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Sulfonated polyether ether ketone based composite polymer electrolyte membranes

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Abstract

Electrochemical properties of a series of composite membranes prepared by incorporation of boron phosphate into polymeric matrix of sulfonated PEEK were studied. The conductivity of the composites was found to exceed largely that of pure SPEEK polymer. It was however lower than predicted by the effective medium theory for these mixtures. This is associated to the formation of a capillary pore system in the membranes. Despite the developed porosity the composite membranes proved to be mechanically strong and not affected by long term storage in water. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Composite membranes; Electrochemistry; Polyether ether ketone (PEEK); Boron phosphate

1. Introduction

Proton conducting polymer electrolyte membranes, designated also as proton exchange membranes (PEM), have currently assumed great importance due to their possible application in many near-ambient temperature electrochemical processes. They are used in various electrochemical devices, such as electrochromic windows, displays or sensors, however their most significant field of application is fuel cells. PEMs are utilized in the fuel cells as separators between cathode and anode compartments where the catalytic reactions of oxygen reduction and fuel oxidation occur respectively. The chief properties required of PEM are therefore the ability to fulfill the separator function as well as a high protonic conductivity to avoid ohmic loss in proton transfer from anode to cathode. Owing to their importance in the fuel cell field, solid polymer electrolytes have received considerable attention over the last years and as a consequence several types of membranes with diverse mechanical and electrical properties have been synthesized and characterized [1–5].

In recent works [4–9] it has been shown that polyether ether ketone (PEEK) is of particularly significant promise as it possesses a good thermal stability, appropriate mechanical properties and some conductivity when sulfonated. However, the mechanical properties of PEEK tend to progressively deteriorate with sulfonation [10] which makes the long term stability of highly sulfonated polymer questionable. As to the low sulfonated PEEK membranes, they are quite strong, yet their proton conductivity σ does not suffice to meet the requirements for PEM which usually comprises $\sigma > 10^{-2}$ S/cm [5].

The composite membranes represent one of the ways to improve the PEM properties as they can presumably combine the assets of the components. This approach was employed in our previous studies [5,11] where in order to build up the proton conductivity of PEEK, several heteropolycompounds (acid and their salts) and polyetherimide doped with some inorganic

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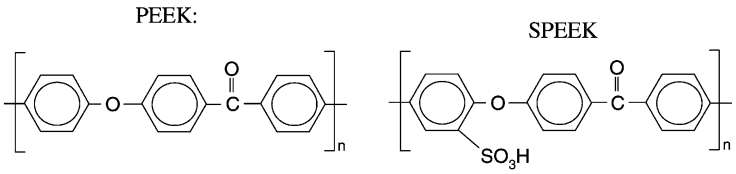

Scheme 1. Structures of PEEK and SPEEK.

acids were used as the second phase. In reference [9] the electrochemical properties of the composite membranes similarly based on sulfonated PEEK embedding some solids (silica, zirconium phosphates) were also reported. It has been shown previously [12,13] that boron orthophosphate (BPO_4) under certain conditions reveals the properties of a proton conductor. The objective of the present work is to explore the possibility to use this solid as a filler in sulfonated PEEK based composite polymer electrolyte membranes. In this study the conductivity of the composites was monitored by impedance spectroscopy as a function of water content, temperature and BPO_4 loading.

2. Experimental

2.1. Materials

PEEK obtained from Polyscience Inc. was sulfonated at room temperature using concentrated H_2SO_4 (95–98%) following the technique described in the literature [10,14]. The chemical structures of the initial and sulfonated PEEK (SPEEK) are shown in Scheme 1. The duration of the reaction was varied from 24 to 112 h in order to increase the sulfonation degree. The degree of sulfonation (DS) was determined both by elemental analysis for sulfur and by titration using the following procedure [8]. 2–5 g of SPEEK was kept in 1 M aqueous NaOH for 1 day and then back titrated with 1 M HCl using phenolphthalein as indicator. BPO_4 (B/P = 0.95) was synthesized from orthophosphoric and boric acids according to the procedure given elsewhere [12]. It was calcined at 550°C and exhibited room temperature conductivity of 7×10^{-2} S/cm at 100%RH. H_2SO_4, H_3PO_4, H_3BO_3 and all solvents used in the work were of reagent grade or better and were used as received.

2.2. Membrane preparation

The pure SPEEK membrane and composite SPEEK/BPO_4 membranes were prepared by solution casting. The SPEEK polymer was first dissolved in

Table 1
Description of membranes (all 200 μm thick)

PEEK DS (%)	BPO_4 content (wt.%)	Water uptake (wt.%)	Conductivity at (S/cm×10^3)	
			25°C	100°C
50	0	28	0.4	2.0
	20	35	0.6	9.9
	40	40	0.8	8.1
	60	55	1.1	6.6
72	0	52	2.8	14.0
	20	66	3.2	28.0
	40	79	5.0	33.0
	60	105	1.0	49.0
80	0	54	4.3	27.0
	20	74	5.1	38.0
	40	116	6.1	45.0
	60	–	20.0	45.0

dimethylacetamide (DMAc) to form a 5–10% solution and appropriate weights of BPO_4 were then added to the solution. The resulting mixture was stirred for 16–24 h. After evaporation of most of the solvent the mixture was cast onto a glass plate using a casting knife. The cast membranes were dried at room temperature overnight and then for 4–6 h at 60°C and for 12 h more at 80–120°C.

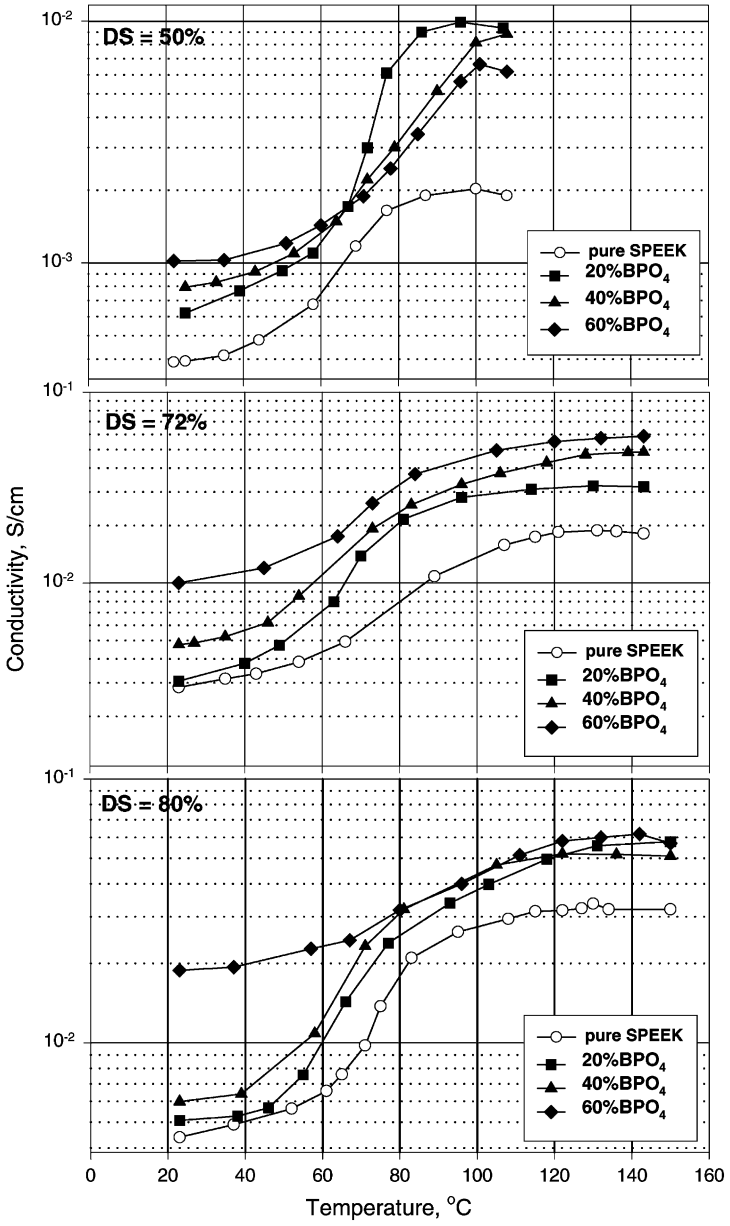

Fig. 1. Conductivity of composite BPO_4/SPEEK membranes as a function of temperature.

2.3. Electron microscopy

The morphologies of the composite polymer membranes were investigated using a scanning electron microscope (JSM-849, JEOL). Specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen and breaking them to produce a cross-section. Fresh cryogenic fractures of the samples were vacuum spray-coated with a thin layer of Au/Pd prior to viewing in SEM.

2.4. Water absorption of membranes

The water absorption of SPEEK membranes was determined from the difference in weight (W) between the dry and the swollen membranes. The membrane cast from DMAc solution after drying was weighed and then soaked in water until the weight remained constant. It was then taken out, wiped with blotting paper and weighed again. The percentage of water absorbed was calculated with reference to the weight of the dry specimen, $((W_{\text{wet}}/W_{\text{dry}}) - 1) \times 100$.

2.5. Conductivity measurements

The proton conductivity of the membrane samples was measured by ac impedance spectroscopy using a Solarton 1260 gain phase analyzer. The frequency range was $1–10^7$ Hz and oscillating voltage 50–500 mV. A sample of the fully hydrated membrane

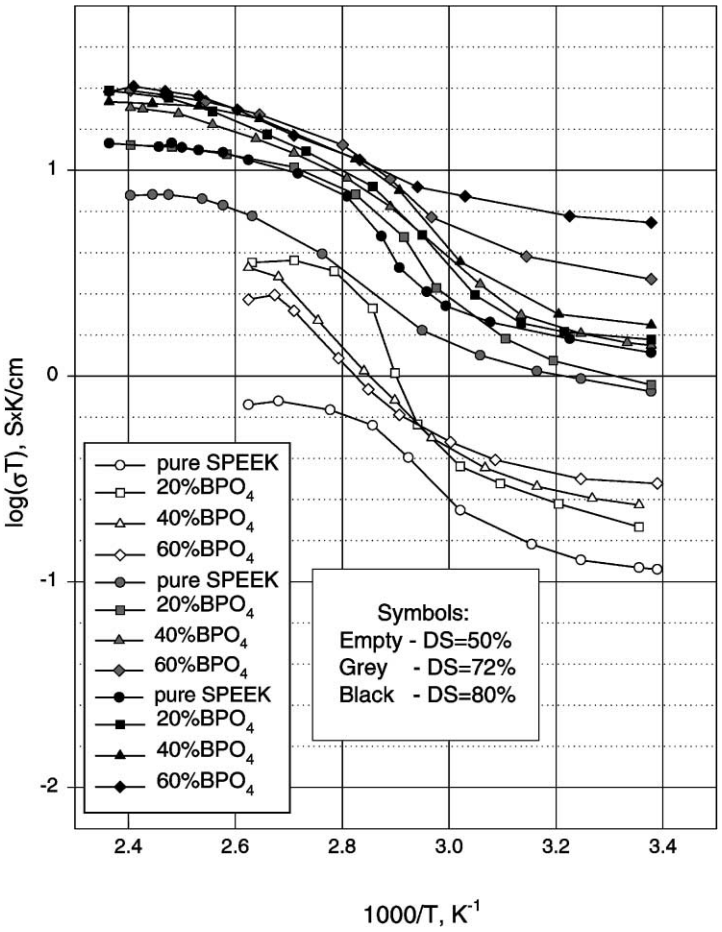

Fig. 2. Arrhenius plot for conductivity of composite BPO_4/SPEEK membranes.

with diameter 13 mm was placed in an open, temperature controlled test cell, where it was clamped between two blocking stainless steel electrodes with a permanent pressure of about 3 kg/cm^2. The electrodes have form of pistons which slide within a thick-walled glass cylinder. The disadvantage of such a cell is that it is not completely closed and the specimen may sustain some dehydration during the measurement. However, it allows to provide good electrode–specimen contact (by applying sufficient mechanical pressure using an external load) and gives an access to a larger temperature range (typically up to 150°C). Besides, the thin specimen discs (∼200 μm) are tightly compressed between blocking electrodes, and can lose water only through their edges. This loss is found negligible at low temperature over the experimental time scale.

The conductivity σ of the samples in transverse direction was calculated from the impedance data using the relation $\sigma = d/RS$ where d and S are the thickness and face area of the sample respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis. The impedance data were corrected for the contribution from the empty and short-circuited cell.

3. Results

Sulfonation of PEEK up to DS $\leq$ 45% yields membranes with poor conductivity [5] typically less than 10^{-5} S/cm. Therefore, only membranes with DS $\geq$ 50% are discussed in this communication. In Table 1 the composition of the samples is presented together with their water uptake at room temperature and their conductivity at 25 and 100°C. All the samples were 0.2 mm thick. The curves of temperature dependence of the membrane conductivity are shown in Fig. 1. It can be seen from the figure that composite membranes always exhibit higher conductivity than the pure SPEEK samples. The greatest increase in σ is observed for 50%DS SPEEK, where it is in average five-fold, while in the case of 72% SPEEK it is three-fold and for 80%DS the gain in conductivity does not exceed 100% at least above 70°C. That is evidently due to the fact that the intrinsic conductivity of 50%DS polymer is about one order of magnitude lower than that of 72%DS and 80%DS materials and thus the impact of the highly conductive BPO_4 in the former case is better pronounced.

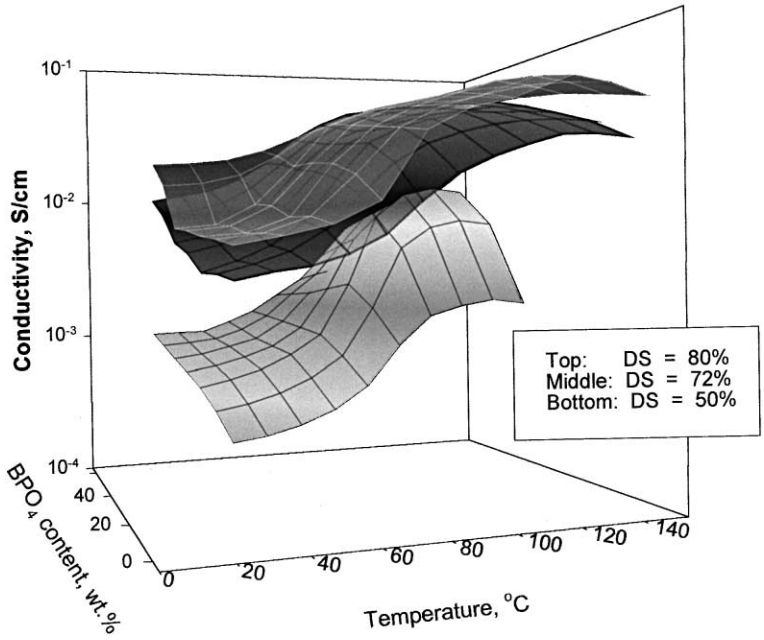

Fig. 3. Influence of temperature and BPO_4 content on the conductivity of composite membranes with various DS.

It is worth noting that the conductivity of 50%DS membranes decreases drastically above 110°C (the values beyond plot range not shown in the Fig. 1) which signals that the thermal stability of their proton conductivity is significantly inferior to that of the higher sulfonated materials. Data presented in Fig. 1 are also plotted in the Arrhenius coordinates (Fig. 2). The form of the curves in the plot is different from the straight lines which suggests that the charge transfer mechanism in the composite membranes is controlled not only by thermally activated diffusion, but depends also on some other phenomenon. This will be dealt with in the following discussion.

The conductivity of the three batches of PEM as a three dimensional function of BPO_4 content and temperature is depicted in Fig. 3. It gives a clear illustration of the fact that with increasing DS the surface of response σ is shifting upward almost proportionally to the sulfonation degree. It should be mentioned that the conductivity measurements have been repeated over several months on the specimens kept in water between the tests, and were found to display reasonably good reproducibility.

Comparing the foregoing results with the electrical properties of some other composite solid electrolytes reported in the literature, it can be seen that the SPEEK/BPO_4 membrane surpasses many of them in conductivity. For example sulfonated polysulfone/heteropolyacids (HPA) composite membranes [15] exhibited $\sigma_{(70^\circ C)} = 2 \times 10^{-3}$ S/cm, while

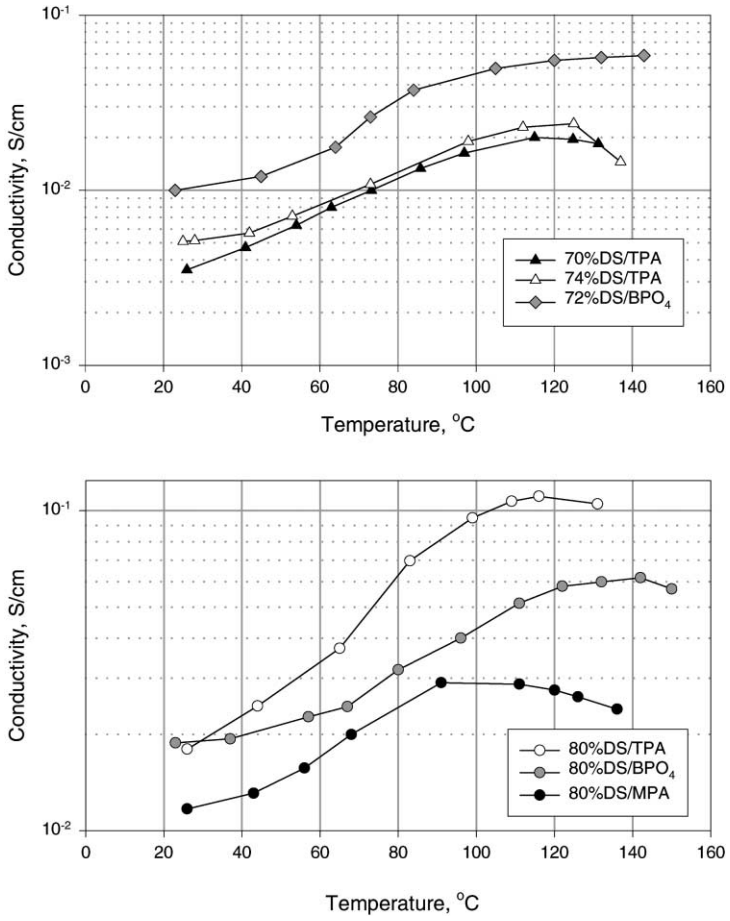

Fig. 4. Conductivity of SPEEK composite membranes containing BPO_4 along with the conductivity of same membranes containing HPAs.

tin–mordenite solid electrolyte embedded into polyacrylates [16] displayed room temperature conductivity below $\sigma = 5 \times 10^{-4}$ S/cm. In Fig. 4 some results of our previous study on HPA/SPEEK membranes are depicted in common plots along with the data of this work. All these data were obtained at the same 60 wt.% loading of the solid. One can see that the BPO_4–SPEEK composite at 72%DS is superior to both 70 and 74% SPEEK mixed with tungstophosphoric acid (TPA) which is the most efficient among HPAs. At 80%DS the SPEEK–BPO_4 membrane is surpassed in conductivity only by TPA–SPEEK composite, while molybdophosphoric acid (MPA) is less efficient as solid electrolyte filler than BPO_4.

4. Discussion

In Fig. 5 the apparent activation energies E_a for composite membrane conduction are depicted as functions of content of solid. It can be seen that these values fall on unexpectedly smooth curves passing through maximums, whose heights decrease with DS. Such an ordered pattern is suggestive of the presence of a phenomenon attendant on BPO_4 embedding, which produces strong impact on the polymer properties. It can be assumed that the formation of a new interface with the solid in the bulk of SPEEK is responsible for the increase of the apparent activation energy. Following decrease of E_a with content of solid is obviously due to the increase in the composite of the volume fraction of highly conductive solid electrolyte.

It can be instructive to consider how the observed conductivity of the polymer–solid electrolyte composites correlate with the theoretically calculated conductivity of two phase mixtures. Both phases (SPEEK and solid electrolyte: HPA or BPO_4) contribute to the proton conductivity of the mixture and therefore an effective medium theory (EMT) can reasonably be applied to describe the conductivity isotherms. It is assumed that solid electrolyte particles have spherical symmetry and are embedded in the polymer matrix to produce space filling random mixture. The general self-consistent equation for the conductivity (σ) of multiphase macroscopically uniform mixture within the framework of EMT has the form [17,18]

$$\sum_{i=1}^{n} \frac{v_i(\sigma_i - \sigma)}{L^*\sigma_i + (1 - L^*)\sigma} = 0 \quad (1)$$

Here σ_i are the conductivities of the individual phases (polymer or solid electrolyte), participating in proton transport, L^* the depolarization factor and v_i the volume fraction of the corresponding phase. Solutions of Eq. (1) were obtained with the fixed parameters as follows. σ_1 corresponded to the room temperature

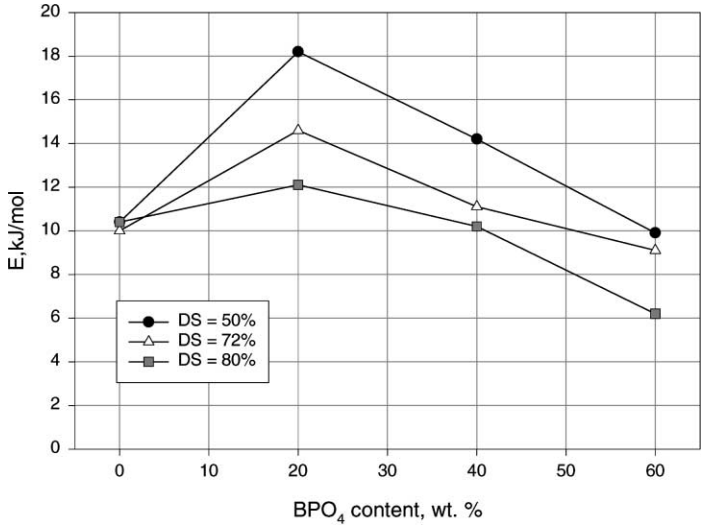

Fig. 5. Apparent activation energies for conductivity of the composite membranes as function of solid electrolyte content.

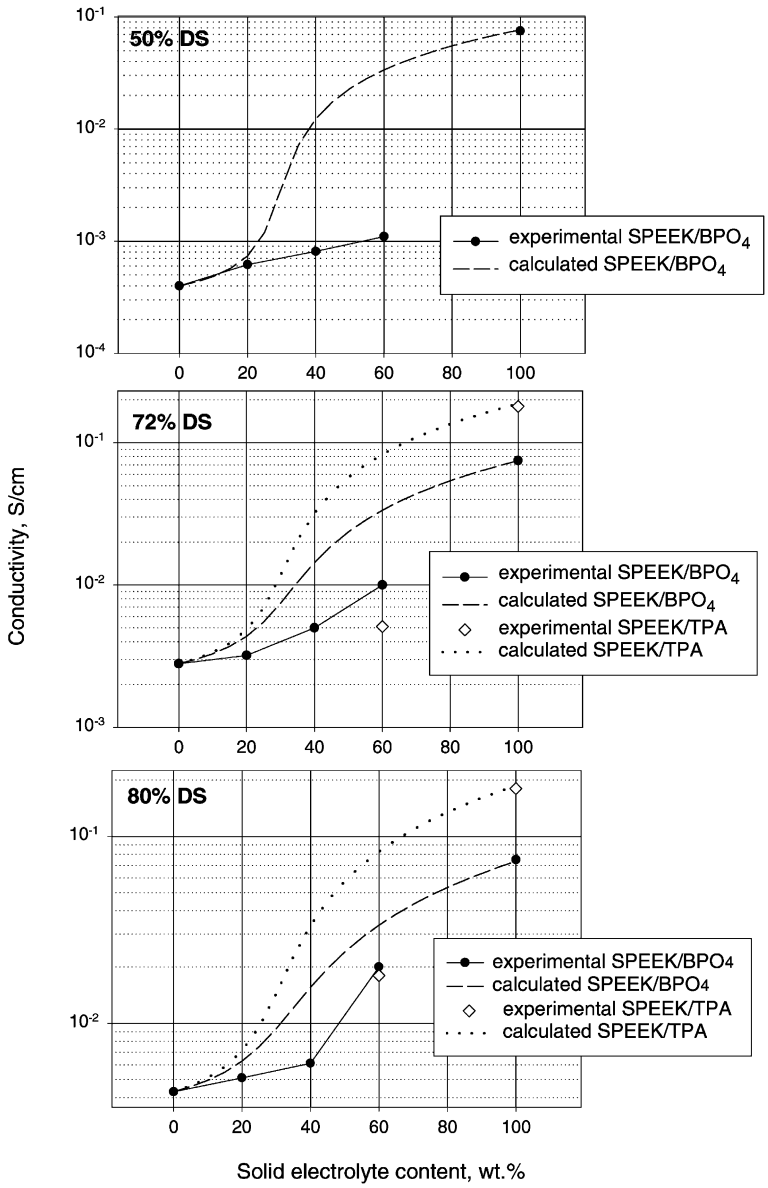

Fig. 6. Comparison of experimentally measured ambient temperature conductivity with that calculated using the EMT approach.

conductivity of pure SPEEK polymer with appropriate DS, σ_2 was the conductivity of solid electrolyte which was equal to $\sigma_2 = 7.5 \times 10^{-2}$ S/cm for BPO_4 and $\sigma_2 = 1.7 \times 10^{-1}$ S/cm for TPA, and the depolarization factor was chosen as $L^* = 0.3$ corresponding to single sphere as indicated in [18].

From Fig. 6, where the curves of calculated conductivities are shown along with experimental results, it can be seen that all the composite membranes display much lower conductivity than is predicted by EMT. The source of this discrepancy may presumably be the difference between the properties of unsupported

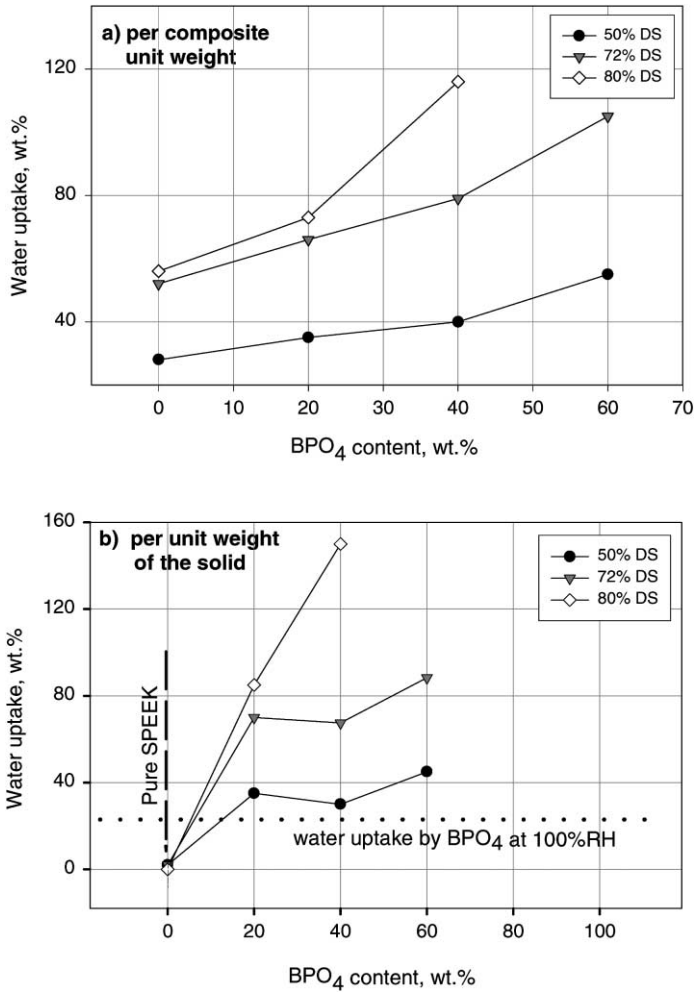

Fig. 7. Water uptake of composite membranes as function of BPO_4 content.

hydrated solid electrolytes and that of solid electrolytes embedded into the polymeric matrix. Enfolded by the polymer matrix, some grains of BPO_4 or HPA may occur to be protected from contact with water which is why they may be much less conductive than fully hydrated unsupported solids. Conductivity of solid electrolytes is strongly dependent on their hydration degree since the transport of protons essentially involves hydrated species, such as the hydronium ion etc. Moreover, the formation of mobile protons from acid sites generally occurs through hydrolysis which makes water the indispensable component of the solid electrolytes.

Ambient temperature isotherms of water absorption by BPO_4/SPEEK membranes are depicted in Fig. 7a. It can clearly be seen that swelling increases both with DS and with BPO_4 content, and this increase as function of the latter variable is most pronounced for specimens with higher DS. Fig. 7b depicts the water uptake calculated per unit mass of the solid as function of the solid content. It is evident that the water uptake accounted for by BPO_4 incorporated into composite membranes substantially exceeds the sorption capacity of the unsupported solid electrolyte. It can be observed that the amount of this extra water per unit mass of the solid increases with both DS and BPO_4

content. The reason for this can only be the emerged porosity of the composite membranes while the pure SPEEK is known as essentially nonporous [5–11].

This is indeed confirmed by the results of SEM analysis, some examples of which can be seen on the micrographs presented in Fig. 8. It is evident (Fig. 8a) that pure SPEEK polymer is nonporous. Introducing the solid electrolyte into the polymer matrix had a profound impact on the polymer structure. Fig. 8b indicates that the composite membranes are highly

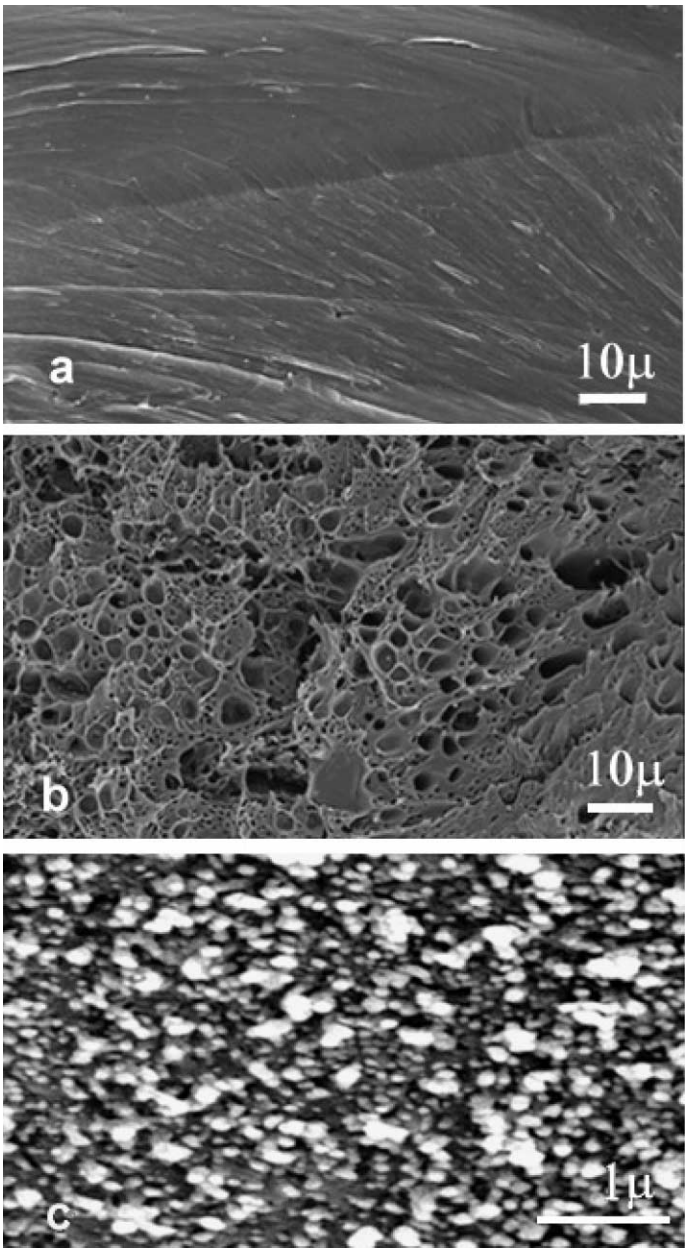

Fig. 8. SEM micrographs of pure SPEEK (a) and composite BPO_4/SPEEK membranes at (b) 40 wt.% and (c) 60 wt.% loading.

porous showing pore diameters in the range 3–10 μm. A higher magnification (Fig. 8c) reveals the structure of the pore walls, which consist of BPO_4 particles of 0.1–0.3 μm, apparently embedded in the SPEEK matrix. A similar structure was observed in the case of HPA/SPEEK composite membranes. The pore formation in the composite BPO_4/SPEEK membranes could also be responsible for the increase of the conduction activation energy compared to pure SPEEK membranes (Fig. 5). It is interesting to note that the highest maximum in E_a versus BPO_4 content dependencies in Fig. 5 is consistent with greatest discrepancy between calculated and measured conductivity (Fig. 6) which was observed for DS = 50%. As to DS = 80%, in this case the calculated conductivity was much closer to the measured values (Fig. 6), which also accords with the smallest maximum in Fig. 5. Thus one may conclude that the influence of solid electrolyte incorporation into the polymer matrix is twofold; on the one hand it gives rise to some porosity which is not beneficial for the membrane electric properties, and on the other hand it increases the composite conductivity due to higher intrinsic conductivity of the solid electrolyte.

The mechanism of pore formation during the preparation process seems to be elusive. It can be assumed however, that in the course of stirring of the mixture of close-grained powder of BPO_4 with SPEEK dissolved in DMAc, fine air bubbles could occur within solidifying mass. It is also conceivable as another possibility, that the solid powder introduced into the polymer solution contains some humidity, in spite of the fact that it was dried before mixing. As DMAc, the solvent used in membrane preparation is completely miscible with water, the presence of water may initiate a process similar to phase-inversion. Therefore, it may bring about the formation of solid layers of the polymer (with BPO_4 occluded in it) while water-diluted solvent will segregate into zones which then form the pores.

As the pores in composite SPEEK based membranes are of capillary size, their elimination could provide a challenging task. It must, however, be emphasized that as SPEEK is not intrinsically porous, there should exist a way to prepare a composite free from the pores. More experiments are needed to improve the preparation technique in order to obtain nonporous membranes which in compliance with theoretical prediction would presumably possess still higher conductivity.

5. Conclusion

A series of composite membranes have been prepared by incorporation of the BPO_4 fine powder into partially sulfonated PEEK polymer. The conductivity of these membranes largely exceeds that of the pure SPEEK polymer. In some instances it was even higher than the conductivity of HPAs/SPEEK composites, despite the fact that the intrinsic conductivity of HPAs is about twice that of BPO_4 under the same conditions (ambient temperature, fully hydrated). The composite membranes proved to be mechanically strong and flexible at DS < 80% and their conductivity has not been affected by storage in water for several months.

However the observed conductivity of the composite membranes did not reach the values predicted by the EMT. For example, according to EMT, mixing with 60 wt.% of BPO_4 which possesses an ambient temperature conductivity of 7.5×10^{-2} S/cm, should endow the membranes with the conductivity of about 2×10^{-2} S/cm. In fact it was 50% less for DS = 80%, half as much when DS = 72% and more than one order of magnitude less in the case of DS = 50%. It was found that the reason for that is associated with the largely increased porosity of the membranes which accompanies composite preparation. The preparation technique should therefore be improved in order to diminish the composite membrane porosity.

The results of the present study nevertheless evidences that BPO_4/SPEEK membranes outperform all the other SPEEK based membranes and can therefore be regarded as having some potential in electrochemical applications, such as fuel cells or hydrogen sensors. It may be worth recalling that BPO_4 is a quite inexpensive solid made by a simple reaction between inexpensive phosphoric and boric acids.

References

[1] G. Pourcelly, C. Gavach, in: Ph. Colomban (Ed.), Proton Conductors: solids, membranes and gels, Materials and Devices, Cambridge University Press, New York, 1992, p. 294.
[2] K.D. Kreuer, Chem. Mater. 8 (1996) 610.
[3] A.E. Steck, C. Stone, in: 2nd International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Montreal, July 1997, p. 792.
[4] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 66.

[5] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, J. Membr. Sci. 173 (2000) 17.
[6] T. Kobayashi, M. Rikukawa, K. Sanui, N. Ogata, Solid State Ionics 106 (1998) 219.
[7] J. Kerres, A. Ullrich, Th. Haring, in: 3rd International Symposium on New Materials for Electrochemical Systems, Montreal, July 1999, p. 230.
[8] D.J. Jones, J. Rozière, L. Tchicaya, in: 3rd International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Montreal, July 1999, p. 248.
[9] B. Bonnet, D.J. Jones, J. Rosière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, B. Bauer, A. Peraio, E. Ramunni, J. New Mater. Electrochem. Syst. 3 (2000) 87.
[10] X. Jin, M.T. Bishop, T.S. Ellis, F.E. Karasz, British Polym J. 17 (1985) 4.
[11] S.D. Mikhailenko, S.M.J. Zaidi, S. Kaliaguine, Polymer Sci. B Polymer Physics 38 (2000) 1386.
[12] S.D. Mikhailenko, J. Zaidi, S. Kaliaguine, J. Chem. Soc., Faraday Trans. 94 (1998) 1613.
[13] S.D. Mikhailenko, J. Zaidi, E. Ghali, S. Kaliaguine, J. New Mater. Electrochem. Syst. 2 (1999) 161.
[14] M.T. Bishop, F.E. Karasz, P.S. Russo, K.H. Langley, Macromolecules 18 (1985) 86.
[15] M.W. Park, J.C. Yang, H.S. Han, Y.G. Shul, T.H. Lee, Y. Cho, Denki Kagaku 64 (1996) 743.
[16] N. Rao, T.P. Andersen, P. Ge, Solid State Ionics 72 (1994) 334.
[17] C.W. Nan, D.M. Smith, Mater. Sci. Eng. B 10 (1991) 99.
[18] C.W. Nan, Prog. Mater. Sci. 37 (1993) 1.