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Sulfonated Polyether Ether Ketone-Based Composite Membranes Doped with a Tungsten-Based Inorganic Proton Conductor for Fuel Cell Applications

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Sulfonated polyether ether ketone (SPEEK)-based composite membranes doped with hydrated tungsten oxide were prepared and studied for proton exchange membrane applications. Hydrated tungsten oxide ($WO_3 \cdot 2H_2O$) was synthesized via acidic hydrolysis of sodium tungstate and its structure and physicochemical features were investigated by thermogravimetric analysis (TG), X-ray diffraction (XRD), and electrochemical impedance spectroscopy (EIS). SPEEK/$WO_3 \cdot 2H_2O$ composite membranes were prepared by mixing proper amounts of SPEEK and hydrated WO_3 in dimethylacetamide as casting solvent. The composite membranes were characterized by XRD, TG-DTA, EIS, and water uptake measurements as a function of the oxide content in the membrane. In particular, XRD patterns as well as TG measurements indicated the existence of a coordinative interaction between the water molecules of tungsten oxide and the SPEEK sulfonic acid groups. This interaction lead to the enhancement of the membrane proton conductivity, as well as of their properties, from the point of view of heat resistance and water solubility. In fact, the addition of tungsten oxide resulted in higher proton conductivity, improved heat resistance, and lower water solubility.
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During the past two decades, significant worldwide efforts have been devoted to develop fuel cell materials and systems for electrochemical energy conversion. Among various types of fuel cells, the proton exchange membrane fuel cell (PEMFC) is one of the most promising candidates for portable technologies and electric vehicles. For these applications, it is important to develop new membranes capable of operating at intermediate temperatures (90–130°C) to enhance fuel oxidation kinetics and reduce heat exchange requirements.[1]

Several methods have been proposed to increase the performance of PEMs and promising results have been obtained with the use of composite membranes, where inorganic particles are embedded in a conducting polymer matrix.[2-6]

In the present work a similar approach was followed and the polymer chosen for the fabrication of proton conductive membranes was sulfonated polyetheretherketone (SPEEK). Polyetheretherketone (PEEK) is a semicrystalline thermoplastic polymer known for its good thermal stability and excellent mechanical properties. As for most sulfonated arylene main chain polymers, its conductivity strongly depends on the degree of sulfonation (DS=number of $-SO_3H$ groups per repeat unit): at reduced levels of sulfonation the hydrophilicity of aromatic polymers is too low to reach the water content needed to ensure values of proton conductivity acceptable for use in fuel cells.[7] Conversely, at high sulfonation degrees, the mechanical properties of the membrane deteriorate.[3] This drawback can be overcome producing hybrid organic–inorganic membranes with controlled mechanical, physical, and chemical properties.[8]

Among several general approaches to increase proton transport as well as the mechanical properties through the use of hybrid membranes, in this work our strategy was to use a proton conductive filler. The filler was introduced with the aim of reducing both the membrane permeability to methanol and the conduction losses at low humidity contents.[9] For these reasons, the incorporation of a hydrophilic oxide into a SPEEK matrix was carried out.

Among inorganic proton conductors, di-hydrated tungsten oxide ($WO_3 \cdot 2H_2O$) exhibits relatively high proton conductivity up to 150°C.[10] This compound crystallizes in a layered structure, analogous to that of $MoO_3 \cdot 2H_2O$, in which infinite layers of corner-shared deformed MoO_5 (H_2O) octahedra are stacked above each other with interlayered water molecules connected by hydrogen bonding between the two kinds of water molecules.[11] This ceramic material cannot be easily shaped in the form of a membrane, a problem that might be solved with the formation of a composite system where an organic polymer may supply the needed plastic properties for fuel cell applications.

SPEEK/$WO_3 \cdot 2H_2O$ composite membranes were prepared by mixing proper amounts of SPEEK and hydrated WO_3 in *N*,*N*-dimethylacetamide (DMA); the structural and electrochemical performance of the resulting membranes was evaluated.

Experimental

Materials.— PEEK was obtained by VICTREX in the form of extrudate (Mw: 38,300 g/mol, 132 repeat units per mole). SPEEK was obtained in concentrated sulfuric acid (H_2SO_4 96%, Aldrich) according to published procedure.[7] The DS was determined by titration and by ^1H NMR, resulting to be 0.8. DMA (98%) was obtained by Wako. Hydrated tungsten oxide ($WO_3 \cdot 2H_2O$) was synthesized as previously reported.[11,12] 50 mL of a 1 M (saturated) sodium tungstate(VI) dihydrate ($Na_2WO_4 \cdot 2H_2O$ 99%, Wako) solution in water were added dropwise into 450 mL of 3 M HCl solution at 5°C. A white precipitate appeared immediately and it turned yellow in 30 min. The precipitate was filtered and washed with 250 mL of 0.1 M HCl. The solid was then rinsed several times with water until no chloride ions were detectable. The yellow powder thus obtained was dried in a desiccator.

Membrane preparation.— Composite membranes were prepared at two different oxide contents, i.e., 23 and 50 wt %. SPEEK (0.4 g) was dissolved in DMA (15 mL) at 40°C under stirring. After complete dissolution of the polymer, the proper amount of hydrated tungsten oxide was added. The yellow suspension was kept stirring for 5 min, treated in an ultrasonic bath for 5 min, then kept stirring at 40°C for 2 h, and finally cast on a Teflon plate. The Teflon plate was kept at 40°C overnight. Membranes were peeled off and dried in a desiccator at room temperature. The thickness of the membrane falls in the range 140–240 μm.

Reference pure SPEEK membranes were prepared following the same procedure.

Methods.— X-ray diffraction (XRD) patterns were recorded at room temperature by means of a PW 1729 X-ray generator (Philips

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International, Inc.) using Cu Kα radiation. Data were collected by the step-scanning mode with steps of 0.05° (time per step: 1 s).

Thermal analysis was performed by using a Thermoplus TG 8120 apparatus (Rigaku, Japan) in dry air with a heating rate of 2°C/min.

Water uptake (W.U.) was calculated as reported in the literature[7] using the following equation

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

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 20 mL of water and kept in water for different times (from 15 to 145 min) at room temperature, then dried with absorbent paper, and weighted.

Conductivity measurements on powders were performed using pellets (4 mm diameter and 1 mm thickness) of hydrated tungsten oxide formed by a cold pressing technique at a pressure of 230 MPa. Carbon (acetylene black) electrodes were attached on both sides of the pellet simultaneously when it was pressed. The pellet was inserted between Pt-current collectors using a spring setup. Conductivity measurements on membranes were performed inserting them between Pt-current collectors using the same setup. A silver paste (Ag dispersion in ethanol) was used for improving the contact between Pt and the membranes. The sample holder containing the membrane was dried at 40°C for 2 h to dry the silver paste before impedance measurements. The conductivity was determined by electrochemical impedance spectroscopy (EIS) measurements using a Hewlett Packard 4192A impedance analyzer at the oscillation amplitude of 0.1 V in the frequency range of 5 Hz to 5 MHz. The water vapor pressure was controlled using a thermostatic compartment in which water-saturated air was introduced. The sample temperature was monitored using a thermocouple placed near the sample pellet. The resistance of the tungsten oxide pellets was obtained from the intersection of the semicircle on the real axis. The resistance of the membranes, and hence, their conductivity, was calculated by a linear fit of the impedance spectra in their linear portion. From the resistance values we obtained the conductivity (σ) value using the following equation

$$\sigma = (d/RA)$$

where R is the resistance, d is the distance between electrodes, and A is the electrode area.

EIS and water uptake measurements were performed before and after the activation of the membranes with sulfuric acid. The activation procedure was carried out as follows: The membranes were immersed in 5 M H_2SO_4 for 1 h at room temperature, then rinsed with water. The membranes were dried in a desiccator for 2 days and disks of 8-mm diam were cut from the membranes and weighed. The disks were then soaked in water at room temperature and weighed after blotting with absorbent paper.

Results and Discussion

Characterization of $WO_3 \cdot 2H_2O$.— Figure 1 shows the XRD pattern of $WO_3 \cdot 2H_2O$ powder (pattern a); patterns (b) and (c) are explained later. The pattern is in good agreement with previous literature reports on the structural data of dihydrated tungsten oxide.[11] The compound is characterized by a layered structure in which each W atom has one terminal oxygen, one coordinated water, and four bridging oxygen atoms with which $WO_5(H_2O)$ octahedra are connected with each other to form a neutral $WO_3[H_2O]$ layer. The second water molecule, not bound to W, lies between such layers as interlayer crystal water.

Figure 2 shows the thermogravimetric (TG) curve of $WO_3 \cdot 2H_2O$ powder, which confirmed the existence of two differently bound water molecules. Two distinct weight losses were, in fact, observed, each one corresponding to the loss of one water molecule. According to previous work, the first weight loss step, at about 70°C, was attributed to the loss of interlayer water and the second one, at higher temperatures, to the loss of coordinated water.[11]

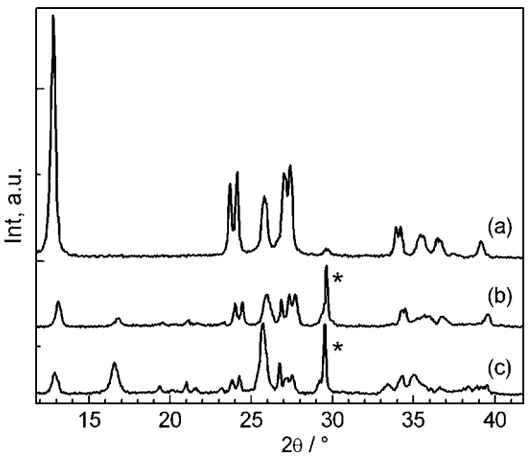

Figure 1. XRD patterns of $WO_3 \cdot 2H_2O$ powder (a), SPEEK/$WO_3 \cdot 2H_2O$ (23 wt %) membrane (b), and SPEEK/$WO_3 \cdot 2H_2O$ (50 wt %) membrane (c). The asterisk refers to a sample holder peak.

The proton conductivity of the $WO_3 \cdot 2H_2O$ pellet at different temperatures and at saturated water vapor pressure was evaluated.

Figure 3 shows the Arrhenius plot for the dihydrated tungsten oxide pellet. Conductivity increased with temperature, showing two different linear trends above and below 60°C. The activation energies (calculated independently in the low- and high-temperature regions) were 0.13 and 0.31 eV, respectively.[11] The two different energy activation values are indicative of two different proton conduction mechanisms. At low temperatures, in fact, the low activation energy value suggests a surface mechanism with protons migrating through surface-adsorbed water.[13] At higher temperatures a bulk mechanism occurred in which conduction takes place through the hydrogen bond network formed by the interlayer and coordinated water molecules.[11]

Characterization of SPEEK.— The proton conductivity of SPEEK membranes was evaluated using EIS measurements. Figure 4 shows the comparison between the complex impedance plots of as-prepared and activated SPEEK membranes at 100% relative humidity (RH) at room temperature. The coordination of SPEEK sulfonic groups with the solvent used for casting is known to induce a decrease in proton conductivity.[14,15] Activation of the membranes with sulfuric acid allows breakup of the acid-base interaction be-

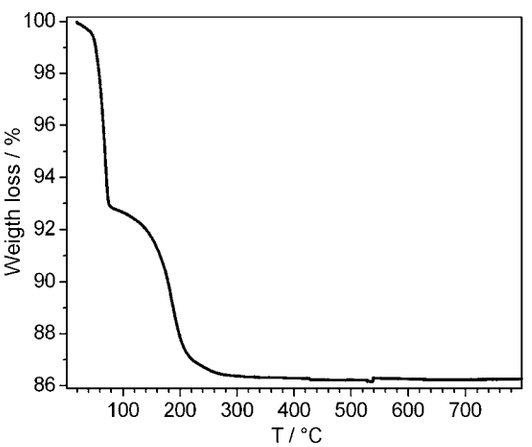

Figure 2. TG curve of $WO_3 \cdot 2H_2O$ powder.

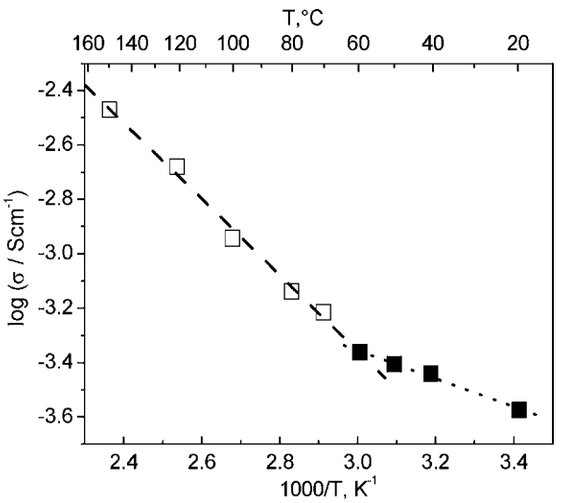

Figure 3. Arrhenius plot of $WO_3 \cdot 2H_2O$ pellet at 100% RH. The fitting was done using the data above 60°C (empty symbols) and below 60°C (filled symbols) separately.

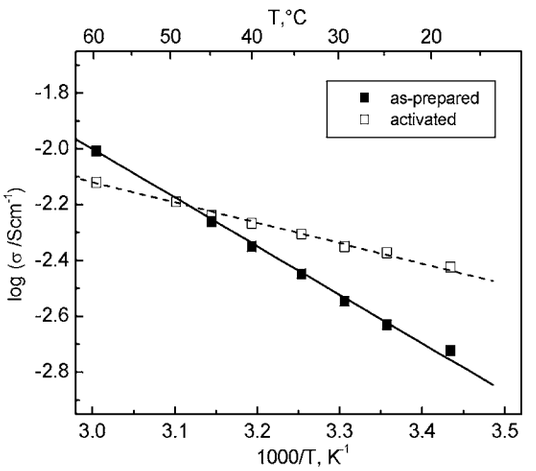

Figure 5. Arrhenius plot for as-prepared and activated pure SPEEK membranes at 100% RH.

tween SPEEK and DMA, without heating the membrane at high temperature, which would induce water loss from the hydrated tungsten oxide to be used as filler. The EIS measurements confirmed that the activation procedure was successful; in fact, the high-frequency semicircle observed for the as-prepared membrane disappeared upon activation (see inset in Fig. 4), demonstrating the removal of the polymer/solvent acid-base interactions that are known to produce discontinuities hindering the migration of H^+ ions.[16]

Figure 5 shows the Arrhenius plots, obtained from EIS measurements, of as-prepared and activated SPEEK membranes. At temperatures above 50°C and at 100% RH, partial dissolution of the polymer in water was observed. However, in the temperature range investigated, conductivity increased with temperature for both as-prepared and activated membranes, and almost the same conductivity value was reached at 50°C when the interaction with the casting solvent is substituted by that with water. It is interesting to point out that the activation energy was higher for the as-prepared membrane (0.37 eV) than for the activated one (0.17 eV), in agreement with previous literature reports on the variation of activation energy with the membrane water content.[17] Eikerling and Kornyshev found that in a dry membrane, which contains only residual water molecules that are strongly bound to the pore surfaces, the activation energy is in the range 0.4–0.5 eV. In the highly swollen membrane, the activation energy is 0.1 eV, which is close to the bulk water value. At intermediate degrees of wetting, the activation energy varies between these two values, allowing the conclusion that in a swollen membrane the influence of interfaces and fixed groups is probably negligible and only the bulk water degrees of freedom contribute to the proton transfer, while in narrow pores, the surface mechanisms of conductivity are dominant.

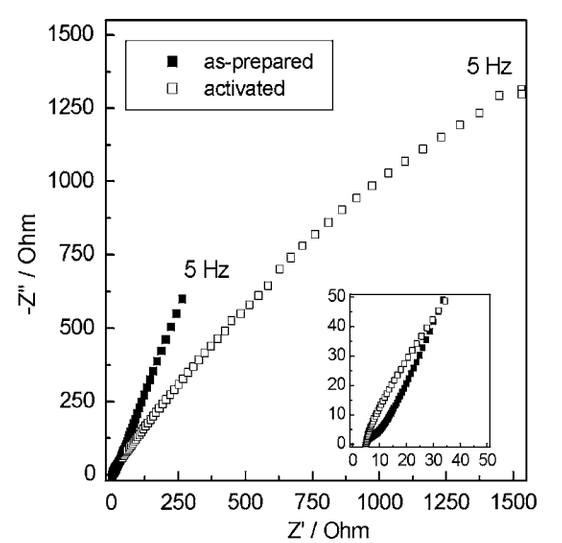

Figure 4. Typical complex impedance plane plot for pure SPEEK membranes measured at 100% RH and at room temperature. A high-frequency zoom of this plot is reported in the inset.

Characterization of SPEEK/$WO_3 \cdot 2H_2O$ *composite membranes.*— Composite membranes SPEEK/$WO_3 \cdot 2H_2O$ at two different oxide contents, i.e., 23 and 50 wt %, were prepared. Figure 1 shows the comparison between the XRD pattern of $WO_3 \cdot 2H_2O$ powder (Fig. 1a) and the SPEEK/$WO_3 \cdot 2H_2O$ composite membranes (Fig. 1b and c); the XRD pattern of a pure SPEEK membrane (not shown) is typical of an amorphous structure. The peaks due to tungsten oxide could clearly be identified in the XRD patterns of the composite membranes, although with some differences with respect to the pattern of the pure oxide. Such differences can be ascribed to a structural modification of the oxide occurring upon membrane formation. In fact, patterns (b) and (c) showed a new peak at $2\vartheta = 17°$ due to the monohydrate phase[11] that was absent in pattern (a). This finding indicates that the hydration grade of the oxide in the membrane changed with respect to the precursor powder and, in particular, it decreased with increasing oxide content in the membrane because of coordination of the oxide interlayer water molecules with the sulfonic acid groups of the polymer.

Such coordinative interaction resulted also from the TG analysis carried out on the membranes. Figure 6 shows the TG curves of the three tested SPEEK-based membranes. After two weight losses due to evaporation of residual water and DMA, which ended at about 260°C, a third step was observed. This step can be attributed to the splitting-off of sulfonic acid groups.[7] It is interesting to observe that the temperature at which the splitting-off of the SO_3H groups of SPEEK (T_S) occurred varied with inorganic filler content, as shown in the inset in Fig. 6. The presence of the filler induced an increase in T_S, thereby supporting the hypothesis of a coordinative interaction between interlayer water molecules of the oxide and SO_3H groups of SPEEK. The fourth step in the TG curves, ending at 525°C, is due to polymer pyrolysis.[7]

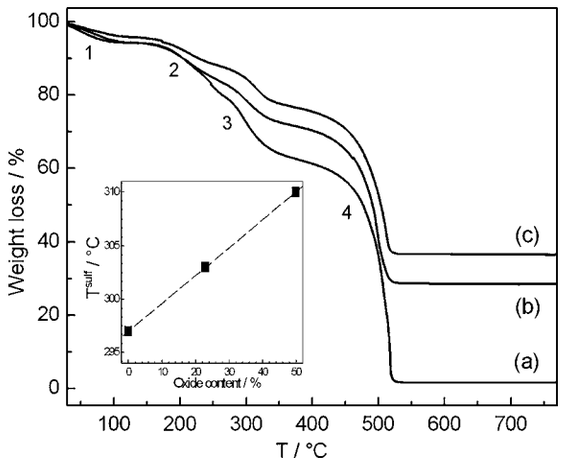

Figure 6. TG curves of pure SPEEK membrane (a), SPEEK/WO_3·$2H_2O$ (23 wt %) membrane (b), and SPEEK/WO_3·$2H_2O$ (50 wt %) membrane (c). (Inset) The temperature at which the splitting-off of the -SO_3H of SPEEK (T_S) occurred *vs* the oxide content in the membrane.

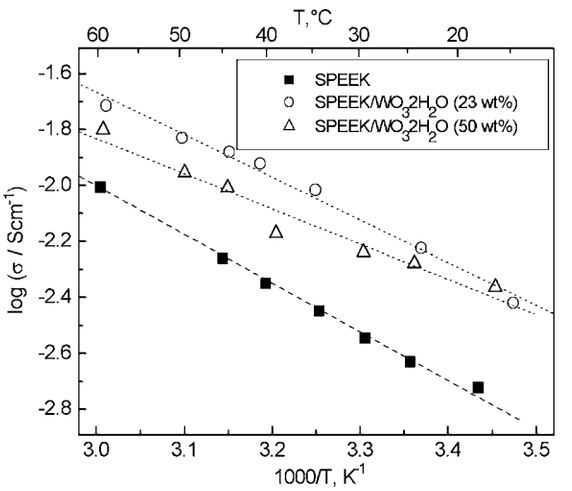

Figure 8. Arrhenius plot for as-prepared SPEEK-based membrane at 100% RH.

Figure 7 shows the comparison of the complex impedance plots for the as-prepared and activated SPEEK/WO_3·$2H_2O$ 23 wt % membranes at room temperature and at 100% RH. The high-frequency resistance was much lower than that observed for the reference SPEEK membranes (Fig. 4), demonstrating that the activation procedure did not significantly affect the conductivity of composite membranes. Both the as-prepared and activated composite membranes showed in fact similar σ values, at variance with what observed for pure SPEEK. The same behavior was observed for the composite membrane containing 50 wt % filler. These observations indicate that the water molecules of tungsten oxide are coordinated by the SO_3H groups of SPEEK, resulting in removal of residual DMA and, therefore, in electrical discontinuities of the membrane.

Figure 8 shows the Arrhenius plots of the composite membranes compared with the as-prepared SPEEK reference membrane. The proton conductivity of the composite membranes was higher in the whole range of temperatures, and at variance with what was observed for pure SPEEK, the activation procedure did not modify their electrochemical performance, in agreement with the existence of a coordinative interaction between SPEEK sulfonic acid groups and tungsten oxide water molecules. The activation energy for the SPEEK/WO_3 composite membranes was found to be 0.33 and 0.28 eV for 23 and 50 wt %, respectively. These values are lower than the activation energy for the as-prepared SPEEK membrane (0.37 eV). It is noteworthy, however, that the conductivity of the composite membranes was larger than that of the activated SPEEK membranes, even though the activation energy for the latter was smaller (0.17 eV).

As already mentioned, one of the main drawbacks for membranes prepared with SPEEK with high sulfonation degree is their water solubility. Therefore, the water uptake behavior and the heat resistance of the membranes in saturated water vapor pressure conditions were investigated.

Figure 9 shows the water uptake of the three SPEEK-based membranes as a function of time. The SPEEK/WO_3 (50 wt %) membrane showed much lower water uptake values only slightly increasing with time, whereas the pure SPEEK membrane and the composite membrane containing lower oxide concentration showed larger water uptake values, increasing with time up to 100–120%. These findings indicate that a large oxide content drastically reduced

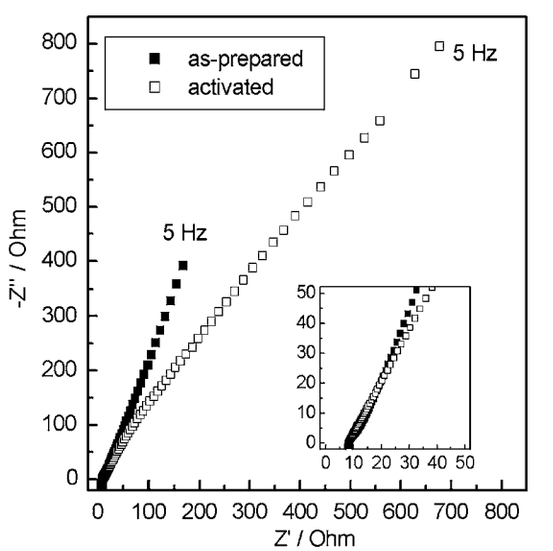

Figure 7. Typical complex impedance plane plot for SPEEK/WO_3·$2H_2O$ (23 wt %) membrane measured at 100% RH and at room temperature. (Inset) A high-frequency zoom of this plot.

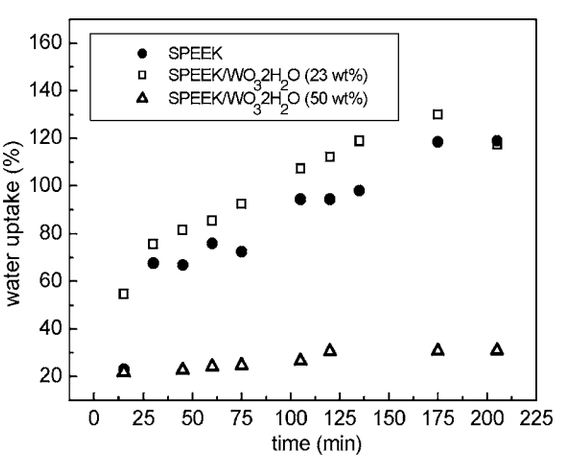

Figure 9. Water uptake values of activated SPEEK-based membranes as a function of time.

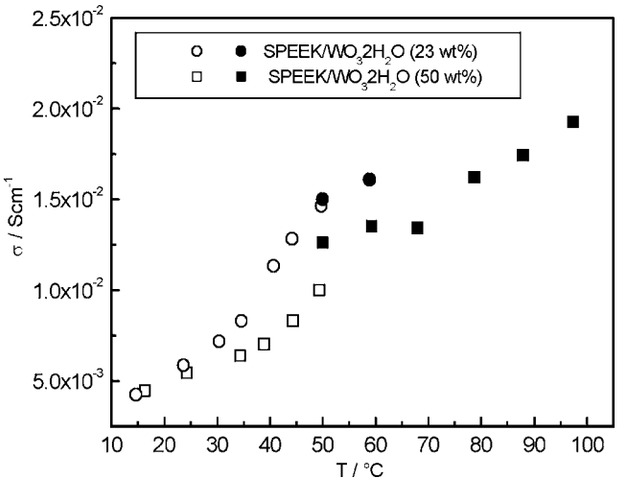

Figure 10. Proton conductivity as a function of temperature of activated SPEEK/$WO_3 \cdot 2H_2O$ membranes. Filled symbols: data collected after keeping the membrane at 50°C overnight at 100% RH.

the water uptake capacity of SPEEK. The control of water uptake allows balance of the need of ion-rich regions that favor proton transfer and excessive swelling, eventually leading to water solubility.

The stability of the membranes as a function of temperature in saturated water environments was investigated. Proton conductivity was measured for the three membranes with increasing temperature from room temperature up to 50°C. Then, after keeping the membranes at 50°C and at 100% RH overnight, the proton conductivity was measured again until dissolution of the membranes. Figure 10 shows the results for the composite SPEEK/WO_3 membranes. The pure SPEEK and the composite SPEEK/WO_3 (23 wt %) dissolved in the temperature range 60–70°C, whereas the membrane with higher oxide content showed an increase in proton conductivity up to 1.9×10^{-2} S cm^{-1} at 100°C. After overnight exposure to saturated water vapor pressure at 50°C, an increase in proton conductivity was measured probably because of a larger hydration of the membrane.

The composition SPEEK/WO_3 50% resulted in a synergic merge of the electrical and physicochemical properties of the two components: the proton conductivity of the composite membrane was larger than those of the pure components; the heat resistance and solubility characteristics were improved with respect to pure SPEEK; moreover, it was possible to prepare flexible membranes with hydrated tungsten oxide, the conductivity properties of which were suitable for the foreseen application.

Conclusions

Polymer electrolyte membranes doped with inorganic proton conductors were successfully prepared. Our strategy to improve proton conductivity of both SPEEK and hydrated tungsten oxide consisted of the combination of the two materials. The composite membrane showed improved conductivity with respect to the single components, probably due to the existence of a coordinative interaction between the water molecules of tungsten oxide and the sulfonic acid (-SO_3H)) groups of SPEEK.

The presence of the oxide not only led to enhancement of the proton conductivity of the SPEEK membranes but also to the improvement of their heat resistance as well as to a decrease in their water solubility. In fact, doping a SPEEK-based material with 50 wt % tungsten oxide allowed preparation of a proton-conducting membrane having low swelling and high proton conductivity up to 100°C. The combination of $WO_3 \cdot 2H_2O$ in the polymeric matrix allowed fabrication of a membrane suitable for fuel cell applications.

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