

Short communication

Effect of an ormosil-based filler on the physico-chemical and electrochemical properties of Nafion membranes

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Abstract

Composite Nafion-based membranes were prepared and characterized, using an organosilane derivative (sulfonated diphenylsilanediol, SDPSD) as a filler. The physico-chemical and electrochemical properties of the composite membranes were investigated using differential scanning calorimetry (DSC), field emission scanning electron microscopy (FE-SEM), water uptake (W.U.), and electrochemical impedance spectroscopy (EIS). Both conductivity values and thermal features of the composite demonstrated that the presence of SDPSD as a filler significantly modified the properties of the Nafion matrix, allowing to increase its performance in terms of proton conductivity as well as thermal stability. In particular, the interaction between Nafion and SDPSD was found to improve the mechanical stiffness of the Nafion matrix, leading to an increase in the temperature range at which the Nafion membrane maintains proper hydration requirements and hence satisfactory proton conductivity values, allowing its use as an electrolyte in Polymer Electrolyte Fuel Cells operating at intermediate temperatures.

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1. Introduction

Nafion is a well-known perfluorinated ionomeric polymer widely used for electrolytic membranes in several electrochemical devices [1]. Among them, proton exchange membrane fuel cells (PEMFCs) are one of the most interesting devices under development for low-emission energy production for transportation and stationary applications, due to their high energy conversion efficiency and environmental benefits [2].

Although Nafion is today the most widely used electrolyte material, it is well-known that current PEMFCs based on Nafion membranes can operate at temperatures lower than 90 °C, since their performance is strongly reduced at higher temperatures. The fall in performance of Nafion-based membranes has been generally ascribed to the loss of water from the membrane and/or to morphological modifications, and many efforts have been directed to the preparation of composite membranes filling the ionomeric matrix with several kind of materials [3–5].

Hybrid systems that have been investigated for electrochemical applications are the so-called ormolytes (organically modified silane electrolytes), where the combination of organic and inorganic moieties is expected to lead to improvement of both components features [6–8]. In this work we chose to use as a filler an organosilane derivative, sulfonated diphenylsilanediol (SDPSD), since it possesses not only inorganic silicon but also organic moieties that can be easily sulfonated, thus adding a contribution to the overall conductivity [9]. Moreover, the sulfonic acid groups present in the structure of SDPSD may interact with the hydrophilic moiety of Nafion avoiding discontinuities at the interface between Nafion and the filler. The SDPSD structure is also expected to undergo to π - π^* interactions [10] as well as condensation reactions [9] leading to a layered filler that is expected to reduce the methanol crossover of the Nafion membrane [11–13]. The effect of SDPSD as a filler on the physico-chemical and the electrochemical properties of a Nafion membrane was investigated with several techniques including differential scanning calorimetry (DSC), field emission scanning electronic microscopy (FE-SEM), water uptake (W.U.), and electrochemical impedance spectroscopy (EIS).

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2. Experimental

2.1. Materials

Nafion 117 (5 wt.% solution) was obtained from Sigma–Aldrich. Sulfonated diphenylsilanediol (SDPSD) was synthesized as previously reported [9]. Hydrogen peroxide was obtained from Carlo Erba (Milan, Italy). All other solvents were reagent grade (Sigma–Aldrich) and were used without further purification.

Composite membranes were prepared at 10 and 30 wt.% SDPSD content (labeled in the text as “Nafion/SDPSD 90:10” and “Nafion/SDPSD 70:30”) according to the following procedure.

Nafion solution was stirred at 80 °C and, once the solvent removal was complete, dimethylacetamide (DMA, 10 mL) was added. The proper amount of SDPSD (dissolved in acetylacetone) was mixed with the resulting Nafion solution in an ultrasonic bath, then cast in a Teflon dish and maintained at 100 °C for 5 h.

The membranes were post-treated as follows: refluxing in H₂O₂ (3 wt.%) for 1 h, refluxing in 0.5 M H₂SO₄ for 1 h, refluxing in deionized H₂O for 1 h [5]. The membranes prepared with this procedure are labeled “as-prepared” in the text. The “as-prepared” membranes were post-treated again, heating them at 170 °C for 2 h. The thermal treated membranes are called “heated” in the text. Reference pure Nafion membranes were prepared following the same procedure.

The thickness of the membrane fell in the range: 150–200 μm.

2.2. Methods

Water uptake (W.U.) was calculated as reported in the literature [14], using the following equation:

$$\text{W.U.}(\%) = \left[\left(\frac{W_{\text{wet}}}{W_{\text{dry}}} \right) - 1 \right] \times 100 \quad (1)$$

where W.U. is expressed in percentage units, W_{wet} is the weight of the wet membrane, and W_{dry} is the weight of the dry membrane. The dry membranes were immersed in water at room temperature for 12 h, then dried with absorbent paper and weighted.

SEM imaging was acquired using FE-SEM, LEO mod. Supra 35, the electron beam energy being 2 keV.

DSC measurements were carried out by using a DSC 821 Mettler Toledo Differential Scanning Calorimeter. Experiments were run from 30 to 280 °C with a heating rate of 20 °C min⁻¹. The experiments were carried out under N₂ flow (40 mL min⁻¹), placing the samples in aluminium pans. Three heating–cooling cycles were carried out, the second cycle was recorded immediately after the first one, whereas the third was recorded 3 days after the first one.

Proton conductivity of the membranes was measured using electrochemical impedance spectroscopy (EIS). An applied voltage of 20 mV and a frequency range of 10 Hz to 1 MHz were

used using a PARSTAT 2273A. Membranes were sandwiched between commercial electrodes (E-Tek ELAT HT 140E-W with a platinum loading of 5 g m⁻²). EIS measurements were performed as a function of temperature and relative humidity (RH). The EIS spectra as a function of RH were collected using an in-home made apparatus, the system consisting in two compartments connected and hold at different temperatures. The cold compartment contains water, while the hot compartment houses the cell test [15]. RH was monitored by a humidity sensor (VAISALA HMP237) in the 20–100% RH range.

3. Results and discussion

Fig. 1 shows the proton conductivity (σ) plot of unfilled Nafion and Nafion/SDPSD composite membranes as a function of $1/T$. In all cases, three different regions can be observed.

In the first region (30–90 °C), conductivity increased with increasing the temperature for all samples, reaching values in the range 0.01–0.02 S cm⁻¹. In particular, the conductivity of the composite membranes was slightly higher than that of the unfilled Nafion, the Nafion/SDPSD 90:10 composite membrane reaching the highest conductivity value.

Above 90 °C, a different behavior was observed for the unfilled Nafion and the Nafion/SDPSD composite membranes. In agreement with previously reported data [1], the proton conductivity of the unfilled Nafion membrane slowly decreased in the 90–160 °C range, and an abrupt loss of performance was observed above 160 °C, leading to the complete loss of the membrane stability.

The conductivity values measured for the Nafion/SDPSD composite membranes remained almost constant, about 0.015 S cm⁻¹, at temperatures between 90 and 160 °C, always higher than those of the Nafion membrane in the same temperature range. In particular, σ of Nafion/SDPSD 90:10 was slightly higher than σ of Nafion/SDPSD 70:30. Although maintaining higher performance than the reference pure Nafion membrane,

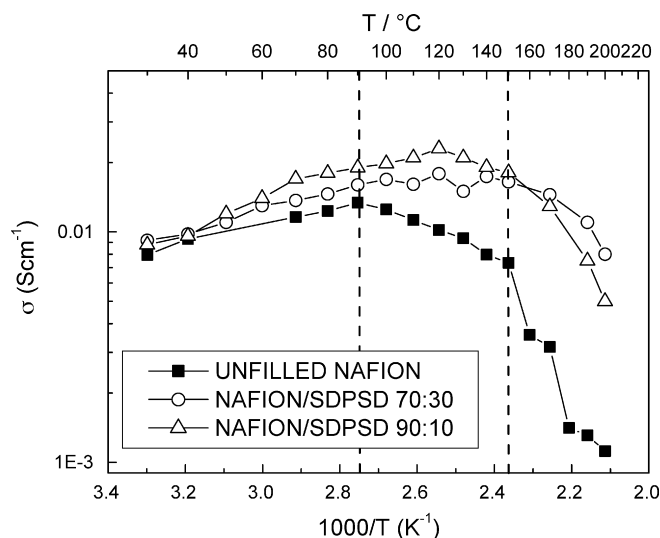


Fig. 1. Arrhenius plots of unfilled Nafion and composite membranes.

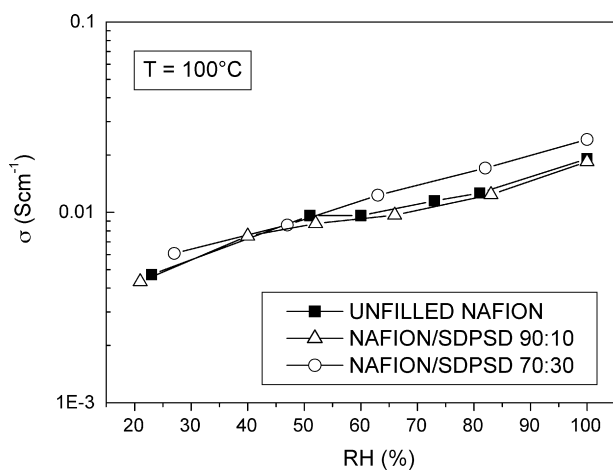


Fig. 2. Proton conductivity vs. relative humidity plots at $T=100^{\circ}\text{C}$ for unfilled Nafion and composite membranes.

a drop in the proton conductivity was observed also for the composite samples above 160°C .

The comparison of conductivity data for the composite and unfilled Nafion membranes demonstrated that the presence of SDPSD in the Nafion matrix improved both proton conductivity and membrane stability with respect to the unfilled Nafion membrane up to 160°C .

Early reports ascribed the decrease in conductivity at elevated temperatures to dehydration, even though more recent work showed similar performance decrements under humidified conditions [4,5]. To check the membrane stability under controlled humidified condition, we measured the proton conductivity of the membranes as a function of relative humidity (RH). Figs. 2 and 3 show the data recorded at 100 and 130°C , respectively.

Similar conductivity values were determined for unfilled Nafion and composite membranes at 100°C . For all samples, σ increased with increasing RH, from 0.005 to 0.02 S cm^{-1} , in the whole range of RH. A different behavior was observed at 130°C . Increasing RH did not lead to significant variation of the conductivity of the reference unfilled Nafion membrane which remained almost constant (around 0.005 S cm^{-1}) and

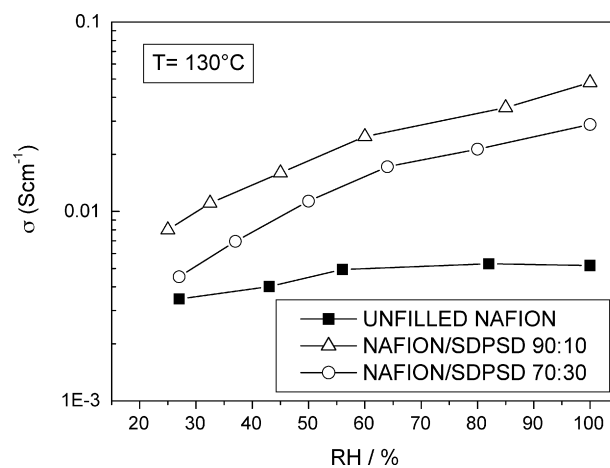


Fig. 3. Proton conductivity vs. relative humidity plots at $T=130^{\circ}\text{C}$ for unfilled Nafion and composite membranes.

lower than that recorded at 100°C . On the contrary, the proton conductivity values of the composite membranes, increased with increasing RH, and they were higher than the σ values recorded at 100°C . Again, the best performance was observed for the Nafion/SDPSD 90:10 membrane.

The morphology of the membranes was examined by scanning electron microscopy to examine the influence of the filler concentration in the polymer matrix. Fig. 4 shows the SEM micrographs for the two composite membranes. SEM images of pure Nafion membranes were also acquired (data not shown) and they appeared completely dark, featureless. The presence of SDPSD can be clearly observed in the composite membranes. In particular, the Nafion/SDPSD 90:10 membrane (Fig. 4a) showed high homogeneity, being SDPSD well dispersed in the Nafion matrix. In the Nafion/SDPSD 70:30 membrane (Fig. 4b), the presence of larger aggregates can be observed. As previously observed with different fillers, the size of SDPSD clusters increased with increasing the filler content in the membrane [16]. Also, it cannot be excluded that some condensation of the silanol units occurred during the process of membrane preparation [9]. In both cases, the presence of the SDPSD did not introduce any porosity in the membrane

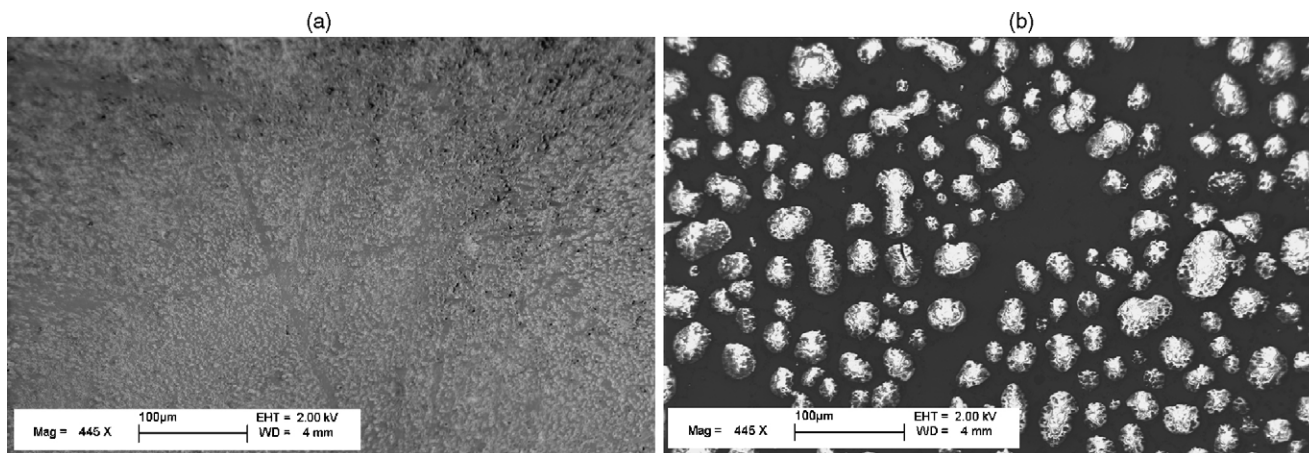


Fig. 4. SEM micrographs of composite membranes. (a) Nafion/SDPSD 90:10; (b) Nafion/SDPSD 70:30.

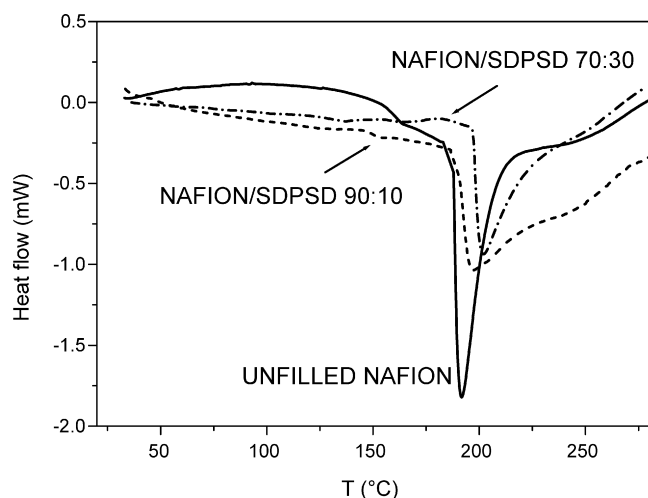


Fig. 5. DSC thermograms of unfilled Nafion and composite membranes (1st run).

that could negatively affect performance [17]. The body of electrochemical data demonstrated that the proton conductivity of unfilled Nafion membranes dramatically decreased at temperatures as high as 100 °C even under fully humidified conditions. On the other hand, the presence of SDPSD allowed to increase the temperature range at which the Nafion-based membranes maintain their stability and thus to shift the temperature at which a transition to a less conducting phase takes place.

To investigate the thermal stability and the occurring of morphological transitions of the Nafion-based membranes, DSC thermograms of the unfilled Nafion membrane and composite membranes were performed, and the results are shown in Fig. 5.

All samples showed an intense endothermic peak in the region between 180 and 200 °C (T_1) and a broad endothermic peak in the range 220–270 °C (T_2). A shoulder in the temperature range 145–160 °C (T_0) was also detectable. During the cooling run (data not shown), no peaks were detected.

On the basis of previous works, it was possible to assign the first endothermic peak at T_0 to molecular rearrangements inside the polar clusters of the polymer [18], and the peak at T_2 to the melting of crystalline regions [19,20]. The endothermic peaks at T_1 seems to be due to the loss of water molecules surrounding the SO_3H groups, as suggested by the following consideration. When a second heating cycle was performed immediately after the first running, all three peaks disappeared (data not shown). On the contrary, DSC thermograms recorded 3 days after the first measurement showed a different behavior. At variance with the peaks at T_0 and T_2 that appeared again, the strong endothermic peak at T_1 was not present in spite of the increased aging time. It seems reasonable assuming that with increasing aging time the polymer is allowed to return to conformational equilibrium and for this reason the peak at T_0 and T_2 are visible again. On the other hand, the absence of the peak at T_1 during the last heating cycle confirms that it can be assigned to an irreversible water loss [20]. Fig. 6 shows details of the peak at T_0 observed during the third heating cycle. The endothermic peak was centered at $T = 147$ °C for the unfilled Nafion and

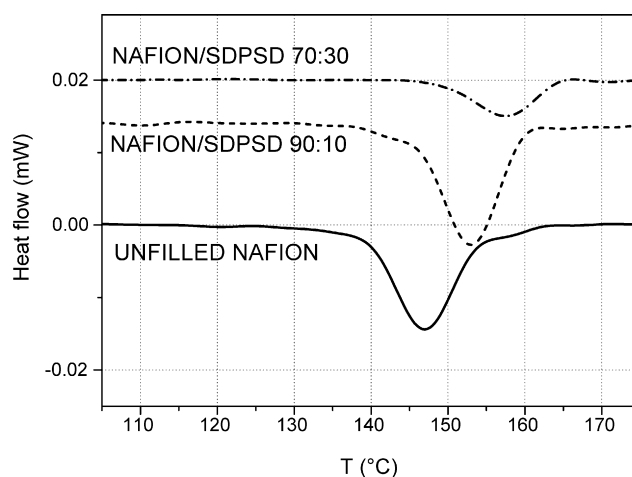


Fig. 6. DSC thermograms of unfilled Nafion and composite membranes (3rd run).

at $T = 153$ °C and $T = 158$ °C for the Nafion/SDPSD 90:10 and Nafion/SDPSD 70:30 composite membranes, respectively.

When the Nafion matrix is filled with SDPSD, the peak is shifted towards higher temperature, and the shift is larger as the SDPSD content increases. This indicates that the thermal transition is modified by the establishment of an interaction of the filler with the polar clusters of Nafion that improves the mechanical stiffness of the matrix. This finding can be easily related to the improvement of the conductivity performance of the composite membrane with respect to the unfilled Nafion. On the contrary, regarding the endothermic peak at T_2 (data not shown) no shifts were observed. These findings indicate that the interaction between the sulfonic acid groups present in the structures of both polymer and filler affects the Nafion polar cluster region without affecting the main chain region restricting the hydrophilic cluster mobility. Once this thermal transition (T_0) due to a change in the polymer structure takes place, the polymer matrix does not maintain proper hydration requirements, losing its mechanical stiffness. The presence of SDPSD allows to shift this transition toward higher temperatures improving the thermal stability and the hydration requirements of the Nafion membrane.

Further indications on the thermally induced variation in the polymer structure can be achieved by water uptake (W.U.) measurements on the Nafion-based membranes, below and above the afore-mentioned transition temperature at T_0 (Table 1). The membranes were heated to 170 °C for 2 h and the W.U. values were compared with W.U. values obtained for the “as-prepared” samples. Table 1 shows that in the case of “as-prepared” samples, the water uptake value of the composite

Table 1
Water uptake values of Nafion-based membranes

Sample	Water uptake (%)	
	“As-prepared” membrane	“Heated” membrane
Unfilled Nafion	30	9
Nafion/SDPSD 90:10	21	11
Nafion/SDPSD 70:30	16	9

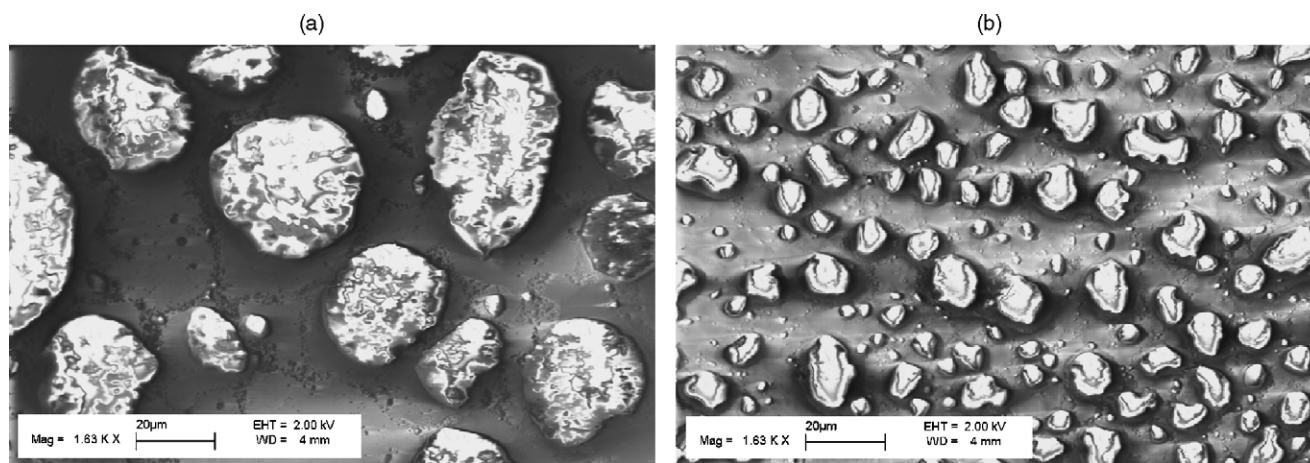


Fig. 7. SEM micrographs of Nafion/SDPSD 70:30 composite membranes. (a) “As-prepared” sample; (b) “heated” sample.

membranes was lower than the W.U. value of the unfilled Nafion, and decreased as the SDPSD content increased. On the contrary, the presence of SDPSD did not affect the W.U. values of the “heated” Nafion membranes. Moreover, the W.U. values of the “heated” samples were lower than the W.U. values of the “as-prepared” samples, indicating that the two different polymer conformations have different hydrophilicity.

SEM investigations were also carried out on the membranes below and above the transition temperature. Fig. 7a and b shows typical SEM pictures of the “as-prepared” and “heated” Nafion/SDPSD 70:30 membrane, respectively. The figures show the presence of SDPSD in the composite membranes, being the filler differently dispersed in the matrix depending on the thermal treatment. In the case of the “as-prepared” sample (Fig. 7a), SDPSD appears aggregated into large clusters. In the case of the “heated” sample (Fig. 7b), the average dimensions of the SDPSD clusters are smaller. The thermal treatment at 170 °C allowed to redistribute the content of SDPSD in the membrane because of the change in the polymer structure that leads to softening of the matrix. SEM images of the unfilled Nafion and Nafion/SDPSD 90:10 membranes were also acquired (data not shown). Regarding the unfilled Nafion membrane, the images appeared completely dark, featureless in both cases; regarding the Nafion/SDPSD 90:10 membrane, SEM images revealed that the thermal treatment affects the filler distribution in the same way of the Nafion/SDPSD 70:30 membranes, even though this effect is less amplified.

4. Conclusions

The effect of a functionalized ormosil sulfonated diphenylsilanediol (SDPSD) as a filler in Nafion-based membranes was investigated. The structural affinities between Nafion and SDPSD enhanced the performance of the composite membranes in terms of morphological stability as well as water retention, improving electrical properties. The interaction between the two components was indicated by the increased thermal stability and proton conductivity. In fact, the composite membranes showed

high conductivity at severe conditions of temperature and relative humidity whereas the unfilled Nafion membrane lost its stability. The enlargement of the temperature range at which the Nafion-based composite membranes can be used as electrolytes make them promising for applications in polymeric Fuel Cells.

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