPSF could probably interact with the basic PEO groups of polyether sulfone, hence promoting miscibility. However, the miscibility is favored only for PES-g-PEO contents higher than 20 wt %, demonstrating the effect of the concentration of the basic (PEO) groups. The influence of the molecular weight of PEO on miscibility has also been studied. Comparison between blends with the same composition 80/20, the blend with the higher PEO molecular weight (5000) shows one sharp peak at  $140^{\circ}\text{C}$ , implying miscibility between blend components. As already mentioned, the  $T_g$  of the blend with the lower PEO molecular weight is higher ( $165^{\circ}\text{C}$ ) compared to that of the former one suggesting that as PEO molecular weight of the PES-g-PEO component is increased, the glass transition temperature of the blend is decreased.

The thermal stability of the synthesized blends was investigated by TGA at a heating rate of  $10^{\circ}\text{C min}^{-1}$  under an argon



**Figure 2.** Comparative TGA curves of blend SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> with composition 90/10, pure SPSF, and pure PES-g-PEO<sub>2000</sub> homopolymer.

atmosphere. TGA curves of blend SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 2000$ ) with composition 90/10 as well as pure polymers are given in Figure 2. PES-g-PEO<sub>x</sub> ( $x = 2000$ ) homopolymer has one weight loss step with an onset at around 340°C, corresponding to the loss of PEO groups and degradation of the polymer backbone<sup>34,35</sup> while SPSF and the former blend show three weight loss stages. Regarding SPSF, the first low temperature weight loss can be attributed to desorption of water bonded to the sulfonate groups while the second one at around 240°C is due to the partial desulfonation as proved by thermogravimetric studies connected to an infrared spectrometer or mass spectrometry.<sup>36</sup> The third one, observed at 460°C, could mark the beginning of decomposition of the main chain of the polymer. Similar TGA data for SPSF were also reported by other groups.<sup>21,37</sup> The blend membrane exhibits weight loss stages like SPSF but its final decomposition could be observed at 420°C. Although a reduction in the decomposition temperature of the



**Figure 3.** XRD patterns of the neat PES-g-PEO<sub>x</sub> ( $x = 2000$  and 5000), SPSF(Na)<sub>45</sub> polymers as well as SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 2000$  and 5000) blend membranes with 80/20 composition.

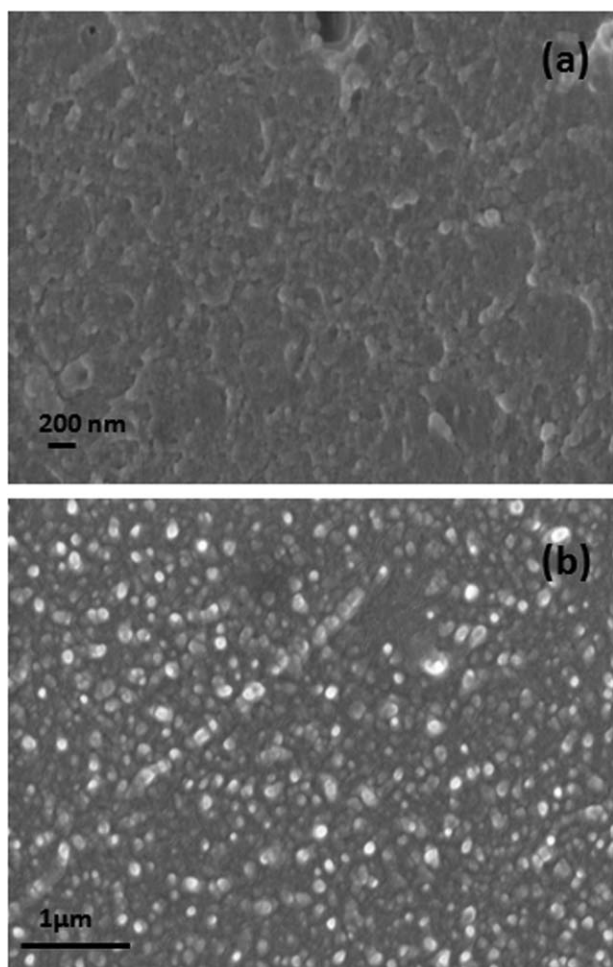
**Table I.** Water Uptake Properties of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 2000$  and 5000) and pure SPSF(Na)<sub>45</sub> Membranes at Different Temperatures

Blend membrane	Composition	Water uptake (%)	
		20°C	85°C
SPSF(Na) <sub>45</sub>	-	3	19
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>2000</sub>	70/30	22	370
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>2000</sub>	80/20	15	120
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>2000</sub>	90/10	6	20
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>5000</sub>	70/30	15	80
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>5000</sub>	80/20	13	75
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>5000</sub>	90/10	11	30

blend is observed, it exhibits the required stability to enable steady operation of the water electrolysis cell.

XRD investigation was used to deduce information about the microstructure of the SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> blend membranes as one of the basic requirements for high conductivity in solid polymer electrolytes is the lack of crystallinity.<sup>26,38</sup> In the case of pristine PES-g-PEO<sub>5000</sub> and PES-g-PEO<sub>2000</sub> homopolymers, the presence of the characteristic diffraction peaks at 19° and 23.3°, respectively, shown in Figure 3, confirms the semicrystalline nature of PEO.<sup>39</sup> In the case of blends, it is evident that the crystallinity suppresses as the PEO molecular weight decreases. With the addition of 80 wt % SPSF(Na)<sub>45</sub>, the amorphous state becomes dominant, independently of PEO molecular weight, due to the disruption of the PEO chains ordering, thus resulting in the loss of its crystallinity. It is well established that conductivity occurs in the amorphous state, above the glass transition temperature ( $T_g$ ), facilitated by the polymer chain segmental motions.<sup>40</sup>

As water is needed as the mobile phase to facilitate proton conductivity, the water uptake ability of these blends was also evaluated. In all cases, the doping level was increased with increasing temperature (from 20 to 85°C) as well as with increasing PES-g-PEO content as PEO shows high hydrophilicity (Table I). In detail, in the case of blend SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 2000$ ) with composition 70/30 the water uptake at 85°C reached values up to 370 wt % while the corresponding blends with 80/20 and 90/10 compositions had 120 and 20 wt %, respectively, denoting the important role of PES-g-PEO content on the water uptake ability. It is worth noticed that in the case of blends SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 5000$ ), much lower doping levels have been obtained (up to 80 wt %, Table I) compared to the corresponding ones of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 2000$ ) blends. When the doping temperature was further increased (100°C), the doping level was also increased. In detail, both SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> and SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> blends with 90/10 and 80/20 compositions, respectively, have showed much improved water uptake up to 120 wt %. Moreover, while in boiling water conditions the maximum water uptake for all blends was reached very fast (within 10–15 min), at 85°C it was achieved within 1–2 h. However, it should be taken into consideration that highly hydrated membranes suffer from low mechanical strength due to excessive swelling. Thus,

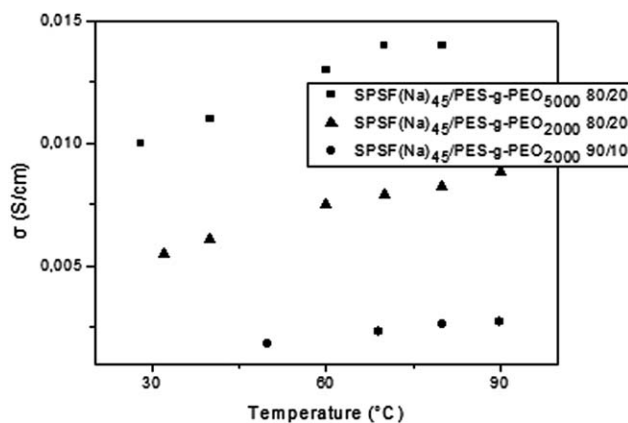


**Figure 4.** Cross-sectional SEM images of blend SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> with composition 90/10 before (a) and after water treatment (b).

careful control of the doping level is required to avoid any mechanical stability problem, arising from the high doping level.

It is well established the importance of morphology on the proton transport, therefore cryofractured blends have been studied by SEM. Cross-sectional SEM images of blend SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x=2000$ ) with 90/10 composition before and after water treatment at 85°C are shown in Figure 4. As it is observed, the blend before water treatment is partially nanophase separated, whose spherical hydrophilic ion-conducting clusters formed by sulfonate and PEO groups are embedded in the matrix [Figure 4(a)]. These observations correlate well with the DMA results where this blend exhibited two  $T_g$ s, implying partial miscibility. After water treatment, the brighter regions corresponding to the spherical clusters are more pronounced and uniformly distributed across membrane. Their diameter size ranges between 90 and 140 nm [Figure 4(b)].

As blends fulfill the requirements of mechanical stability combined with high doping levels, the last prerequisite of high proton conductivity must be satisfied. Figure 5 presents the temperature dependence of the ionic conductivity

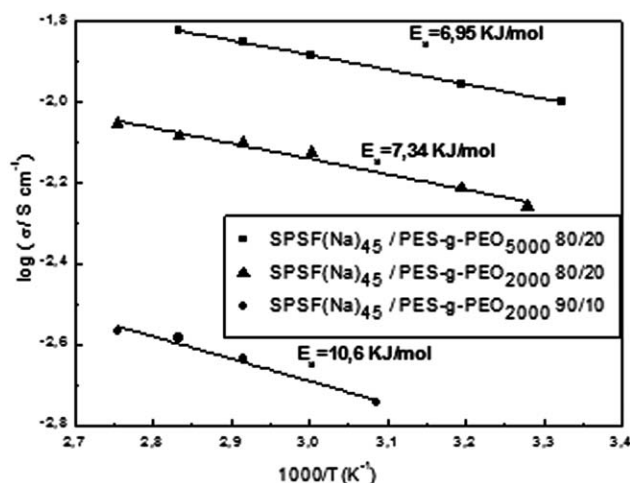


**Figure 5.** Temperature dependence of the proton conductivity of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> and SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> polymer electrolyte membranes.

ity for SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> and SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> blends having the same initial water uptake (120 wt %). The proton conductivity is significantly improved by increasing PEO molecular weight as well as PES-g-PEO content implying that not only water but also PEO due to its basic nature promotes the proton conduction, as already reported by other groups.<sup>41</sup> In particular, the maximum ionic conductivity of  $1.4 \times 10^{-2} \text{ S cm}^{-1}$  obtained at 80°C corresponds to the membrane containing PEO with 5000 molecular weight while the blend with PEO molecular weight 2000 and the same composition (80/20) reached its maximum conductivity value of  $8.8 \times 10^{-3} \text{ S cm}^{-1}$  at 90°C (Table II). The observed high ionic conductivities are mainly attributed to the high water uptake ability of PES-g-PEO component. Namely, as blend miscibility also greatly affects conductivity,<sup>42</sup> in the aforementioned miscible blends, the polymer matrix behaves as a continuous ionic pathway consisting of sulfonate groups and basic (ether-oxygen atoms) PEO groups. As PEO groups act as Lewis bases, the proton transport is promoted via hydrogen bonding between oxygen of PEO groups and water molecules. Even though the two blends contain the same PES-g-PEO weight fraction, the one with the longer PEO chains (PEO<sub>5000</sub>) showed enhanced conductivity. Having in mind that both blends are amorphous, the blend with the longer PEO chains shows improved segmental mobility due to its lower

**Table II.** Maximum Proton Conductivity Values and Activation Energy Values for SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x=2000$  and 5000) Membranes

Blend membrane	Composition	$\sigma_{\max}$ (S cm <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>5000</sub>	80/20	$1.4 \times 10^{-2}$	7.34
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>2000</sub>	80/20	$8.8 \times 10^{-3}$	6.95
SPSF(Na) <sub>45</sub> /PES-g-PEO <sub>2000</sub>	90/10	$2.7 \times 10^{-3}$	10.6



**Figure 6.** Arrhenius plots of the different blends SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> and SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub>.

$T_g$  value (which is further reduced by water plasticization), thus enabling the faster proton conduction. The previous trends evidence the influence of the water uptake ability, the phase behavior as well as the chain mobility on the proton transport. When the PES-g-PEO content is reduced from 20 to 10 wt % for SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> blends, a pronounced decrease of the conductivity to  $2.7 \times 10^{-3}$  S cm<sup>-1</sup> is observed, although an increased number of ionic sites (sulfonated groups) exist, indicating that the concentration of basic PEO moieties greatly affects the proton transport. A possible explanation of this behavior is the following: the polymer electrolyte membrane is hydrated and swollen by water molecules, whereas hydrated protons can be transported through the membrane, hence leading to ionic conductivity enhancement. At low concentrations of PEO units, the limited number of proton carriers (PEO groups) is not capable to form a continuous proton pathway together with the sulfonate groups, thus resulting in reduced conductivity. On the contrary, by increasing the PEO concentration, an increased number of proton carriers exists, leading to the formation of a continuous proton pathway thus resulting in faster ion conduction. This speculation is further supported by the SEM data, as the decreased conductivity of the blend with composition 90/10 could be attributed to the formation of a non-well-connected proton pathway [Figure 4(b)] related to its partially phase separated behavior.

The maximum conductivity value obtained at 80°C is comparable with the corresponding one of SPSF-co-polyphenylene sulfide sulfone (SPSF-co-PPSS)/TPA composite membranes used for water electrolysis.<sup>18</sup>

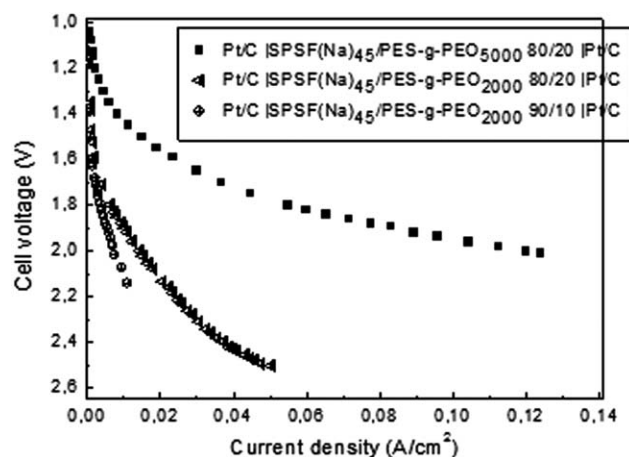
Figure 6 shows the Arrhenius plots of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> and SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> blends where the logarithm of conductivity is plotted against the inverse of temperature. The relationship between conductivity and the inverse of temperature follows a linear dependence, suggesting a thermally activated process within the temperature window from 20 to 90°C. The apparent activation energy ( $E_a$ ) mean-

ing the minimum energy required for proton transport across the blend membrane was calculated using the following equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{RT}\right),$$

where  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy, and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ) and  $T$  is the absolute temperature (K). The  $E_a$  values for the different blend membranes estimated by the slopes of the straight lines shown in Figure 6 are presented in Table II. In particular, the  $E_a$  values decrease slightly from 7.34 to 6.95 kJ mol<sup>-1</sup> by increasing the PEO molecular weight from 2000 to 5000, respectively, while keeping the same blend composition (80/20). When PES-g-PEO content is reduced to 10 wt % for blend SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub>, the activation energy is 10.6 kJ mol<sup>-1</sup>, the highest among the studied blends. All calculated  $E_a$  values are higher related to the corresponding value of Nafion 117 ( $5.45 \text{ kJ mol}^{-1}$  with water uptake 41.57 wt %).<sup>43</sup> It is well known that water promotes proton mobility via both structural diffusion (Grotthuss-type hopping of the proton through the hydrogen-bonded network of water molecules) and vehicular motion (coupled proton-water transport of hydronium ions).<sup>44</sup> However, the Grotthuss mechanism is known to require lower activation energy values<sup>45</sup> for proton conduction varying between 14 and 40 kJ mol<sup>-1</sup>, which are very close with the corresponding ones calculated for the synthesized blends, implying that the conductivity is governed by the former mechanism.

The performance of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> membranes was investigated at low temperature PEM electrolyzer. Figure 7 presents the polarization curves of MEAs prepared from different polymer electrolytes in terms of composition and PEO molecular weight at 80°C and ambient pressure. It is well established that the rate-determining step in PEMWE is associated with the oxygen evolution process occurring at the anode.<sup>46</sup> Consequently, the poor performance observed is originated mainly from the use of Pt anode due to its low reaction rate for oxygen evolution. The MEA based on SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> electrolyte exhibits better performance compared to the



**Figure 7.** Water electrolysis performance using Pt/C|SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>x</sub> ( $x = 2000$  and  $5000$ )|Pt/C MEAs at 80°C.

corresponding one based on SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> electrolyte, as the current density increases from 15 to 112 mA cm<sup>-2</sup> at 2 V. Even though the cell performance of the former MEA is assisted by the increased Pt loading, which is twice higher than SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>2000</sub> electrolyte based MEA, it is the overall lower ohmic resistance (higher conductivity) of the interface that mainly improves its performance. Another important observation addresses the significant role of the polymer binder used on performance. The PES-g-PEO<sub>x</sub> homopolymer that was added as a binder to the catalytic powder can be reflected in the low current density region (~1 mA cm<sup>-2</sup>), where the influence of the ohmic resistivity is almost negligible. The catalyst layer itself can be considered as hydrophilic and the water film existed due to the intense hydrated conditions, may expand the three phase region by acting as a transport layer for protons thus activating catalyst particles.<sup>47</sup> In particular, the addition of the PES-g-PEO<sub>5000</sub> with the longer PEO chains onto the catalytic layer, due to its very hydrophilic character and improved mobility, in combination with the intense hydrated conditions of the cell, can probably expand/improve the three phase region, and consequently, enhance the oxygen evolution reaction (OER) as it is well known that its kinetics are favored by extremely hydrated environments.<sup>47</sup> For comparison reasons, the cell performance for the system SPSF-co-polyphenylene sulfide sulfone (SPSF-co-PPSS)/TPA was 1.83 V at 1 A cm<sup>-2</sup> at 80°C under ambient pressure,<sup>18</sup> which is higher than that of SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> with composition 80/20 (0.062 A cm<sup>-2</sup> at 1.83 V).

The effect of reducing PES-g-PEO<sub>2000</sub> weight content on cell performance is also shown in Figure 7. In particular, it is observed that in the case of blend with 10 wt % PES-g-PEO<sub>2000</sub> content, the performance is decreased as neither the membrane (due to the reduced amount of the hydrophilic agent [PES-g-PEO]) nor the electrode can withstand the intense hydrated conditions existing in the cell. It should be stressed that these results are preliminary and electrolytic cell performance has to be much improved by optimization of the electrolyte–electrode interface, for example, using other anode electrocatalysts instead of Pt, different electrode preparation method.

## CONCLUSIONS

Focused on the development of new nonfluorinated low cost membranes capable to operate in PEM electrolyzers, a series of solid polymer electrolyte membranes were synthesized by blending polyether sulfones bearing side chain PEO groups with SPSF. The produced amorphous SPSF(Na)<sub>45</sub>/PES-g-PEO blends have shown high glass transition temperatures ( $T_g$ s up to 165°C), high thermal stability and high water uptakes. The proton conductivity of the hydrated membranes is dependant on the molecular weight of PEO as well as the weight fraction of PES-g-PEO. In the case of miscible blends where a continuous proton conductive pathway is formed and consisted of sulfonate/PEO groups, the proton transport is promoted via hydrogen bonding between oxygen (acts as Lewis base) of PEO groups and water molecules. Once this pathway is formed, the proton transport is greatly affected by the polymer chain mobility. The proton conductivity was increased by increasing temperature and the SPSF(Na)<sub>45</sub>/PES-g-PEO<sub>5000</sub> blend with

composition 80/20 showed maximum conductivity value of  $1.4 \times 10^{-2}$  S cm<sup>-1</sup> at 80°C. The  $E_a$  values were also estimated and varied between 6.95 and 10.6 kJ mol<sup>-1</sup>, implying that Grotthuss mechanism is the dominant for proton conduction. Regarding the cell performance, the electrolyte with the lower ohmic resistance (higher conductivity) showed better performance, although is still poor due to the use of Pt as anode. Moreover, as the longer PEO chains facilitate the fast ion conduction, the use of the PES-g-PEO component with PEO molecular weight 5000 as a binder probably improves the three phase boundary region of the anode, thus enhancing the kinetics of OER.

A detailed study regarding the effect of different parameters on the electrolytic cell performance is under progress.

## ACKNOWLEDGMENTS

This article has been supported by and performed within EU project “Prometheas,” Contract Nr ICA2-2001-10037 and by GSRT, Ministry for Development of Greece in the framework of the bilateral project GR-BG, Contract Nr 098G.

## REFERENCES

1. Barbir, F. *Sol. Energy* **2005**, *78*, 661–669.
2. Dunn, S. *Int. J. Hydrogen Energy* **2002**, *27*, 235–264.
3. Rasten, E.; Hagen, G.; Tunold, R. *Electrochim. Acta* **2003**, *48*, 3945–3952.
4. Grigoriev, S. A.; Porembsky, V. I.; Fattev, V. N. *Int. J. Hydrogen Energy* **2006**, *31*, 171–175.
5. Hossain, S. K. M.; Das, M. *Chem. Eng. World* **2008**, *43*, 112–118.
6. Tanekaka H.; Torikai, E.; Kawami, Y.; Wakabayashi, N. *Int. J. Hydrogen Energy* **1982**, *7*, 397–403.
7. Kato, M.; Maezawa, S.; Sato, K.; Oguro, K. *Appl. Energy* **1998**, *59*, 261–271.
8. Leonida, A.; Mc Elroy, J. F.; Sexauer, R. N. *SAE Tech. Pap. Ser.* **1992**, 1–5.
9. Erickson, A. C.; Puskar M. C.; Zagaja, J. A.; Miller, P. S. *SAE Tech. Pap. Ser.* **1987**.
10. Vielstich, W.; Lamm, A.; Gasteiger, H. A. In *Handbook of Fuel Cells: Fundamentals Technology and Applications*; Wiley: Chichester, **2003**; Vol. 2.
11. Kondoh, M.; Yokoyama, N.; Inazumi, C.; Maezawa, S.; Fujiwara, N.; Nishimura, Y.; Oguro, H.; Tanenaka, K. *J. New Mater. Electrochem. Syst.* **2000**, *3*, 61–65.
12. Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535–4585.
13. Bae, J. M.; Honma, I. *Solid State Ionics* **2002**, *147*, 189–194.
14. Holze, R.; Ahn, J. J. *Membr. Sci.* **1992**, *73*, 87–97.
15. Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587–4612.
16. Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463–1502.
17. Ng, F.; Péron, J.; Jones, D. J.; Roziere, J. J. *Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2107–2117.

18. Jang, I.-Y.; Kweon, O.-H.; Kim, K.-E.; Hwang, G.-J.; Moon, S.-B.; Kang, A.-S. *J. Membr. Sci.* **2008**, *322*, 154–161.
19. Jang, I.-Y.; Kweon, O.-H.; Kim, K.-E.; Hwang, G.-J.; Moon, S.-B.; Kang, A.-S. *J. Power Sources* **2008**, *181*, 127–134.
20. Aricò, S.; Siracusano, S.; Briguglio, N.; Baglio, V.; Di Blasi, A.; Antonucci, V. *J. Appl. Electrochem.* **2013**, *43*, 107–118.
21. Lufrano, F.; Squadrito, G.; Patti, A.; Passalacqua, E. *J. Appl. Polym. Sci.* **2000**, *77*, 1250–1256.
22. Kim, D. H.; Choi, J.; Hong, Y. T.; Kim, S. C. *J. Membr. Sci.* **2007**, *299*, 19–27.
23. Krishnan, N. N.; Lee, H.-J.; Kim, H.-J.; Kim, J.-Y.; Hwang, I.; Jang, J. H.; Cho, E. A.; Kim, S.-K.; Henkensmeier, D.; Homg, S.-A.; Lim, T.-H. *Eur. Polym. J.* **2010**, *46*, 1633–1641.
24. Devrim, Y.; Erkan, S.; Baç, N.; Eroğlu, I. *Int. J. Hydrogen Energy* **2009**, *34*, 3467–3475.
25. Lufrano, F.; Baglio, V.; Di Blasi, O.; Staiti, P.; Antonucci, V.; Aricò, S.; *Solid State Ionics*, **2012**, *216*, 90–94.
26. Tarascon, J. M.; Armand, M. *Nature (London)* **2001**, *414*, 359–367.
27. Armand, M. *Solid State Ionics* **1983**, *9/10*, 745–754.
28. Gray F. M.; Mac Callum, J. R.; Vincent, C. A. *Solid State Ionics* **1986**, *18/19*, 282–286.
29. Chiu, C.-Y.; Chen, H.-W.; Kuo, S.-W.; Huang, C.-F.; Chang, F.-C. *Macromolecules* **2004**, *37*, 8424–8430.
30. Deimede, V.; Voyiatzis, G. A.; Kallitsis, J. K.; Qingfeng, L.; Bjerrum, N. *J. Macromolecules* **2000**, *33*, 7609–7617.
31. Deimede, V.; Kallitsis, J. K. *Macromolecules* **2005**, *38*, 9594–9601.
32. Kerres J.; Ullrich A.; Meier F. *Solid State Ionics* **1999**, *125*, 243–249.
33. Jang, W.; Sundar, S.; Choi, S.; Shul, Y.-G.; Han, H. *J. Membr. Sci.* **2006**, *280*, 321–329.
34. Lauter, U.; Meyer, W. H.; Wegner, G. *Macromolecules* **1997**, *30*, 2092–2101.
35. Zhang, Q.; Zhang, S.; Bi, W. *Polymer* **2011**, *52*, 5471–5478.
36. Samms, S. R.; Wasmus, S.; Savinell, R. F. *J. Electrochem. Soc.* **1996**, *143*, 1498–1505.
37. Smitha, B.; Anjali Devi, D.; Sridhar, S. *Int. J. Hydrogen Energy* **2008**, *33*, 4138–4146.
38. Nishimoto, A.; Agehara, K.; Furuya, N.; Watanabe, T.; Watanabe, M. *Macromolecules* **1999**, *32*, 1541–1548.
39. Park, J. K.; Kang, Y. S.; Won, J. *J. Membr. Sci.* **2008**, *313*, 217–223.
40. Lightfoot, P.; Mehta, M. A.; Bruce, P. G. *J. Mater. Chem.* **1992**, *2*, 379–381.
41. Raducha, D.; Wiczorek, W.; Florjanczyk, Z.; Stevens, J. R. *J. Phys. Chem.* **1996**, *100*, 20126–20133.
42. Gasa, J. V.; Weiss, R. A.; Shaw, M. T. *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 2253–2266.
43. Shahi, V. K. *Solid State Ionics* **2007**, *177*, 3395–3404.
44. Smitha, B.; Sridhar, S.; Khan, A. A. *Macromolecules* **2004**, *37*, 2233–2239.
45. Colombari, P.; Novak A. In *Proton Conductors*; Colombari P., Ed.; Cambridge University Press: Cambridge, England, **1992**.
46. Marshall, A.; Børresen, B.; Hagen, G.; Tsympkin, M.; Tunold, R. *Energy* **2007**, *32*, 431–436.
47. Labou, D.; Slavcheva, E.; Schnakenberg, U.; Neophytides, S. *J. Power Sources* **2008**, *185*, 1073–1078.