

Alternative Fuel Technologies

This paper is published as part of the high-profile series of PCCP special issues on Alternative Fuel Technologies.

Guest edited by Joachim Maier (MPI Stuttgart), Dirk Guldi (Universität Erlangen-Nürnberg), and Adriano Zecchina (University of Torino), and published in selected 2007 print issues of PCCP, all papers are collected online on a dedicated website:

www.rsc.org/pccp/altfuel

Visit the website for both cutting edge research papers and authoritative review articles by leaders in a range of fields of critical importance to the world today

- ▶ fuel cells
- ▶ electrochemical energy conversion
- ▶ supercapacitors and molecular materials
- ▶ hydrogen storage
- ▶ solar energy conversion
- ▶ biohydrogen

Sign up for RSS alerts to have the latest articles delivered directly to your desktop



RSC Publishing

www.rsc.org/pccp/altfuel

Registered Charity Number 207890

Intermediate temperature proton conductors for PEM fuel cells based on phosphonic acid as protogenic group: A progress report

H. Steininger,^a M. Schuster,^b K. D. Kreuer,^{*a} A. Kaltbeitzel,^c B. Bingöl,^c W. H. Meyer,^c S. Schauff,^c G. Brunklaus,^c J. Maier^a and H. W. Spiess^c

Received 21st December 2006, Accepted 30th January 2007

First published as an Advance Article on the web 27th February 2007

DOI: 10.1039/b618686f

The melting behaviour and transport properties of straight chain alkanes mono- and difunctionalized with phosphonic acid groups have been investigated as a function of their length. The increase of melting temperature and decrease of proton conductivity with increasing chain length is suggested to be the consequence of an increasing ordering of the alkane segments which constrains the free aggregation of the phosphonic acid groups. However, the proton mobility is reduced to a greater extent than the proton diffusion coefficient indicating an increasing cooperativity of proton transport with increasing length of the alkane segment. The results clearly indicate that the “spacer concept”, which had been proven successful in the optimization of the proton conductivity of heterocycle based systems, fails in the case of phosphonic acid functionalized polymers. Instead, a very high concentration of phosphonic acid functional groups forming “bulky” hydrogen bonded aggregates is suggested to be essential for obtaining very high proton conductivity. Aggregation is also suggested to reduce condensation reactions generally observed in phosphonic acid containing systems. On the basis of this understanding, the proton conductivities of *poly(vinyl phosphonic acid)* and *poly(meta-phenylene phosphonic acid)* are discussed. Though both polymers exhibit a substantial concentration of phosphonic acid groups, aggregation seems to be constrained to such an extent that intrinsic proton conductivity is limited to values below $\sigma = 10^{-3} \text{ S cm}^{-1}$ at $T = 150^\circ\text{C}$. The results suggest that different immobilization concepts have to be developed in order to minimize the conductivity reduction compared to the very high intrinsic proton conductivity of neat phosphonic acid under quasi dry conditions. In the presence of high water activities, however, (as usually present in PEM fuel cells) the very high ion exchange capacities (IEC) possible for phosphonic acid functionalized ionomers ($\text{IEC} > 10 \text{ meq g}^{-1}$) may allow for high proton conductivities in the intermediate temperature range ($T \sim 120\text{--}160^\circ\text{C}$).

1. Introduction

Ionomers containing immobilised sulfonic acid as the *protogenic group* (source of excess protons) and water as a *proton solvent* (stabilising excess protons and allowing for high proton mobility) are generally used as electrolytes in polymer electrolyte membrane (PEM) fuel cells. Because of the limitations connected to the humidification requirement of such membrane materials (in particular the limited operation temperature of about $T = 90^\circ\text{C}$ and significant water and methanol transport) a separator material, which exclusively transports protons in a low humidity environment while operating at temperatures higher than $T = 100^\circ\text{C}$, is widely considered to be one of the keys to further progress in PEM fuel cell technology (e.g. ref. 1).

One promising approach in the development of such a material is to combine the functions of the *protogenic group*

and the *proton solvent* in a single molecule.^{2,3} Such molecules must be amphoteric in the sense that they behave as both a proton donor (acid) and proton acceptor (base), and they must form dynamical hydrogen bond networks. The first leads to the formation of a high concentration of intrinsic protonic defects as a result of self-dissociation, and the latter may promote a high mobility of these protonic charge carriers (excess and deficient protons). It should be noted that the mobility of intrinsic defects is generally higher than that of extrinsic defects, which may be introduced by acid or basic doping disturbing the local symmetry of the hydrogen bond network.^{4,5}

Typical amphoteric liquids include *phosphoric acid* and diverse *heterocycles* such as imidazole, pyrazole, benzimidazole and triazole. In the liquid state, they all show relatively high conductivities with significant contributions from *structure diffusion*, i.e. the motion of protonic defects (excess or deficient protons) *via* intermolecular proton transfer coupled to hydrogen bond breaking and forming processes.⁵ Although this mechanism relies on hydrogen bonding, the highest rates are observed for the liquid state, where the short lifetime of this interaction may be in the ps range. The dynamics of the

^a Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany. E-mail: kreuer@fkf.mpg.de

^b FuMATech, Am Grubenstollen 11, 66386 St. Ingbert, Germany

^c Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

hydrogen bonding and the high dielectric constant favouring charge separation are making hydrogen bonded liquids ideal media for obtaining high proton conductivity.^{6,7} Unlike water, which has a low viscosity and a high molecular diffusion coefficient giving rise to some proton conductivity as a result of the diffusion of hydrated protons as a whole (in concentrated aqueous solutions of acids⁸ and most hydrates, such as heteropolyacids⁹ layered hydrates¹⁰ and zeolites,¹¹ the mobility of *e.g.* H_3O^+ or NH_4^+ is indeed the dominating proton conduction mechanism (*vehicle mechanism*^{12,13}), some of the above mentioned hydrogen bonded liquids show high conductivity contributions from *structure diffusion* (up to 98% in the case of phosphoric acid¹⁴). Another essential difference compared to water is that apart from the hydrogen bond donor and acceptor sites there are other sites available for immobilization to a polymeric structure. In the case of heterocycles, this may be achieved by *e.g.* C–O–C, C–C or C–SO₂–C bonds, but because of the hydrolytic sensitivity of the C–O–P bond involved in the immobilisation of phosphoric acid, phosphonic acid ($\text{HPO}(\text{OH})_2$), which also shows high proton conductivity as a neat compound,¹⁵ has been suggested as protogenic group. This may be immobilised *via* more stable C–P bonds.¹⁶

In the case of heterocycles, the first immobilisation attempts were undertaken for imidazole, pyrazole and benzimidazole tethered to small molecules and various oligomers^{17–21} before the first heterocycle functionalized fully polymeric systems based on styrene²² and siloxane backbones²³ were demonstrated to show proton conductivity in the complete absence of water. In some cases the conductivity reduction compared to the conductivity of the corresponding liquid heterocycle is only a little more than one order of magnitude. The results of this work are of paramount importance, because they clearly prove that protons may be decoupled from their binding sites, which are covalently bonded to polymeric structures. In other words, protons are the only diffusing species in these structures, and proton conduction is exclusively due to *structure diffusion*. Later, similar conductivities of fully polymeric structures at even lower temperatures were demonstrated by using triazole as a protogenic group.^{24,25} In the case of imidazole and benzimidazole, these encouraging results were obtained by a “spacer concept”: the heterocycles were attached to polymer backbones *via* flexible spacers such as ethylenoxide or alkane segments. Surprisingly, proton mobilities increase with increasing spacer length, and this increase even overcompensates the dilution effect. According to the current understanding, the flexibility of long spacers facilitates the aggregation of the terminating protogenic groups which corresponds to the formation of extended hydrogen bonded structures. The manner in which the protogenic group is tethered to the spacer segment (preferentially by a σ -bond) does not disturb the symmetry (the chemical equivalence of two nitrogens) and still allows for rapid reorientation, *i.e.* rapid hydrogen bond breaking and forming processes. Recent electronic structure calculations at the B3LYP/6-311G(d,p) level of theory of the corresponding barriers for isolated (non hydrogen bonded) heptyl segments terminated by a sulfonic, phosphonic or imidazole function,²⁶ has revealed that the barriers for reorientation are particularly low for imidazole as a protogenic

group ($\sim 3.9 \text{ kJ mol}^{-1}$). Of course, intermolecular interactions (*e.g.* hydrogen bonding) increase this barrier, but also in the bulk, imidazole reorientation going along with hydrogen bond breaking and forming processes is still very fast as shown by NMR spectroscopy^{27–29} and by a molecular dynamics simulation.³⁰ In the case of heterocycles, the covalent immobilisation *via* spacers is therefore a viable route to form a dynamical hydrogen bond network within a true solid, *i.e.* a solid with liquid-like properties.¹

But when it comes to the use of imidazole based polymers as the separator material in PEM fuel cells, inherent limitations have to be considered. A recent critical discussion on the choice of the protogenic group in PEM separator materials¹⁶ provides a basis for the understanding of these limitations: (i) the moderate amphotericity of imidazole limiting the intrinsic charge carrier concentration to about 10^{-3} and the significant cooperativity in the diffusion of protons,⁵ showing up as extremely high Haven ratios (up to 15), is limiting the accessible proton conductivity to about $10^{-3} \text{ S cm}^{-1}$, which is far too low for fuel cell applications; (ii) strong adsorption on platinum surfaces leads to very high overpotentials for oxygen reduction; and (iii) direct oxidation by oxygen is limiting the chemical stability to low oxygen activities.

In the same study, phosphonic acid has been suggested as a protogenic group for intrinsically conducting separator materials. Its electrochemical properties are similar to these of commonly used sulfonic acid and its degree of self-dissociation is one reason for the high proton conductivity of neat liquid phosphonic acid, which is about a factor of 15 higher than the conductivity of neat imidazole. The first principle based molecular modelling investigation referred to above²⁶ substantiated this experimental observation with computed energy penalties (endothermicities) for the neat proton transfer between pairs of methyl-phosphonic acid and imidazole molecules of 37.2 and 120.1 kJ mol^{-1} , respectively. Provided that immobilisation effects for phosphonic acid are similarly small to those for heterocycle based systems, phosphonic acid functionalized fully polymeric systems with similar architecture may therefore show conductivities high enough for fuel cell applications.

Indeed, many phosphonated polymers (ionomers) have been suggested for application in fuel cells.^{31–47} Different polymer backbones such as polyaryleneethers,^{31,36} oligotetrafluoroethylenes,^{32–34} polyethersulfones,^{35,40,41–44} polyphosphazenes,^{37,38,47} poly(4-phenoxybenzoyl-1,4-phenylene)s,⁴² polystyrenes grafted on perfluorinated backbones⁴³ and polysiloxanes⁴⁶ have been used. Synthesis methods comprise: the Arbuzov reaction,^{48,49} phosphonation of aromatic bromides (Ni- or Pd-catalyzed),^{49,50} metallation (lithiation) of a bromide or an acidic hydrogen and subsequent reaction with $\text{ClPO}(\text{OR})_2$.^{45,51} However, the majority of these ionomers have low phosphonic acids concentrations (also expressed as ion exchange capacity, IEC), and the proton conduction mechanism is still water based, as in hydrated sulfonic acid functionalized polymers.

In another class of fuel cell electrolytes, phosphoric acid is the main constituent in ionic complexes with polybenzimidazole. Provided that the concentration of phosphoric acid is high ($> 90\%$), these systems show high proton conductivities

also under low humidity conditions and temperatures close to $T = 200\text{ }^{\circ}\text{C}$.^{52–54} But most of the phosphoric acid has little, if any, binding interaction with the basic polymer, and leaching out of phosphoric acid by water is a severe problem when used in a fuel cell.

This paper presents a summary of our recent attempts to access intrinsically proton conducting polymers with tethered phosphonic acid functions. The first part provides data obtained on model compounds. The systematic variation of the architecture of phosphonic acid containing molecules and oligomers reveals insight into the hydrogen bonding, dynamics and proton conduction mechanism. Specially, we examine whether the “spacer concept”, which had been proven successful in the case of heterocycle based polymers (discussed above), may also be adopted to phosphonic acid functionalized proton conducting polymers. Different strategies to access fully polymeric proton conductors can be deduced from this study, and a few selected approaches are presented in the second part of this paper.

Apart from published data, some recent, yet unpublished, data are included into this progress report.

2. Proton conduction in phosphonic acid based model compounds

As a first step towards full immobilisation of phosphonic acid, diphosphonic acids, in which two phosphonic acid functions terminate the ends of flexible segments, have been prepared and characterised with respect to melting point, molecular diffusion and proton conductivity.¹⁶ Although the chosen alkane segments are less polar and less flexible than the ethylenoxide spacers used for preparing similar di-imidazoles¹⁸ (just for preparative reasons), the qualitative comparison of the properties of these two type of model compounds reveal distinct differences in the structure, bonding and dynamics of imidazole and phosphonic acid based systems. The conclusions are actually confirmed by including a comparison of the properties of heptyl-imidazole (I-C7) and heptyl-phosphonic acid (P-C7) into considerations.

Although the melting points of neat phosphonic acid ($T_m = 74\text{ }^{\circ}\text{C}$) and imidazole ($T_m \sim 90\text{ }^{\circ}\text{C}$) are quite similar, the melting behaviour of phosphonic acid and imidazole functionalized alkanes and ethylenoxides are different. While imidazole terminated ethylene oxide segments are highly viscous oils which form glasses with glass transition temperatures ($T_g = -8$ to $-24\text{ }^{\circ}\text{C}$) only somewhat higher than the glass transition temperature of polyethylene oxide ($T_g = -65\text{ }^{\circ}\text{C}$), diphosphonic acids show distinct melting points (for spacer lengths from C_3 to C_{12} , melting temperatures fall into the range $T = 160$ to $220\text{ }^{\circ}\text{C}$, where molecules with an odd number of C-atoms have lower melting temperature ($T_m \sim 160\text{--}170\text{ }^{\circ}\text{C}$) than those with an even number of C-atoms ($T_m \sim 200\text{--}220\text{ }^{\circ}\text{C}$)) well above the melting point of neat phosphonic acid. One possible explanation of this surprising finding is a high local order (low configurational entropy) of the melts of the diphosphonic acids. This assumption is actually supported by the molecular diffusion coefficients, which have been determined by PFG-NMR (Fig. 1). While the reduction of the diffusion coefficients of neat phosphonic acid and imidazole is

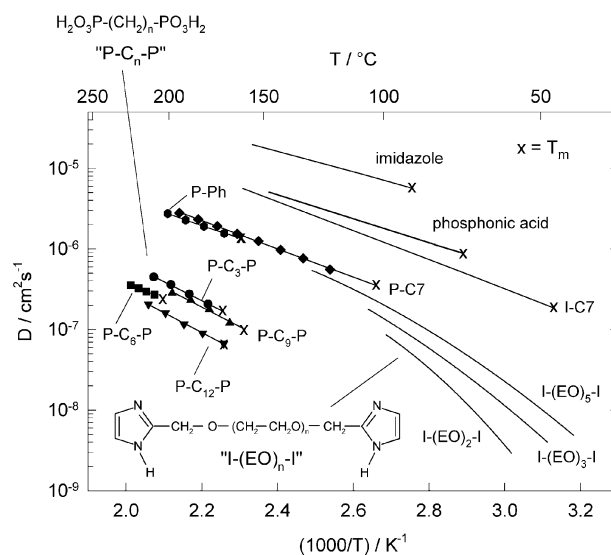


Fig. 1 Molecular diffusion coefficients of different hydrocarbon molecules functionalized with one or two phosphonic acid groups in the liquid state as obtained by PFG-NMR. The diffusion coefficients of imidazole functionalized molecules^{16,18} and neat phosphonic acid¹⁵ and imidazole² are shown for comparison.

comparable for small spacers, the trends for increasing spacer lengths are just opposite for both series: the molecular diffusion coefficient of diphosphonic acids decrease (without significant change in the activation enthalpy) with increasing spacer length, *i.e.* the length of the spacer does not support the mobilisation of the system as observed for di-imidazoles (see introduction and Fig. 1). Not only does the “spacer concept” appears to fail for immobilised phosphonic acids, alkane spacers seem to progressively order with increasing spacer length, which may even reduce the entropy and therefore the pre-exponential factor of the diffusion. A possible reason for this may be the more pronounced difference in hydrophobicity/hydrophilicity in diphosphonic acids compared to di-imidazoles similar to that of phospholipids, which also have a tendency to order especially in aqueous environment (note that phosphonic acid is more polar than imidazole and that the ethylene oxide spacer is more polar and more flexible than the alkane spacer). It is also worth noting that the immobilisation effect is significantly lower for mono-functionalized molecules as can be seen from the molecular diffusion coefficients of phenyl-phosphonic acid (P-Ph), heptyl-phosphonic acid (P-C7) and ethyl-imidazole (I-C7) (Fig. 1). But the trends are in line with these of above discussed difunctionalized molecules, *e.g.* the melting points are shifted into opposite directions for imidazole and phosphonic acid functionalized molecules.

When it comes to proton conductivity, the immobilisation effect is even larger than for long range molecular diffusion. At a first glance, this is surprising considering a proton conduction mechanism comprising only intermolecular proton transfer and structural reorganisation involving hydrogen bond breaking and forming processes, *i.e.* only involving local dynamics of the large molecules. But effects on the *dissociation, cooperativity of proton diffusion and dynamical percolation of the hydrogen bonded network* may explain the conductivity

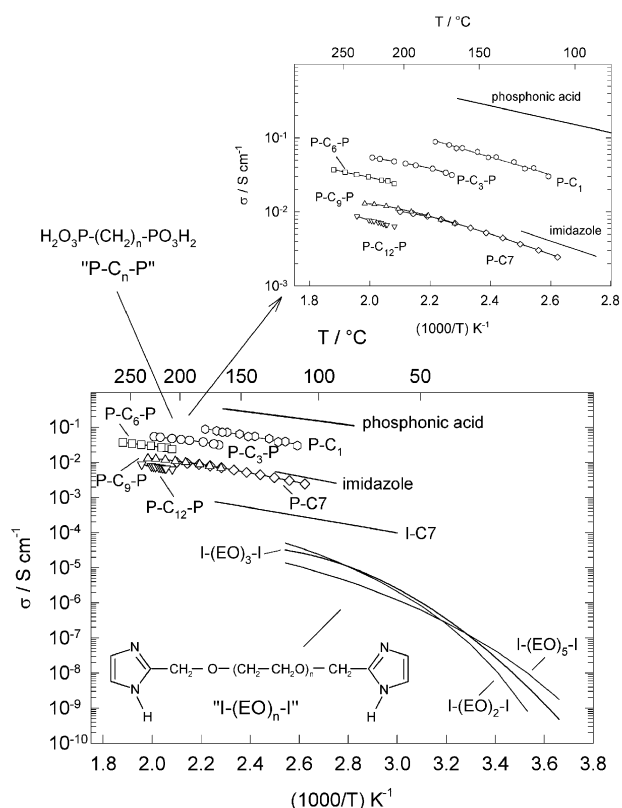


Fig. 2 Ionic conductivities of different hydrocarbon molecules functionalized with one or two phosphonic acid groups in the liquid state as obtained by ac-impedance spectroscopy. The conductivities of imidazole functionalized molecules^{16,18} and neat phosphonic acid¹⁵ and imidazole² are shown for comparison.

data shown in Fig. 2: In the case of the imidazole functionalized oligomers, the conductivity increases with increasing spacer length only at low temperature. Above *ca.* room temperature, this trend is reversed and the conductivities diverge to an extent which can not be completely explained by the reduced imidazole concentration with increasing spacer length. In fact, for a fixed concentration of protonic charge carriers (by defined doping with a strong acid), the conductivity, and therefore the mobility of protonic defects, is almost completely controlled by T_g .²⁰ Therefore, the decreasing conductivity with increasing spacer length is likely the result of reduced self-dissociation. The proton conductivities of phosphonic acid based systems are generally higher because of their significantly higher (about two orders of magnitude) degree of self-dissociation. But apart from concentration effects (the concentration of phosphonic acid decreases by a factor of two from P-C3-P to P-C12-P), there must be other effects reducing the conductivity. These are probably the reduced connectivity among the phosphonic acid functions (percolation) and an increasing cooperativity of proton diffusion with increasing spacer length, *i.e.* increasing dilution of the phosphonic acid functions (Fig. 2). As can be seen from the diffusion coefficient of the OH-protons D_{OH} (average diffusion coefficients of all protons exchanging between phosphonic groups, Fig. 3), this is actually reduced to a lesser extent when compared to the corresponding diffusion coefficient of liquid

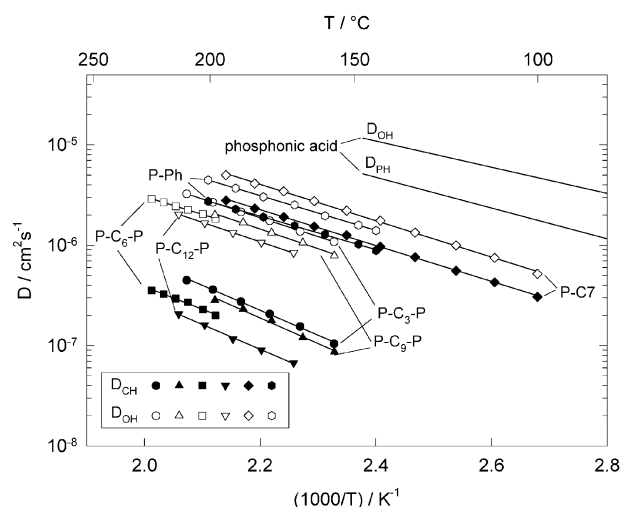


Fig. 3 Diffusion coefficients of the protons bond to phosphonic acid of phosphonic acid functionalized hydrocarbons D_{OH} and the corresponding molecular diffusion coefficients D_{CH} (see also Fig. 1) as obtained by site-selective PFG-NMR. The diffusion coefficients of neat phosphonic acid¹⁵ are shown for comparison.

phosphonic acid, and for the series from P-C3-P to P-C12-P this changes by only a factor of two. However, proton conductivities σD calculated from these diffusion coefficients (*i.e.* via the Nernst–Einstein relationship as explained in detail in ref. 16, Fig. 4) appear to be significantly higher than the experimentally obtained conductivities corresponding to Haven ratios ($D_H/D_\sigma = \sigma_D/\sigma_{H+}$) which increase from a value of 2.7 for P-C3-P to 8.9 for P-C12-P at $T = 180^\circ\text{C}$. This indicates an increasing contribution to proton transport which allows for fast diffusion, but avoids charge separation necessary for proton conductivity. This phenomenon has already been observed for imidazole based systems⁵ and for neat phosphonic acid,¹⁵ and it has been suggested that local ordering and a reduced dielectric constant are the main reasons for

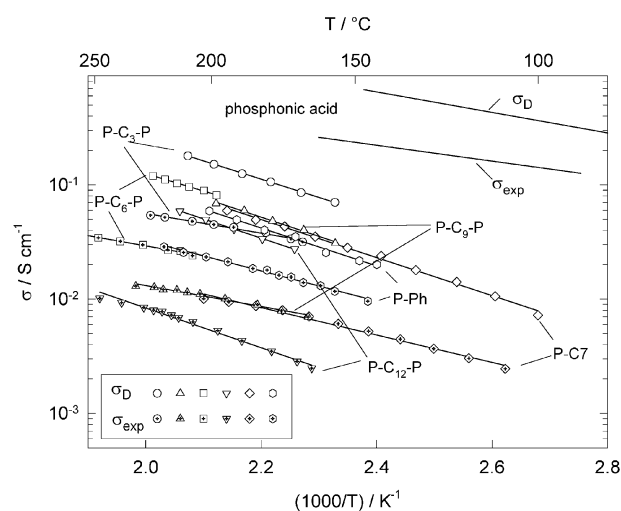


Fig. 4 Proton conductivities obtained from D_{OH} values (see Fig. 3) via the Nernst–Einstein relationship compared to measured conductivities (see Fig. 2) σ_{exp} .

this phenomenon. As a result, protons exchange their positions on closed trajectories in a cooperative way, which still allows for proton diffusion but not for proton conductance. It is worth noting that the relatively high proton conductivities of P-Ph and P-C7 also reflect the relatively small Haven ratios for these monofunctionalized molecules (Fig. 4).

In short, the reduction by an order in the conductivity of P-C12-P compared to the conductivity of P-C3-P is obviously the result of an increased cooperativity of proton diffusion (factor 3.5), a reduced concentration of protonic charge carriers (dilution effect, factor of 2) and some effect of reduced percolation (factor of 1.5). It could also be that the degree of self-dissociation is affected by the immobilisation. This has not been examined yet, but the total immobilisation effect appears to be more pronounced for phosphonic acid compared to imidazole based systems.

The trends are similar for the conductivities of phosphonic acid functionalized siloxanes which are also included in Fig. 5⁵⁵ showing the conductivity of soft covalently immobilised phosphonic acids as a function of the phosphonic acid volume fraction (for a given temperature ($T = 160\text{ }^{\circ}\text{C}$) and estimated volume fractions assuming ideal mixing behaviour). The curve roughly follows a power law with a rather high exponent of around 4.5. It is worth noting that the decrease of the conductivity in the PBI- H_3PO_4 system is even steeper with an exponent close to 6.5, an effect which is not yet understood. Obviously, the proton conductivity of both phosphonic acid and phosphoric acid based systems are very sensitive to dilution (dispersion) of the acid. For a given volume fraction, the highest conductivities are observed for systems in which the free aggregation of phosphonic acid is less constrained (see conductivity of P-C7 in Fig. 5). According to the above considerations, the aggregation of phosphonic acid in diphosphonic acids may be constrained by ordering of the spacer segments, and in the PBI-phosphoric acid system, the strong interaction between the basic polymer and the phosphoric acid may interfere with the hydrogen bonding between phosphoric acid molecules (aggregation). To date, there is only a very rough understanding of the proton conduction mechanism of neat phosphonic acid¹⁵ and neat phosphoric acid:¹⁴ it is

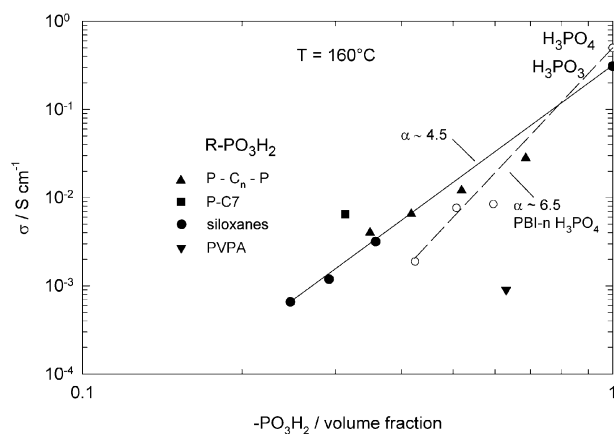


Fig. 5 Conductivity of phosphonic acid (data from Fig. 2 and ref. 55) and phosphoric acid containing polymers⁵³ as a function of the acid volume fraction for a given temperature (see text).

certainly dominated by *structure diffusion*, but details of the mechanism are not yet known. The strong sensitivity towards dilution, however, suggests that the elementary reactions (conduction mechanism) are complex and involve the dynamics of a large number of molecules. The number of molecules participating in the conduction process is most likely larger than in the case of imidazole forming low dimensional aggregates⁵⁶ and probably even larger than in the case of water, in which hydrogen bond rearrangements within the second hydration shell of the hydronium ion determines proton conduction.^{57,58}

When it comes to obtaining high intrinsic proton conductivity in a fully immobilised phosphonic acid based polymer, two major parameters therefore have to be kept in mind: (i) the volume fraction of phosphonic acid has to be as high as possible; and (ii) constraints of phosphonic acid aggregation must be minimised.

Apart from achieving high proton conductivity, this also appears to be advantageous for reducing condensation reactions. Fig. 6 shows the conductivity of neat phosphonic acid, heptyl-phosphonic acid and a phosphonated oligosiloxane in the nominally dry state and under a water partial pressure of $p_{\text{H}_2\text{O}} = 1\text{ bar}$ (10^5 Pa). Under the latter conditions and low temperature, all materials contain excess water, and the conductivity is definitely water based just like in hydrated sulfonic acid based ionomers. At higher temperature, where the conductivity curves cross, also the samples under 1 atm water pressure are nominally dry, *i.e.* the corresponding temperature may formally be considered the onset of condensation (we will later show that free water and condensation products coexist to some extent). For neat phosphonic acid, this temperature is close to $T = 160\text{ }^{\circ}\text{C}$, but it significantly decreases for lower conducting compounds. Conductivity and stability towards condensation, therefore, seem to be affected in a similar way. The hypothesis that aggregation is also thermodynamically

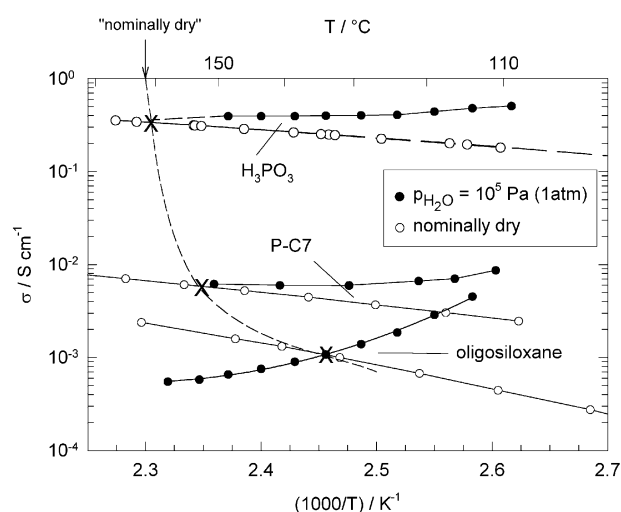


Fig. 6 Conductivities of neat phosphonic acid, heptyl-phosphonic acid P-C7¹⁶ and an oligosiloxane with alkane side chains terminated by phosphonic acid functional groups⁵⁵ in the nominally dry state and under a water pressure of $p_{\text{H}_2\text{O}} = 10^5\text{ Pa}$ (1 atm). The temperatures where the corresponding conductivities equal, *i.e.* at which the samples in pure water atmosphere are nominally dry are indicated (see text).

stabilising the system is reasonable considering the pronounced amphotericity of phosphonic acid: only in extended hydrogen bonded aggregates, is the degree of self-dissociation expected to be high and therefore contribute to an entropic stabilisation.

3. The first steps towards polymeric systems

3.1. Proton conductivity in the dry state

Considering the above results on low molecular weight model compounds, the strategy towards a full immobilisation of the phosphonic acid functional group must be different from the “spacer concept” successfully applied to the immobilisation of heterocycles. For the latter, comb-like architectures in which the functional groups terminate relatively long soft side chains, showed the highest conductivities: *e.g.* a main chain functionalized vinyl imidazole is a brittle polymer with negligible conductivities,²⁰ while a polystyrene with imidazole terminated alkane side chains showed the highest proton conductivities reported so far.²²

The severe dilution associated with the application of long spacers is however anticipated to be detrimental to the conductivity of phosphonic acid based systems. Obtaining a very high concentration of phosphonic acid functional groups, which still aggregate in a relatively unconstrained way appears to be the key challenge in making a polymer with high intrinsic proton conductivity.

In fact, many phosphonic acid based ionomers prepared by post-phosphonation of polymers have already been reported (*e.g.* ref. 31, 36–38, 41–44). Except for very few cases,⁴³ such reactions are rarely quantitative, and hence the resulting IECs are low, and the reported conductivities are always water based. Therefore, the method of choice to obtain high IEC phosphonic acid functionalized polymers is the polymerisation of phosphonated monomers.⁴⁶

We have been following such routes in order to obtain polymers with extremely high concentrations of phosphonic acid functional groups.

Poly(vinyl phosphonic acid), PVPA, of rather high molecular weight ($62\,000\text{ g mol}^{-1}$) was synthesised by free radical polymerisation of vinyl phosphonic acids.⁵⁹ Freeze drying and subsequent drying at $T = 50\text{ }^{\circ}\text{C}$ and $p = 0.1\text{ Pa}$ (10^{-3} mbar) for at least one week leads to nominally dry materials. We are using the term “nominally dry” because the material contains a significant amount of condensation products (30%) and a corresponding amount of free water ($0.15\text{ H}_2\text{O}/\text{PO}_3\text{H}_2$).⁶⁰

Poly(meta-phenylenephosphonic acid), PmPPA, in which each ring has exactly one phosphonic acid functional group, has been synthesised by nickel-catalysed reductive coupling of phosphonated chlorides.⁶¹ Purification and freeze drying results in a product, which we consider to be close to dry.

Poly(vinyl phosphonic acid) has actually the higher concentration of phosphonic acid groups, but in contrast to poly(meta-phenylene phosphonic acid) there is a pronounced polyelectrolyte effect and only one proton per phosphonic acid group is titratable.⁵⁹ In the case of poly(meta-phenylene phosphonic acid) both protons of the phosphonic function may be titrated which corresponds to an IEC of $>10\text{ meq}$

g^{-1} .⁶¹ In both polymers, the phosphonic functions are directly attached to the main chain, but especially for meta connected PmPPA the flexibility of the backbone and the lower concentration of functional groups is anticipated to allow for relatively free aggregation of the phosphonic acid functions.

Of course, the key test for the above described approach is the conductivity measurement of nominally dry materials. Conductivities were recorded for as-prepared samples in closed conductivity cells. Although the total composition does not change under these conditions the concentration of free water and condensation products may change with temperature. The conductivity of nominally dry PVPA is actually relatively low (Fig. 5 and 7) and the conductivity of PmPPA could hardly be measured. Compared to the conductivity of dry, but soft phosphonated oligo siloxanes, which show VTF like behaviour,⁵⁵ the conductivity of dry PVPA is lower and of Arrhenius type. Considering the fact that this material contains some water ($\lambda = 0.15\text{ H}_2\text{O}/\text{PO}_3\text{H}_2$ at room temperature), even this low conductivity could be water based. Indeed, for a nominal water content of $\lambda \sim 0.8\text{ H}_2\text{O}/\text{PO}_3\text{H}_2$ the proton conductivity is probably *vehicular*: PVPA in its potassium form (obtained by ion exchange, using a column) has almost the same conductivity as in its acid form, suggesting that the mobile species are K^+ and H_3O^+ , respectively (Fig. 7). Any contribution from structure diffusion would be much more affected by the introduction of foreign cations into the hydrogen bond network.

In short, the very high concentrations of phosphonic acid functions in PVPA and PmPPA do not lead to high intrinsic proton conductivities. According to the discussion of the conductivity of model compounds (see above), this observation suggests that immobilisation on main chains puts too many constraints on the aggregation of the phosphonic group and therefore severely reduces intrinsic proton conductivity. To what extent cooperativity of proton diffusion contributes to this conductivity reduction is not clear, because proton diffusion data are not available yet.

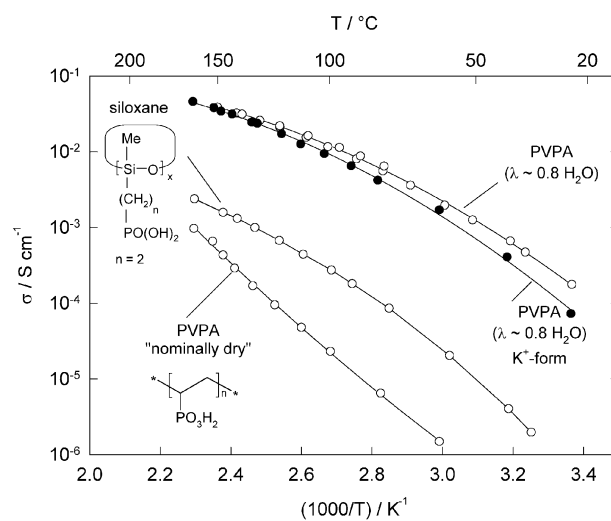


Fig. 7 Conductivity of PVPA in the nominally dry state and with a water content of $\lambda = [\text{H}_2\text{O}]/[\text{PO}_3\text{H}_2] \sim 0.8$. The conductivity of a K^+ exchanged PVPA is also shown, and the conductivity of phosphonic acid functionalized siloxane⁵⁵ is shown for comparison.

The results also indicate that the role of water has to be more carefully considered for phosphonic acid based proton conductors. Water is released in the condensation reaction of phosphonic groups, and is present as solvation water just like in the case of sulfonic acid based ionomers.

We have, therefore, determined both the water content (by gravimetric measurements, Karl-Fischer titration and quantitative analysis of ^1H -NMR chemical shifts of P-OH/ H_2O signals) and the degree of condensation of PVPA by analysing ^{31}P -NMR signals originating from $\text{PO}(\text{OH})_2$ and P-O-P as a function of the relative humidity.⁶⁰ The amount of titratable water expressed in terms of $\lambda = \text{H}_2\text{O}/[-\text{PO}_3\text{H}_2]$ as a function of relative humidity is shown for room temperature in Fig. 8. As expected from the relatively low acidity of phosphonic acid, there is no steep increase at low water activities as observed for super-acidic sulfonic acid based ionomers, where hydration is extremely exothermic for the absorption of the first (*ca.* 5) water molecules.⁶² The shape of the hydration isotherm rather suggest an entropic driving force (most probably osmosis). Unfortunately, modelling of the curve is not yet possible, because this requires the precise knowledge of the dissociation “constant” as a function of the water content. The fact that PVPA finally completely dissolves in liquid water suggests that

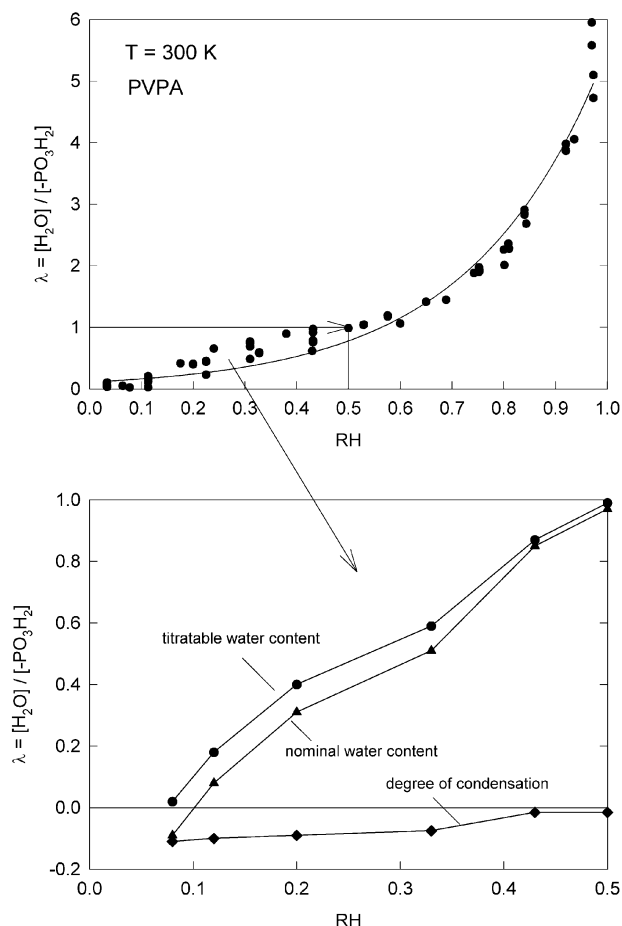


Fig. 8 Hydration isotherm of PVPA as determined by Karl-Fischer titration (above). The degree of condensation (expressed in terms of water content) determined by NMR is additionally shown at the bottom.⁶⁰

the material is very soft and osmotic pressure is only a minor parameter in the chemical potential of water in the membrane. It should also be noted that the water uptake at RH close to the dew point ($\lambda \sim 5$) is small compared to the water uptake of Nafion ($\lambda \sim 14$), but considering the extremely high IEC of PVPA, this corresponds to a water volume fraction which is about a factor of three higher than in Nafion. Of course, this has implications for the water based conductivity, as will be discussed later.

However prior to this discussion, we would like to draw reader's attention to conditions of relatively low humidification. For relative humidity below about $\text{RH} = 50\%$ (at room temperature), condensation products (P-O-P) become visible, and these condensation products coexist with titratable water down to a relative humidity of about $\text{RH} = 8\%$, where the degree of condensation is about 30% corresponding to $\lambda = -0.15 [\text{H}_2\text{O}]/[-\text{PO}_3\text{H}_2]$ (Fig. 8). Therefore, the answer to the question of the proton conduction mechanism of “dry” phosphonic acid based polymers is probably very complex. Also for neat phosphoric acid⁶³ and phosphonic acid condensation products (*e.g.* diphosphoric acid) are coexisting with a corresponding amount of hydronium ions (H_3O^+), but because of the dominance of structure diffusion, the conductivity contribution from hydronium ions is probably negligible for these systems.^{14,15} This may change for small amounts of extra water (nominally wet samples), however this corresponds to a situation which is worth investigating, but not having been examined so far.

3.2. Proton conductivity under humidifying conditions

The envisaged polymeric systems obviously show only very small conductivity at low relative humidities, but the high IECs may render possible high proton conductivity in the hydrated state. Even for low numbers of $\lambda = [\text{H}_2\text{O}]/[-\text{PO}_3\text{H}_2]$, *i.e.* low relative humidities, the total amount of water may be high enough to produce high proton conductivity. As shown recently for highly sulfonated polysulfones, apart from a high concentration of excess protons the main effect of high IEC is to provide a good connectivity within the hydrated hydrophilic domain also at low relative humidity.⁶⁴ We have therefore measured the water uptake and the conductivity of PmPPA and PVPA for a water pressure of $p_{\text{H}_2\text{O}} = 10^5 \text{ Pa}$ (1 atm) from about $T = 110\text{--}160^\circ\text{C}$ corresponding to relative humidities decreasing from about 70 to 15% (Fig. 9). The conductivity of poly(meta-phenylene phosphonic acid), the ionomer with the lower concentration of phosphonic acid functions, is somewhat lower than that of PVPA. However for the conductivity of this ionomer, there is a certain tendency to level off with increasing temperature, which even indicates some intrinsic conductivity (structure diffusion). While this still has to be proven, the relatively low values of the water based conductivities for both PmPPA and PVPA may be the consequence of: (i) a relatively low degree of dissociation (note that despite the high water content in these systems, the number of water molecules per phosphonic function is low, <1 , see Fig. 9); and (ii) the interaction of the water with the phosphonic group, which definitely reduces the water diffusion coefficient, in a similar way as is the case for sulfonic acid

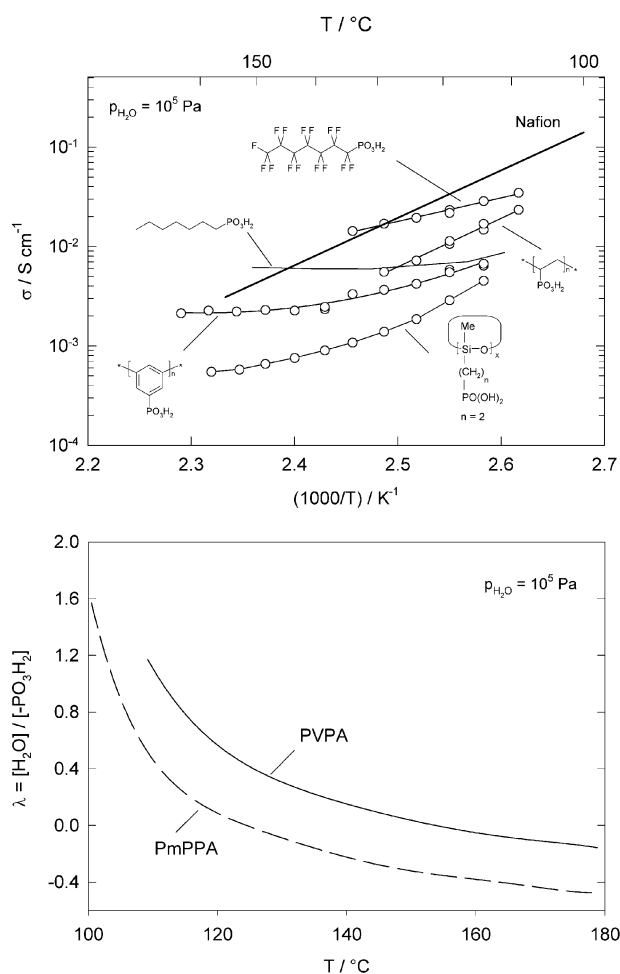


Fig. 9 Conductivities of PVPA and PmPPA⁶¹ at a water partial pressure of $p_{\text{H}_2\text{O}} = 10^5$ Pa (1 atm). The conductivity as a function of temperature of Nafion⁶⁴ and a functionalized oligosiloxane⁵⁵ is shown for comparison. The effect of fluorination is demonstrated by the conductivities of heptyl-phosphonic acid and its fluorinated analogue. Hydration isobars of PVPA and PmPPA obtained by TGA are shown at the bottom. Note that the absolute water content of PVPA is well determined,⁶⁰ while there is some uncertainty in the absolute values for PmPPA.

based ionomers.⁶⁵ But conductivity is still higher than for oligosiloxanes in the hydrated state.⁵⁵

As to a possible application of phosphonic acid based systems in PEM fuel cells, the comparison with the conductivity of Nafion is interesting. This is definitely higher than the ones of phosphonic acid based systems for the given water partial pressure ($p_{\text{H}_2\text{O}} = 1$ atm) and temperatures just above $T = 100$ °C, but the conductivity of Nafion decreases more steeply (Fig. 9), which is probably a consequence of the significantly lower density of acidic sites (IEC) reducing the connectivity within the hydrated domain at low degrees of hydration. Therefore, the conductivity of some phosphonic acid based systems, which decreases less with temperature, exceeds that of Nafion at temperatures above $T = 150$ °C (Fig. 9). While this may be a certain advantage for high temperature low humidity operation, the conductivity at low temperature and high relative humidities is significantly lower

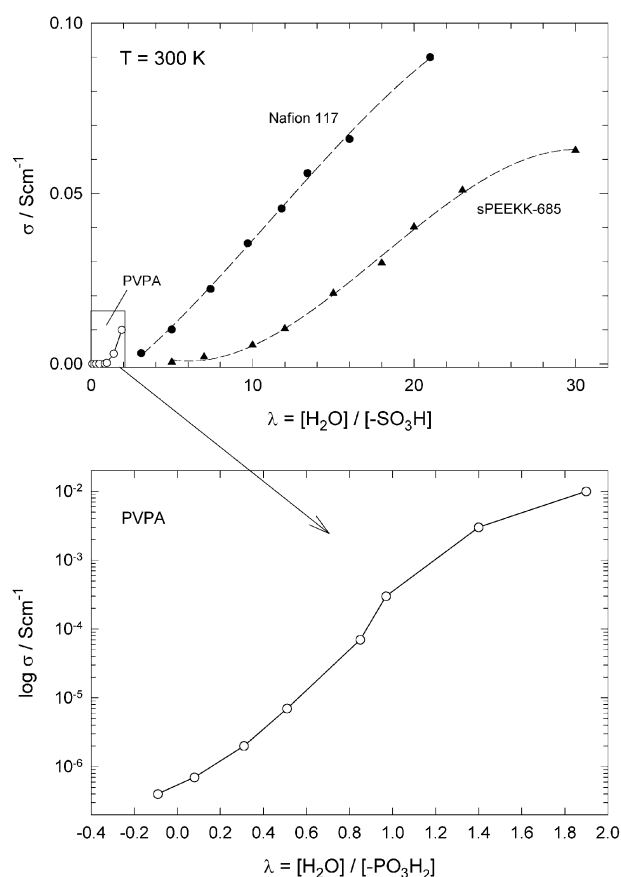


Fig. 10 Room temperature conductivity of PVPA as a function of its water content $\lambda = [\text{H}_2\text{O}] / [-\text{SO}_3\text{H}]$. The conductivities of Nafion and a sulfonated poly(arylene ether ketone)⁵ are shown for comparison.

than for sulfonic acid functionalized systems. The room temperature conductivity of PVPA is actually quite high for a given value of $\lambda = [\text{H}_2\text{O}] / [-\text{PO}_3\text{H}_2]$ (Fig. 10), but for a given relative humidity (for the relation between λ and RH see Fig. 8) or water volume fraction, the conductivities are indeed low.

For the appearance of intrinsic proton conductivity, the amphoteric character of the phosphonic acid function is essential (see Introduction), but when it comes to water based conductivity an increase in acidity will increase the hydrophilicity and hence the conductivity. Phosphonic acid is significantly less acidic (higher $\text{p}K_{\text{a}}$) than the commonly used sulfonic acid, and increase of the acidity is therefore expected to increase both the water uptake and concentration of released protons. We have therefore prepared the fluorinated variety of P-C7 and determined the proton conductivity under hydrous conditions (Fig. 9). Indeed, compared to the hydrocarbon variety, the conductivity is higher, but it should also be noted that there is some indication of reduced hydrolytic stability for this particular compound.

4. Conclusions and outlook

Designing a phosphonic acid functionalized polymer with high intrinsic proton conductivity (conductivity in the nominally dry state) requires a high concentration of functional groups

which are free to aggregate with only minor constraints. This is the major conclusion of a study on model compounds, *i.e.* alkane segments terminated by one or two phosphonic acid functions. The “spacer concept” which had been proven successful in supporting dynamical aggregation within heterocycle functionalized systems appears to fail for phosphonic acid based systems. The dilution of functional groups associated with the tethering of phosphonic acids to some backbone *via* long, flexible spacers is anticipated to be detrimental to high proton conductivity. However, also for polymers in which the phosphonic groups are covalently connected to the main chain (at least for those presented in this study) the signatures of intrinsic proton conductivity are also quite small (about 10^{-3} S cm $^{-1}$ at 150 °C in the case of *poly(meta-phenylene phosphonic acid)*). Obviously, high proton conductivity requires the formation of very “bulky” aggregates of phosphonic acid, which is difficult to achieve in fully polymeric systems. Aggregation also seems to be favourable in minimising condensation reactions, which are also detrimental to proton conductivity. It is worth mentioning that some condensation products and aqueous species (*e.g.* H $_3$ O $^{+}$) always coexist in phosphonic acid functionalized polymers.

We, therefore, conclude that covalent immobilisation strategies are probably not compatible with achieving the very high proton conductivities required for the successful application of such materials as electrolyte in PEM fuel cells at intermediate temperature and quasi dry conditions ($\sigma > 5 \cdot 10^{-2}$ S cm $^{-1}$ at $T \sim 120$ – 160 °C).

However, the very high ion exchange capacities (IEC) achievable for phosphonic ionomers compared to sulfonic ionomers renders possible interesting proton conductivities at high temperature and some humidification. The relatively weak acidity of the phosphonic acid function may be increased by fluorination of the polymer segments next to the phosphonic group. This appears to lead to higher conductivities, probably as a consequence of both a higher water uptake and a higher degree of dissociation under hydrous conditions.

Acknowledgements

The authors thank A. Fuchs for technical support, S. J. Paddison (University of Alabama in Huntsville) for proof reading and the *Bundesministerium für Bildung und Forschung* (project DryD under the contract No. 0329567) and the *Stiftung Energieforschung Baden-Württemberg* (A 19603) for financial support.

References

- 1 K. D. Kreuer, *ChemPhysChem*, 2002, **3**, 771.
- 2 K. D. Kreuer, A. Fuchs, M. Ise, M. Spaeth and J. Maier, *Electrochim. Acta*, 1998, **43**, 1281.
- 3 K. D. Kreuer, Proton Conduction in Fuel Cells, in *Hydrogen Transfer Reactions*, ed. J. T. Hynes, J. P. Klinman, H. H. Limbach and R. L. Schowen, Wiley, VCH, Ch. 23, 2005, pp. 709–736.
- 4 A. Schlechter and R. F. Savinell, *Solid State Ionics*, 2002, **147**, 181.
- 5 K. D. Kreuer, S. J. Paddison, E. Spohr and M. Schuster, *Chem. Rev.*, 2004, **104**, 4637.
- 6 K. D. Kreuer, *Solid State Ionics*, 1997, **94**, 55.
- 7 K. D. Kreuer, *Solid State Ionics*, 2000, **136**–**137**, 149.
- 8 T. Dippel and K. D. Kreuer, *Solid State Ionics*, 1991, **46**, 3.

- 9 K. D. Kreuer, M. Hampele, K. Dolde and A. Rabenau, *Solid State Ionics*, 1988, **28**–**30**, 589.
- 10 K. D. Kreuer, A. Rabenau and R. Messer, *Applied Physics. A Materials Science & Processing*, 1983, **32**, 45.
- 11 K. D. Kreuer, W. Weppner and A. Rabenau, *Mater. Res. Bull.*, 1982, **17**, 501.
- 12 K. D. Kreuer, W. Weppner and A. Rabenau, *Solid State Ionics*, 1981, **3**–**4**, 353.
- 13 K. D. Kreuer, A. Rabenau and W. Weppner, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 208.
- 14 T. Dippel, K. D. Kreuer, J. C. Lassègues and D. Rodriguez, *Solid State Ionics*, 1993, **61**, 41.
- 15 M. Schuster, K. D. Kreuer and J. Maier, *Solid State Ionics*, submitted.
- 16 M. Schuster, T. Rager, A. Noda, K. D. Kreuer and J. Maier, *Fuel Cells*, 2005, **5**, 355.
- 17 K. D. Kreuer, *J. Membr. Sci.*, 2001, **185**, 29.
- 18 M. Schuster, W. H. Meyer, G. Wegner, H. G. Herz, M. Ise, K. D. Kreuer and J. Maier, *Solid State Ionics*, 2001, **145**, 85.
- 19 M. F. H. Schuster, W. H. Meyer, M. Schuster and K. D. Kreuer, *Chem. Mater.*, 2004, **16**, 329.
- 20 M. F. H. Schuster and W. H. Meyer, *Annu. Rev. Mater. Res.*, 2003, **33**, 233.
- 21 J. C. Perrson and P. Jannasch, *Chem. Mater.*, 2003, **15**, 3044.
- 22 H. G. Herz, K. D. Kreuer, J. Maier, G. Scharfenberger, M. F. H. Schuster and W. H. Meyer, *Electrochim. Acta*, 2003, **48**, 2165.
- 23 G. Scharfenberger, W. H. Meyer, G. Wegner, M. Schuster, K. D. Kreuer and J. Maier, *Fuel Cells*, 2006, **3**–**4**, 237.
- 24 Z. Zhou, S. W. Li, Y. L. Zhang, M. L. Liu and W. Li, *J. Am. Chem. Soc.*, 2005, **127**, 10824.
- 25 S. W. Li, Z. Zhou, Y. L. Zhang, M. L. Liu and W. Li, *Chem. Mater.*, 2005, **17**, 5884.
- 26 S. J. Paddison, K. D. Kreuer and J. Maier, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4530.
- 27 G. R. Goward, M. F. H. Schuster, D. Sebastiani, I. Schnell and H. W. Spiess, *J. Phys. Chem. B*, 2002, **106**, 9322.
- 28 I. Fischbach, H. W. Spiess, K. Saalwachter and G. R. Goward, *J. Phys. Chem. B*, 2004, **108**, 18500.
- 29 S. R. Benhabbour, R. P. Chapman, G. Scharfenberger, W. H. Meyer and G. R. Goward, *Chem. Mater.*, 2005, **17**, 1605.
- 30 M. Iannuzzi and M. Parrinello, *Phys. Rev. Lett.*, 2004, **93**, 025901.
- 31 X. Xu and I. Cabasso, *Polym. Mater. Sci. Eng.*, 1993, **68**, 120.
- 32 S. V. Kotov, S. C. Pedersen, W. Qiu, Z. M. Qiu and D. J. Burton, *J. Fluorine Chem.*, 1997, **82**, 13.
- 33 M. Yamabe, K. Akiyama, Y. Akatsuka and M. Kato, *Eur. Polym. J.*, 2000, **36**, 1035.
- 34 C. Stone, T. S. Daynard, L. Q. Hu, C. Mah and A. E. Steck, *J. New Mater. Electrochem. Syst.*, 2000, **3**, 43.
- 35 Y. Z. Meng, S. C. Tjong, A. S. Hay and S. J. Wang, *J. Polym. Sci., Part A*, 2001, **39**, 3218.
- 36 K. Miyatake and A. S. Hay, *J. Polym. Sci., Part A*, 2001, **39**, 3770.
- 37 H. R. Allcock, M. A. Hofmann, C. M. Ambler and R. V. Morford, *Macromolecules*, 2002, **35**, 3484.
- 38 H. R. Allcock, M. A. Hofmann, C. M. Ambler, S. N. Lvov, X. Y. Zhou, E. Chalkova and J. Weston, *J. Membr. Sci.*, 2002, **201**, 47.
- 39 Y. M. Li and K. Hinokuma, *Solid State Ionics*, 2002, **150**, 309.
- 40 Y. Z. Meng, S. C. Tjong, A. S. Hay and S. J. Wang, *Europ. Polymer J.*, 2003, **39**, 627.
- 41 K. Jakoby, K. V. Peinemann and S. P. Nunes, *Macromol. Chem. Phys.*, 2003, **204**, 61.
- 42 S. Yanagimachi, K. Kaneko, Y. Takeoka and M. Rikukawa, *Synthetic Metals*, 2003, **135**–**136**, 69.
- 43 G. Schmidt-Naake, M. Böhme and A. Cabrera, *Chem. Eng. Technol.*, 2005, **28**, 720.
- 44 B. Lafitte and P. Jannasch, *J. Polym. Sci., Part A*, 2005, **43**, 273.
- 45 B. Lafitte and P. Jannasch, On the prospects for phosphonated polymers as proton-exchange fuel cell membranes, in *Advances in Fuel Cells*, ed. T. S. Zhao, K. D. Kreuer and T. Van Nguyen, Elsevier, vol. 1, in press.
- 46 S. Li, Z. Zhou, H. Abernathy, M. Liu, W. Li, J. Ukai, K. Hase and M. Nakanishi, *J. Mater. Chem.*, 2006, **16**, 858.
- 47 H. Allcock and R. M. Wood, *J. Polym. Sci., Part B*, 2006, **44**, 2358.
- 48 L. D. Freedman and G. O. Doak, *Chem. Rev.*, 1957, **57**, 479.
- 49 P. Tavs, *Chem. Ber.*, 1979, **103**, 2428.

- 50 T. Hirao, T. Masunaga, N. Yamada, Y. Ohshiro and T. Agawa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 909.
- 51 F. Eymery, B. Iorga and P. Savignac, *Tetrahedron*, 1999, **55**, 13109.
- 52 J. S. Wainright, J. T. Wang, D. Weng, R. F. Savinell and M. Litt, *J. Electrochem. Soc.*, 1995, **142**, L121.
- 53 Q. Li, R. He, J. O. Jensen and N. J. Bjerrum, *Chem. Mater.*, 2003, **15**, 4896.
- 54 L. X. Xiao, H. F. Zhang, E. Scanlon, L. S. Ramanathan, E. W. Choe, D. Rogers, T. Apple and B. C. Benicewicz, *Chem. Mater.*, 2005, **17**, 5328.
- 55 H. Steininger, M. Schuster, K. D. Kreuer and J. Maier, *Solid State Ionics*, 2006, **177**, 2457.
- 56 W. Münch, K. D. Kreuer, W. Silvestri, J. Maier and G. Seifert, *Solid State Ionics*, 2001, **145**, 437.
- 57 M. Tuckerman, K. Laasonen, M. Sprik and M. Parrinello, *J. Phys. Chem.*, 1995, **99**, 5749.
- 58 N. Agmon, *Chem. Phys. Lett.*, 1995, **244**, 456.
- 59 B. Bingöl, W. H. Meyer, M. Wagner and G. Wegner, *Macromol. Rapid Commun.*, 2006, **27**, 1719.
- 60 A. Kaltbeitzel, S. Schauff, H. Steininger, B. Bingöl, G. Brunklaus, W. H. Meyer and H. W. Spiess, *Solid State Ionics*, in press.
- 61 T. Rager, M. Schuster, H. Steininger and K. D. Kreuer, 2006, submitted.
- 62 M. Escoubes and M. Pineri, Thermodynamic Studies of the Water-Perfluorosulfonated Polymer Interaction: Experimental Results, in *Perfluorinated Ionomer Membranes*, ed. A. Eisenberg and H. L. Yeager, ACS Symposium Series, 1982, **180**, pp. 9–24.
- 63 R. A. Munson, *J. Phys. Chem.*, 1964, **68**, 3374.
- 64 M. Schuster, K. D. Kreuer, H. T. Andersen and J. Maier, *Macromolecules*, 2007, **40**, 598–607.
- 65 S. J. Paddison, R. Paul and K. D. Kreuer, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1151.



90507040

RSCPublishing

**Fast
Publishing?**
Ahead of the field

To find out more about RSC Journals, visit

www.rsc.org/journals