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Proton-conducting hydrogel membranes

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Proton-conducting poly(acryl amide) hydrogels are prospective materials for application in electrochemical devices working at ambient temperatures. In the present paper, the conducting properties of hydrogels doped with H_3PO_4 or H_2SO_4 are analysed in connection with such features of the hydrogel membrane as sorption and permeation of solvents and tensile strength. It is shown that these features depend on the concentration of the acid used as protonic dopant as well as on the composition of the hydrogel membrane, i.e. the amount of crosslinking and gelation agents used in the gel synthesis. © 1998 Elsevier Science Ltd.

(Keywords: hydrogels; conductivity; solvent uptake and permeation)

INTRODUCTION

The growing interest in proton-conducting polymeric electrolytes arises from the possibility of their application in various electrochemical devices such as sensors, electrochromic windows and displays, and ambient-temperature fuel cells[1,2]. Most systems investigated so far[1–4] are based on linear or branched polymers having basic sites in the main chain or a side chain and doped with strong acids such as H_3PO_4 or H_2SO_4. A review of these studies has recently been published[1]. These protonic electrolytes exhibit high ionic conductivity but suffer from a propensity for attack of the acids in the presence of even traces of moisture. This limits their application, especially in fuel cells or humidity sensors.

Recently a new group of proton-conducting polymeric electrolytes, based on poly(acryl amide) hydrogels doped with H_3PO_4 or H_2SO_4, has been developed and described[5–7]. These systems exhibit conductivities exceeding $10^{-2}\,S\,cm^{-1}$ at ambient conditions. Conductivity depends on the acid and water concentration[6]. It has been shown that these hydrogel electrolytes are stable up to 70°C but undergo degradation connected with a loss of ionic conductivity at higher temperatures[7]. The structure and thermal characteristics of these electrolytes have been studied by the techniques of Fourier transform infra-red spectroscopy (*FT*i.r.) and differential scanning calorimetry (d.s.c.), respectively. *FT*i.r. studies showed various degrees of dissociation of H_3PO_4 in the hydrogel electrolytes which can be associated with the possibility of a Grotthus type of proton conduction mechanism[7]. By contrast, mostly HSO_4^- anions are detected by *FT*i.r. in the case of H_2SO_4-doped hydrogels, connected with the vehicle type of the proton conduction for these electrolytes[7]. D.s.c. studies confirmed previous conductivity investigations in showing thermal stability of the hydrogel electrolytes up to 70°C[6].

The hydrogel electrolytes are prospective materials for application in various electrochemical devices working at ambient temperatures, such as electrochromic windows, fuel cells or humidity sensors. Therefore it is important to study water transport through the hydrogel membranes together with the conduction process in these electrolytes. In the present paper, ionic conductivity of the hydrogel electrolytes is analysed in connection with properties of the hydrogel membranes such as water uptake, permeation of water and methanol, and tensile strength. The influence of these properties on the conductivity and structure of the hydrogel electrolytes will be discussed.

EXPERIMENTAL

Sample preparation

Proton-conducting hydrogel electrolytes were prepared according to the procedure described elsewhere[6]. Acrylamide (AAM) (Eastman Kodak, reagent grade), *N,N′*-methylenebisacrylamide (MBAA; acting as a crosslinking agent) and agar (Aldrich, reagent grade; acting as a gelation agent) were mixed together in a glass flask and dissolved in deionized water. The mixture was stirred magnetically until the visible dissolution of all solid components. This was followed by the addition of a few drops of hydrogen peroxide to initiate the polymerization reaction. Finally, stoichiometric amounts of H_3PO_4 (85 mass% water solution) or H_2SO_4 (~50 mass% water solution) were added. The conditions of the polymerization reaction were the same as those described in previous papers on acrylamide hydrogels[6,7]. The final thickness of hydrogel membranes varied between 300 and 500 μm, depending on sample composition. The final concentration of water in the hydrogel electrolytes was checked by a gravimetric method from knowledge of the initial amount of solid components.

Experimental techniques

Impedance spectroscopy. Ionic conductivity of the proton-conducting hydrogels was determined with the complex impedance method. The samples were sandwiched between two stainless steel blocking electrodes and placed in a temperature-controlled furnace. The impedance measurements were carried out on a Solartron Schlumberger impedance analyser type 1255 over the frequency range

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from 5 Hz to 500 kHz. The temperature range of impedance studies was 20–100°C.

Solvent sorption measurements. The hydrogel samples (approximately 1 cm × 1 cm with a thickness around 400 μm) were initially dried in open air up to water content of 15–20 mass%. This was followed by immersion of these samples in the desired solution in a glass container at room temperature for up to 1 day (in the case of water sorption by hydrogel membranes) or up to 1000 s [in the case of studies of the sorption of a water solution of CH_3OH (2 M) and H_2SO_4 (2.5 M) by hydrogels]. Following immersion the gels were removed from the container, blotted dry and weighed immediately in a closed weighing bottle. Mass% of the absorbed solution was calculated with respect to the mass of the dry polymer membrane.

From the absorption data the 'intrinsic' permeation (S) within the membrane can be calculated. The 'intrinsic' permeation is defined as the rate at which a solution is transported within a membrane without application of an external driving force. It is calculated from the initial linear portion of the water sorption *versus* time data. The relationship used is as follows:

S = (grams of the solution absorbed
× thickness of membrane/time of sorption
× area of membrane × pressure)

where pressure = atmospheric pressure exerted on film in cm Hg and area = area of membrane exposed to the solution.

Tensile strength experiments. The tensile strength of hydrogel membranes (T) was calculated as the pressure required to break the hydrogel foil 1 cm wide and 4 cm long. The experiments were performed at room temperature for samples humidified to the saturation level.

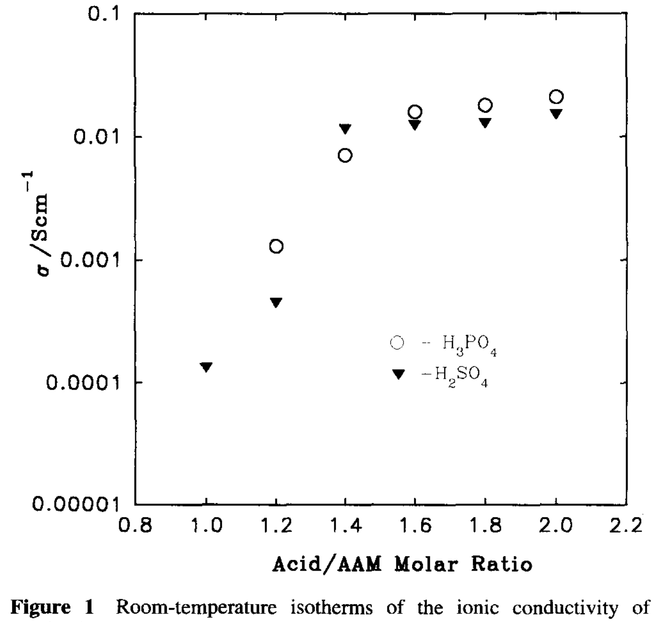

Figure 1 Room-temperature isotherms of the ionic conductivity of acrylamide (AAM) based protonic gel electrolytes as a function of the acid/AAM molar ratio. Data for samples doped with H_3PO_4 or H_2SO_4. Samples contain 20 mass% of water

RESULTS

In *Figure 1* isotherms of ambient-temperature ionic conductivity as a function of the acid concentration are shown for hydrogel electrolytes doped with H_3PO_4 or H_2SO_4. The conductivity data are similar to those presented previously for analogous electrolytes[7]. Conductivity increases with an increase in acid concentration and exceeds 10^{-2} S cm^{-1} for samples with acid/acrylamide (AAM) ratio higher than 1.4:1. For acid/AAM ratios higher than 1.6:1 conductivity remains almost constant and conductivities measured for hydrogels doped with H_3PO_4 and H_2SO_4 are similar.

Figure 2 presents changes in the sorption of a water solution of CH_3OH (2 M) and H_2SO_4 (2.5 M) as a function of acid/AAM ratio. Data obtained for H_2SO_4 (*Figure 2a*) and H_3PO_4 (*Figure 2b*) doped hydrogels are presented. The absorption of this solution by the hydrogel electrolyte after soaking a membrane in the solution for 1000 s is measured according to the procedure described above. Sorption of the

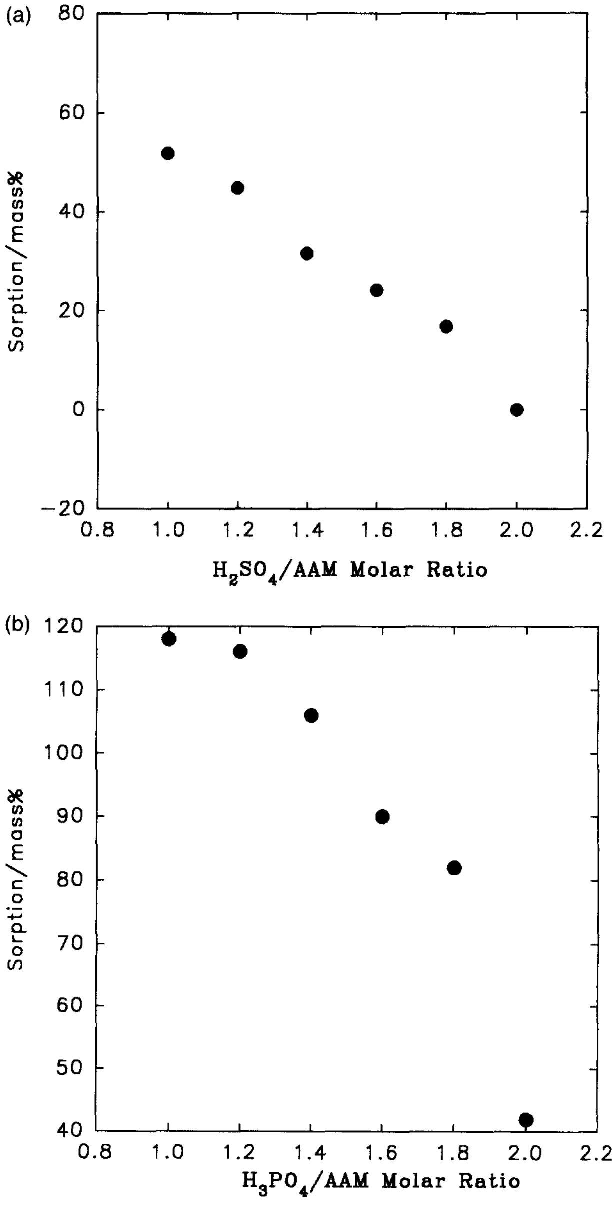

Figure 2 Sorption of the water solution of 2 M CH_3OH and 2.5 M H_2SO_4 by the (a) H_2SO_4- and (b) H_3PO_4-doped hydrogels as a function of acid/AAM molar ratio. Hydrogels were immersed in the solution for 1000 s

solution by the hydrogel decreases with an increase in H_2SO_4/AAM molar ratio. The relationship observed is almost linear. Similar trends are obtained for H_2SO_4- and H_3PO_4-doped hydrogel electrolytes, for which the sorption of water as a function of acid/AAM molar ratio is shown in *Figure 3a* and *Figure 3b*, respectively. Hydrogels were soaked in water for up to 24 h. Absorption of water decreases with a decrease in the agar concentration (see *Figure 4a*) and decreases with an increase in the concentration of MBAA (see *Figure 4b*).

Permeation of the water solution of CH_3OH (2 M) and H_2SO_4 (2.5 M) through the hydrogel membrane doped with H_2SO_4 is shown in *Figure 5a* as a function of H_2SO_4/AAM molar ratio. An initial increase in the permeation is followed by a decrease for samples of H_2SO_4/AAM ratio higher than 1.6:1. In the case of the H_3PO_4-doped electrolytes (see *Figure 5b*) permeation of water initially increases with an increase in H_3PO_4/AAM molar ratio. For H_3PO_4/AAM ratios higher than 1.6:1, a small decrease in the permeation rate is observed.

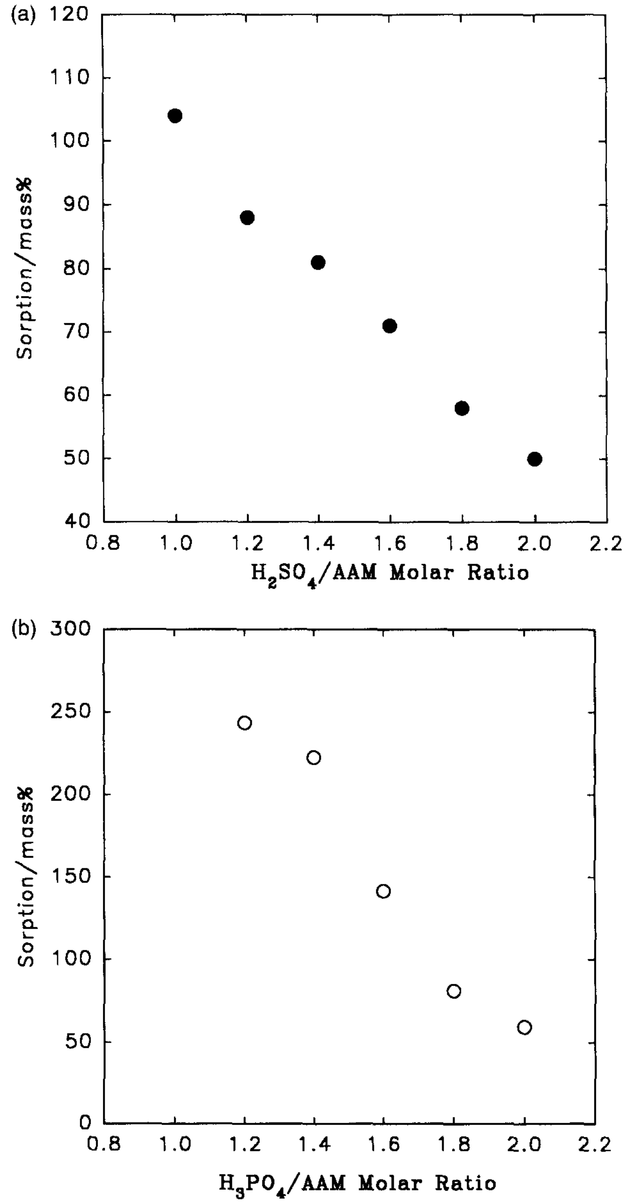

Figure 3 Sorption of water by the (a) H_2SO_4- and (b) H_3PO_4-doped hydrogels as a function of acid/AAM molar ratio. Hydrogels were immersed in water for 24 h

In *Figure 6* changes in the tensile modulus as a function of acid/AAM ratio are compared for H_3PO_4- and H_2SO_4-doped hydrogels. Tensile modulus measured for H_3PO_4-doped hydrogel electrolytes is about one order of magnitude higher than that for the analogous H_2SO_4-doped electrolytes. For both systems tensile modulus decreases with an increase in acid concentration.

DISCUSSION

It was suggested in previous studies that water has a plasticizing effect in H_2SO_4- or H_3PO_4-doped acrylamide hydrogels[6]. D.s.c. studies showed that the glass transition temperature (T_g) of hydrogels decreases with decreasing water concentration[6]. A decrease in T_g has also been seen for samples with high content of crosslinking agent (MBAA) and low amount of gelation agent (agar). This is coupled with a low water uptake of such membranes as shown in *Figure 4a* and *Figure 4b* and confirms the plasticizing effect of water on the hydrogel matrix. Therefore hydrogels containing a higher amount of water should

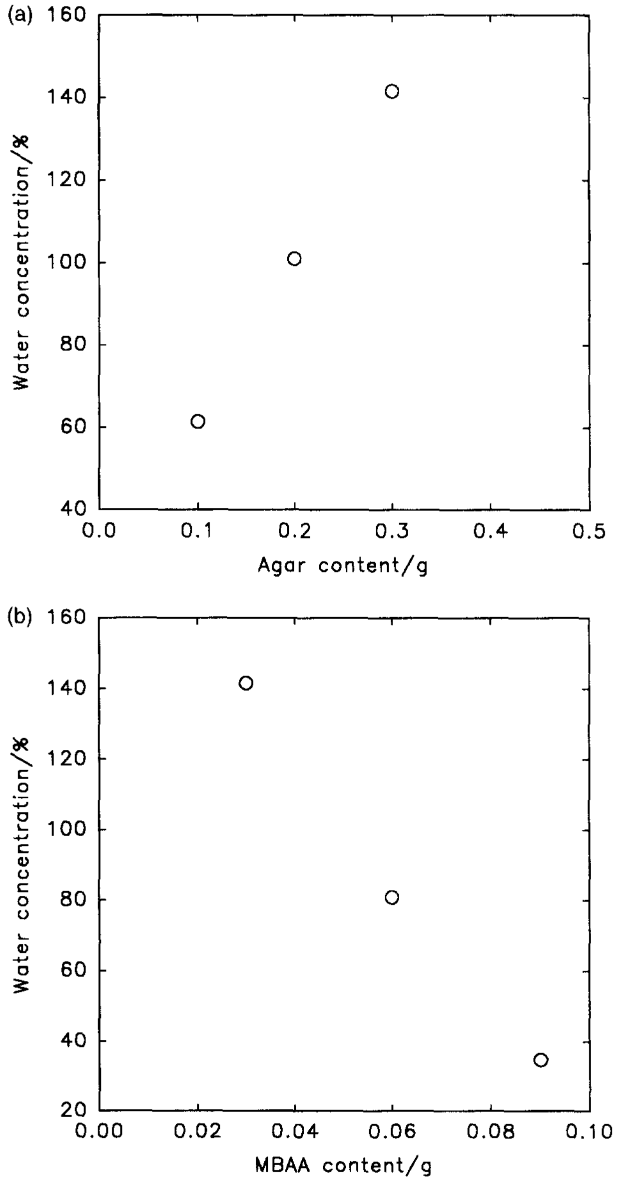

Figure 4 Sorption of water by the AAM/H_3PO_4 hydrogels as a function of (a) agar concentration and (b) MBAA concentration

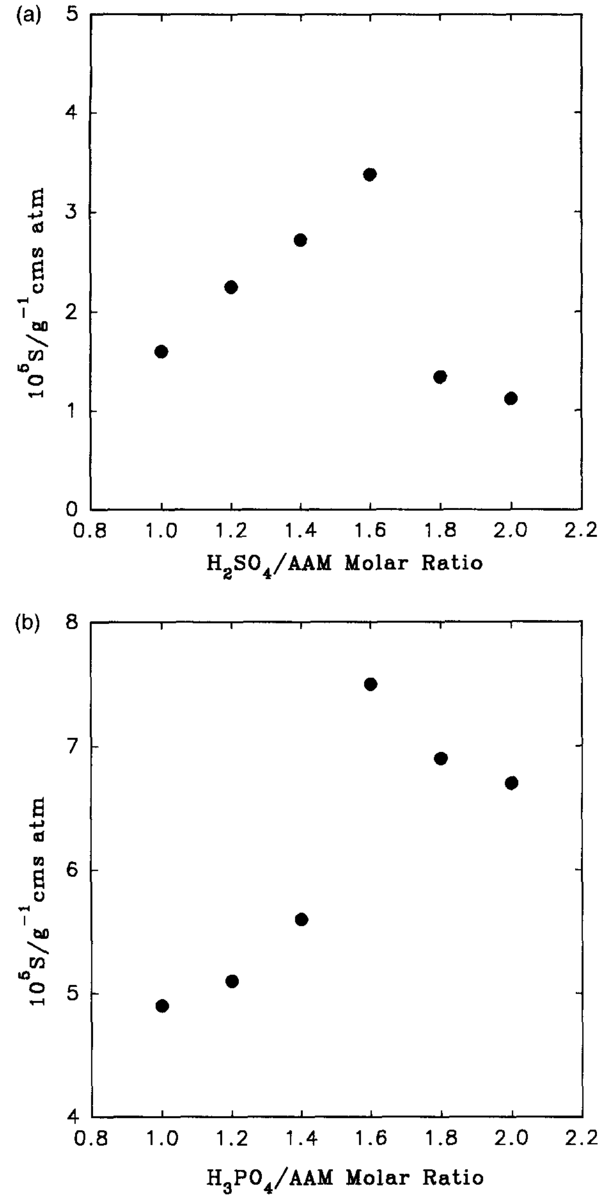

Figure 5 Permeation (*S*) of water solution of 2 M CH_3OH and 2.5 M H_2SO_4 through (a) H_2SO_4- and (b) H_3PO_4-doped hydrogel membranes as a function of acid/AAM molar ratio

be more flexible, which is associated with their higher tensile strength. This latter suggestion is confirmed by the studies of tensile modulus performed for the H_3PO_4- and H_2SO_4-doped hydrogels (see *Figure 6*). Samples with high acid/AAM ratio, i.e. having low water uptake, are less flexible and creep more easily under the applied pressure than hydrogel electrolytes with low acid/AAM ratio (higher flexibility, higher water uptake). As shown in *Figures 2* and *3*, water uptake decreases with an increase in acid concentration. Acid molecules occupy certain positions in the hydrogel matrix and some of them can be chemically bonded to the hydrogel host, as found from *FT*i.r. experiments[7]. Therefore, for the high acid concentration, the availability of 'free volume' inside the hydrogel matrix for water molecules is limited. This is associated with lower water uptake, lower flexibility and lower tensile strength. The trends observed here are similar to those described for a variety of polymeric gels in a recent review[8].

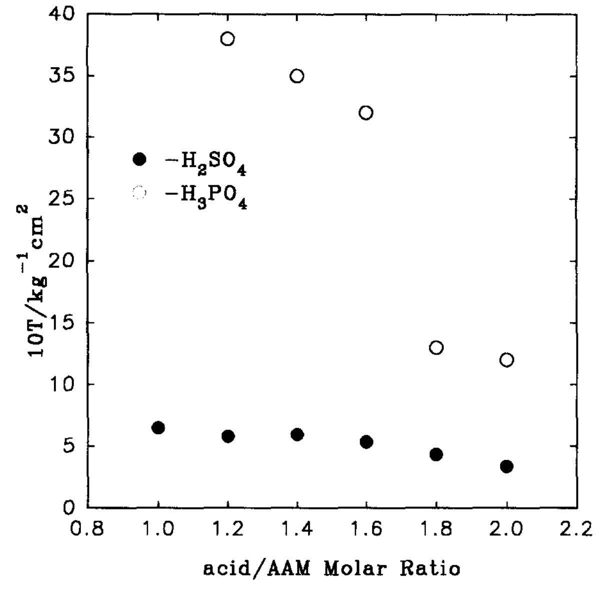

Figure 6 Tensile modulus (*T*) measured as a function of AAM/acid ratio for AAM/H_2SO_4 and AAM/H_3PO_4 hydrogels

The sorption of water by H_3PO_4 membranes is higher than that by H_2SO_4 hydrogels as a consequence of the higher flexibility of the former and its higher tensile strength. An increase in agar concentration additionally increases polymer flexibility owing to the role of agar acting as a sorbent of water molecules, which is also confirmed by d.s.c. studies[6,7] showing a lowering in T_g for samples with high agar concentration. A decrease in the solution uptake is also connected with a decrease in permeation of a particular solution through the hydrogel membrane.

For hydrogel electrolytes of low water content (typically 20–30 mass%) an increase in the conductivity with an increase in acid/AAM molar ratio should not be related to the presence of water. The water content for these samples is too low to account for the ionic transport. For these electrolytes the conduction mechanism is most probably similar to that described by Lassegues and co-workers for 'dry' poly(acryl amide)-based protonic electrolytes[1,4]. Effective medium theory calculations performed for the AAM/H_3PO_4 hydrogels as a function of water concentration in a hydrogel membrane confirmed this hypothesis[7]. However, as has also been shown from these effective medium theory calculations in the presence of an excess of water, the proton transport through the hydrogel is 'liquid-like' and occurs through the residual water present in the hydrogel structure. Above the saturation concentration of water in the hydrogel, the conductivity is weakly dependent on humidity and is higher than 10^{-2} S cm^{-1} at ambient temperatures. Therefore an increase in water concentration resulting from the sorption of water from the water solution of acids results not only in a change in the hydrogels' flexibility, but also in an increase in ionic conductivity.

CONCLUSIONS

It is shown that various physico-chemical properties of hydrogel electrolytes depend on the acid/AAM molar ratio as well as on the concentration of water in the hydrogel membrane. The solution uptake and permeation as well as tensile strength decrease with an increase in the acid/AAM ratio. The higher water content is coupled with flexibility of the hydrogel membrane as well as with the increase in ionic conductivity.

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REFERENCES

1. Lassegues, J. C., in *Proton Conductors: Solids, Membranes and Gel—Materials and Devices*, ed. P. Colomban. Cambridge University Press, Cambridge, 1992, Ch. 20.
2. Przyłuski, J. and Wieczorek, W., *Synth. Met.*, 1991, **45**, 323.
3. Donoso, P., Gorecki, W., Berthier, C., Defendini, F., Poinsignon, C. and Armand, M. B., *Solid State Ionics*, 1988, **28–30**, 969.
4. Lassegues, J. C., Desbat, B., Trinquet, O., Cruegge, F. and Poinsignon, C., *Solid State Ionics*, 1989, **35**, 17.
5. Połtarzewski, Z. and Przyłuski, J., in *Proc. First Int. Symp. New Materials for Fuel Cell Systems*, Montreal, 9–13 July 1995, ed. O. Savadogo. Montreal Polytechnique Publishers, Montreal, 1995.
6. Wieczorek, W., Florjańczyk, Z. and Stevens, J. R., *Electrochim. Acta*, 1995, **40**, 2327.
7. Wieczorek, W. and Stevens, J. R., *Polymer*, **38**, 2057
8. Schroder, U. P. and Opermam, W., in *Physical Properties of Polymeric Gels*, ed. J. P. Cohen Addad. Wiley and Sons Ltd, Chichester, 1996, Ch. 2.