Modeling of Electrochemical Cells:
Proton Exchange Membrane Fuel Cells
HYD7007 – 01

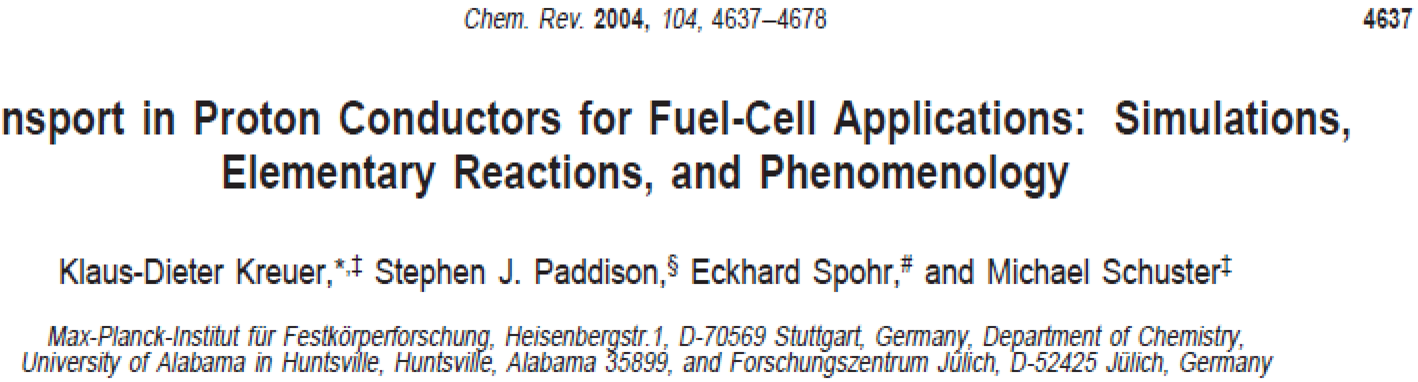
Lecture 09. Membranes of Other Chemistries

Dept. of Chemical & Biomolecular Engineering
Yonsei University
Spring, 2011

Prof. David Keffer
dkeffer@utk.edu

Lecture Outline

This lecture is largely a presentation of material given in the following review article.



Chem. Rev. **2004,** *104,* 4637–4678 **4637**

Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology

Klaus-Dieter Kreuer,*[‡] Stephen J. Paddison,[§] Eckhard Spohr,[#] and Michael Schuster[‡]

Max-Planck-Institut für Festkörperforschung, Heisenbergstr.1, D-70569 Stuttgart, Germany, Department of Chemistry, University of Alabama in Huntsville, Huntsville, Alabama 35899, and Forschungszentrum Jülich, D-52425 Jülich, Germany

Solvents: Water

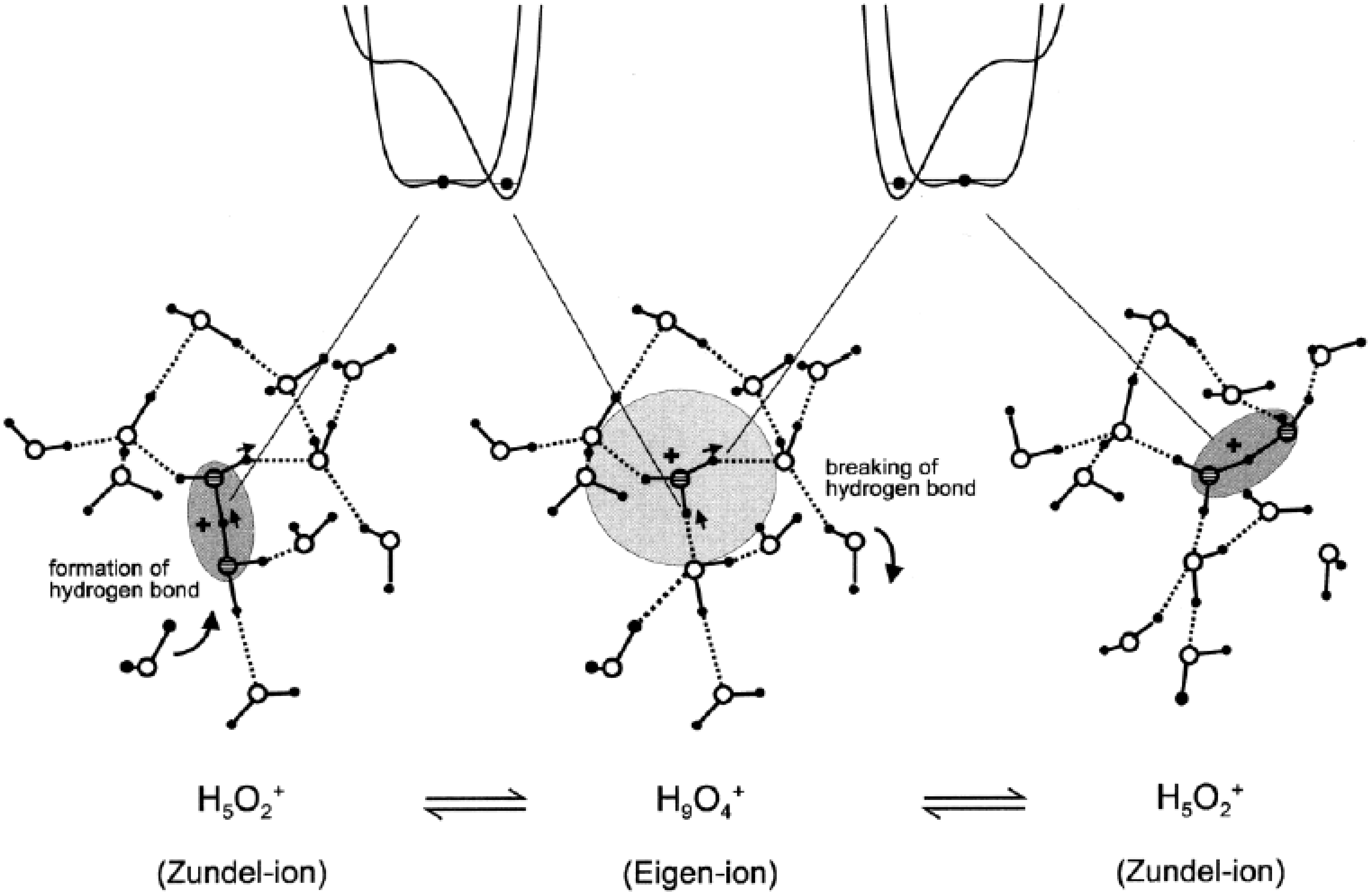


Figure 1. Proton conduction in water. The protonic defect follows the center of symmetry of the hydrogen-bond pattern, which "diffuses" by hydrogen-bond breaking and forming processes; therefore, the mechanism is frequently termed "structure diffusion". Note that the hydrogen bonds in the region of protonic excess charge are contracted, and the hydrogen-bond breaking and forming processes occur in the outer portion of the complexes (see text). Inserted potentials correspond to nonadiabatic transfer of the central proton in the three configurations (atomic coordinates taken from refs 33 and 34).

Kreuer et al., Chem. Rev. 2004.

Solvents: Phosphoric Acid

Phosphoric Acid (H_3PO_4)

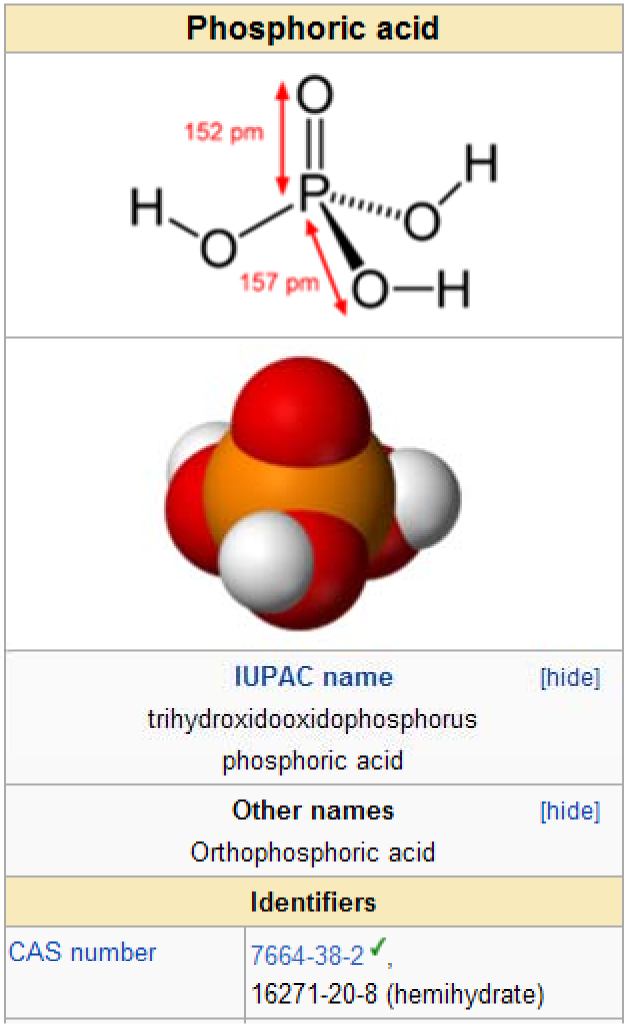
In the presence of water, the following dissociation reactions occur

$$H_3PO_{4(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)} \qquad K_{a1} = 7.25\times10^{-3}$$

$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)} \qquad K_{a2} = 6.31\times10^{-8}$$

$$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)} \qquad K_{a3} = 3.98\times10^{-13}$$

In neat phosphoric acid (no water), there is dissociation into various phosphate ions, $H_2PO_4^-$, $H_4PO_4^+$, H_3O^+, $H_2P_2O_7^{2-}$.



Phosphoric acid

IUPAC name

trihydroxidooxidophosphorus

phosphoric acid

Other names

Orthophosphoric acid

Identifiers

CAS number	7664-38-2 ✓, 16271-20-8 (hemihydrate)

Solvents: Phosphoric Acid

Phosphoric Acid (H_3PO_4)

The mobility of the proton is two orders of magnitude higher than the vehicular mechanism of any of the phosphate species. Therefore structural diffusion is occuring.

At the melting point (T = 42 °C) conductivity is 7.7×10^{-2} S/cm. The diffusivity of the proton is 2×10^{5} cm^2/s. For comparison, the self-diffusivity of charge in bulk water is 9.7×10^{-5} cm^2/s.

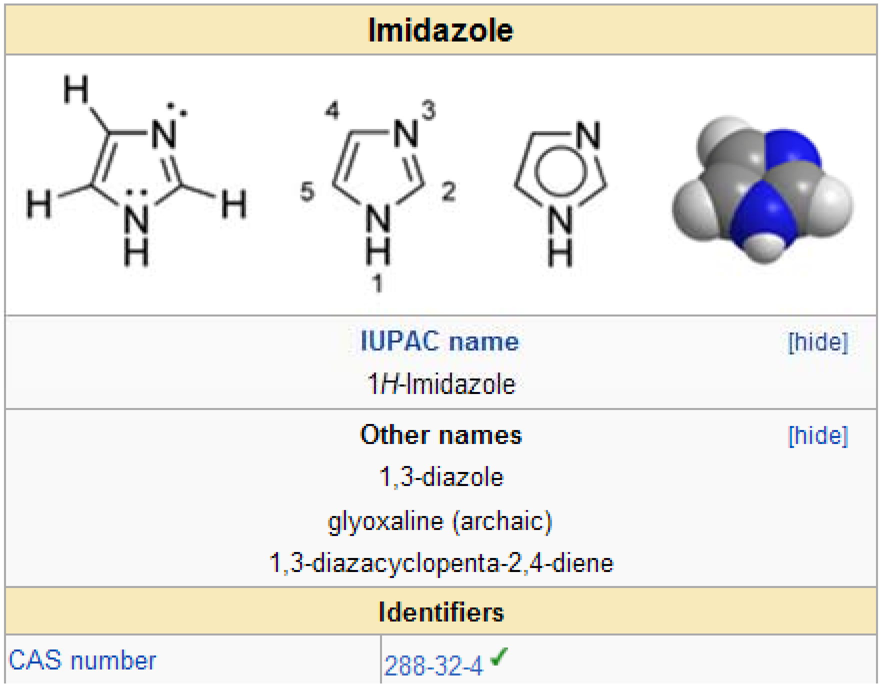
The high concentration of protons and the high mobility make it an attractive fuel cell membrane solvent candidate.

Kreuer et al., Chem. Rev. 2004.

Solvents: Imidazole

Imidazole is an organic compound with the formula $C_3H_4N_2$. This aromatic heterocyclic is a diazole and is classified as an alkaloid. Imidazole refers to the parent compound, whereas imidazoles are a class of heterocycles with similar ring structure, but varying substituents.

Imidazole is amphoteric, i.e., it can function as both an acid and as a base.



Imidazole

IUPAC name [hide]

1*H*-Imidazole

Other names [hide]

1,3-diazole

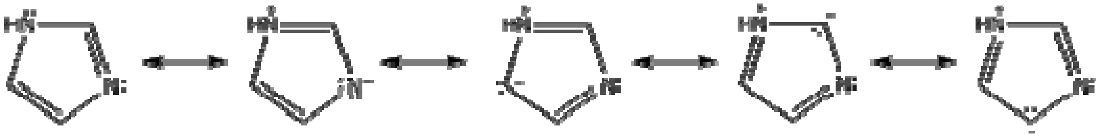
glyoxaline (archaic)

1,3-diazacyclopenta-2,4-diene

Identifiers

CAS number	288-32-4 ✓

Resonance Structures



http://en.wikipedia.org/wiki/Imidazole

Solvents: Imidazole

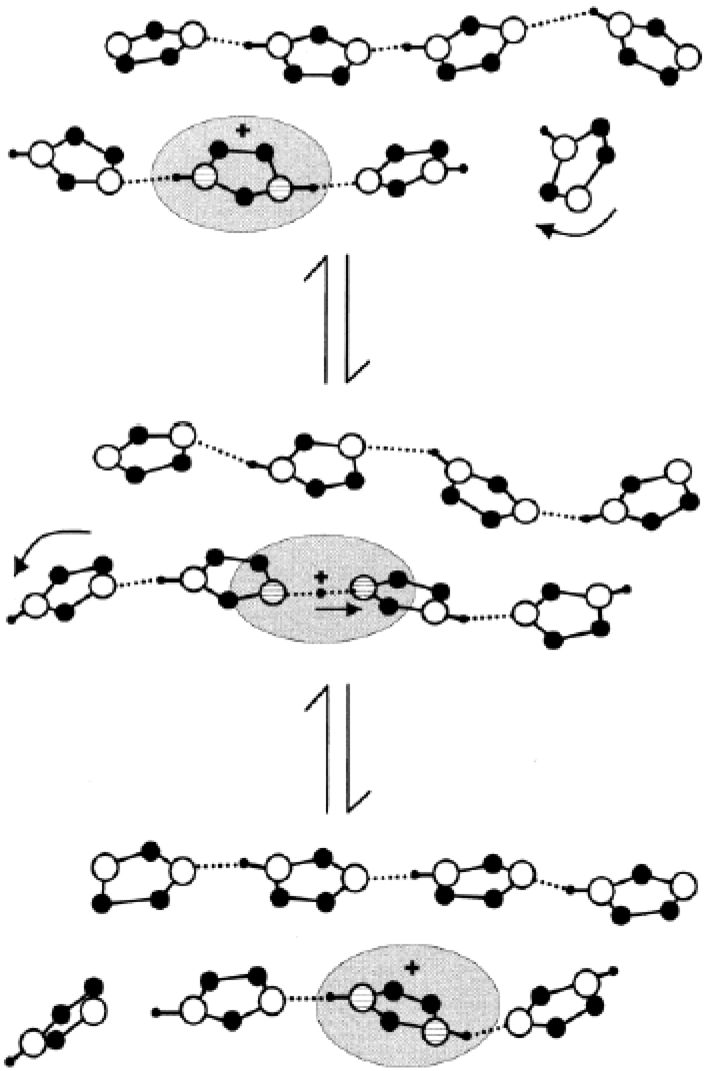


Figure 3. Proton conduction mechanism in liquid imidazole, as revealed by a Car–Parrinello molecular dynamics (CPMD) simulation.[37] Note the similarities with the proton conduction mechanism in water (see Figure 1).

Structural diffusion in Imidazole can also occur.

If the structural diffusion is uncorrelated, it can result in proton conduction.

Kreuer et al., Chem. Rev. 2004.

Solvents: Imidazole

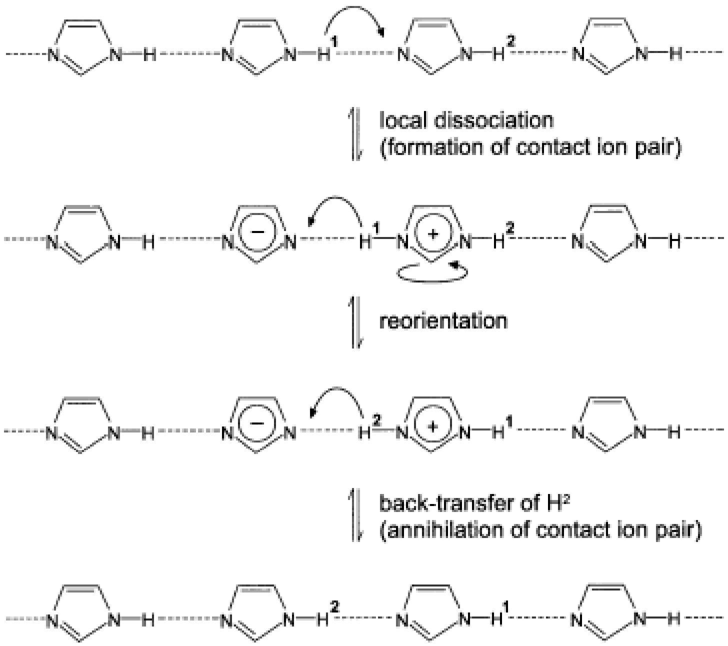


Figure 4. Schematic illustration of correlated proton transfers in pure liquid imidazole leading to proton diffusion but not proton conductivity (see text).

If the structural diffusion is correlated, it does not result in proton conduction.

Kreuer et al., Chem. Rev. 2004.

Membranes: PFSA w/ water

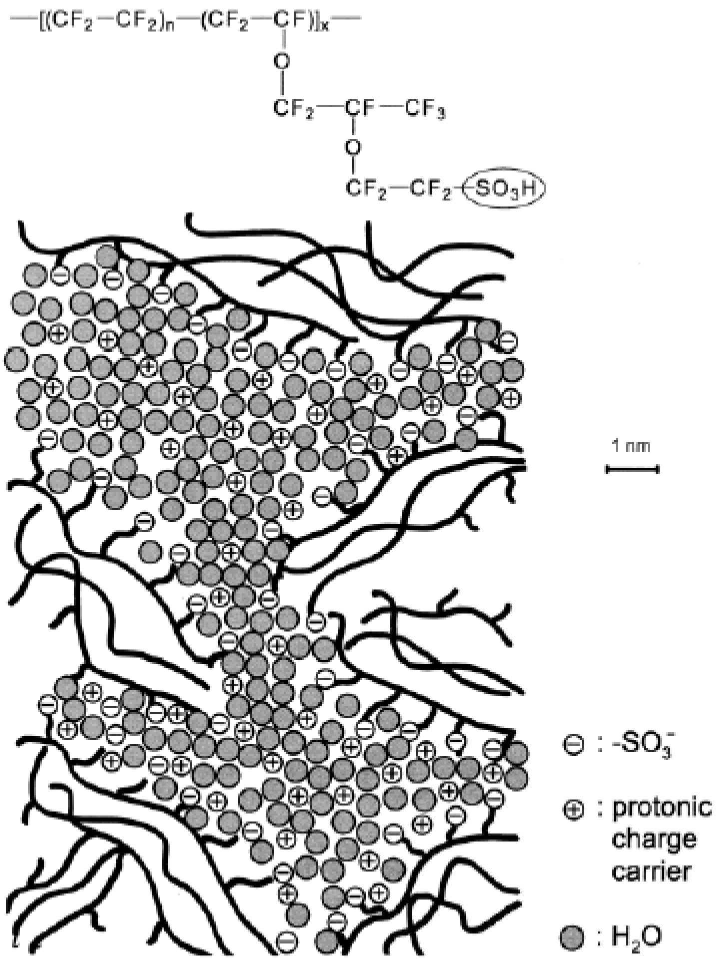


Figure 6. Two-dimensional illustration of some microstructural features of Nafion for an intermediate water content (see text).

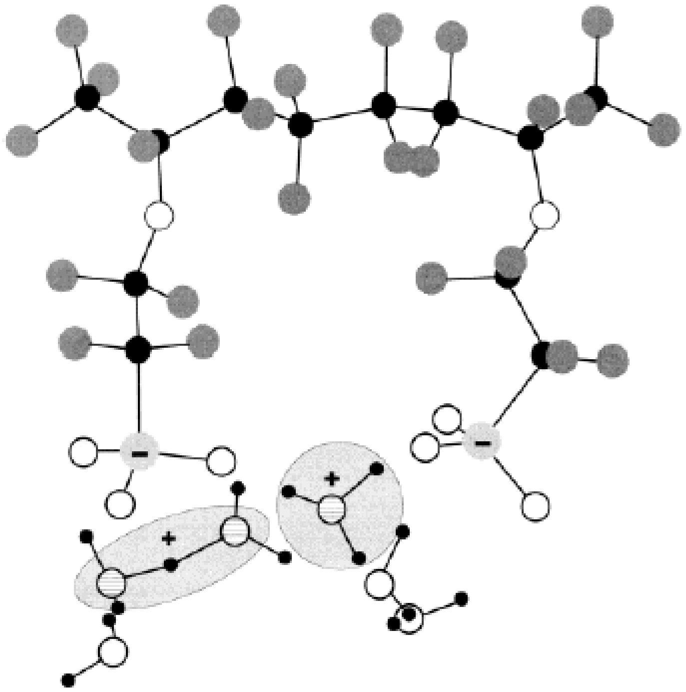


Figure 7. Minimum energy conformation of a two-side-chain fragment of a perfluoro sulfonic acid polymer (Dow) with six water molecules, showing the dissociation of both acidic protons.[23]

As discussed in earlier lectures, these systems have nanosegregation into aqueous and polymer domains. The sulfonic acid groups dissociate, providing protons.

Kreuer et al., Chem. Rev. 2004.

Membranes: PFSA w/ water

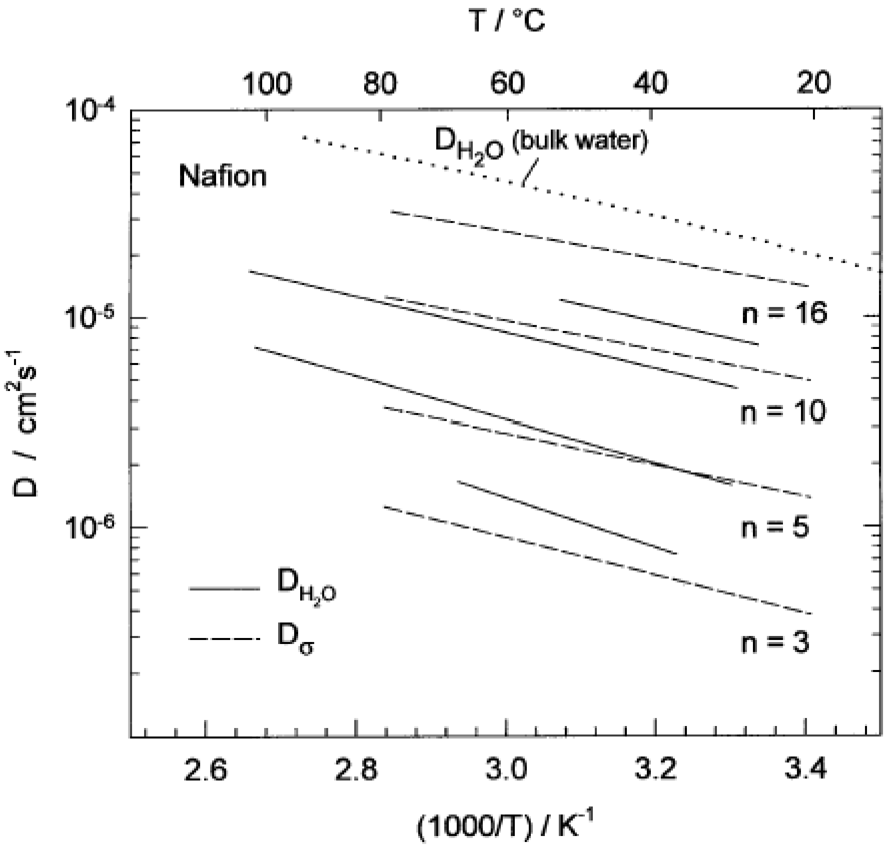


Figure 9. Proton conductivity diffusion coefficient (mobility) and water self-diffusion coefficient of Nafion 117 (EW = 1100 g/equiv), as a function of temperature and the degree of hydration ($n = [H_2O]/[-SO_3H]$).[197]

As discussed in earlier lectures, the proton mobility decreases as the water content decreases.

Kreuer et al., Chem. Rev. 2004.

Membranes: $(PAMA^{+}H_2PO_4)\cdot H_3PO_4$

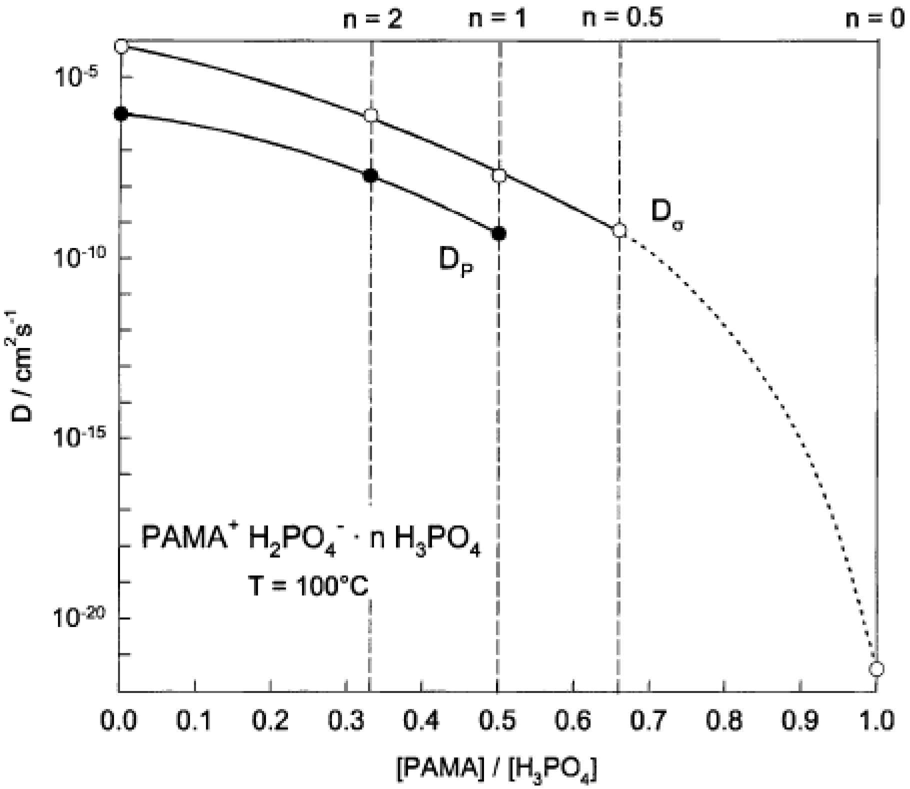


Figure 10. Proton conductivity diffusion coefficient (mobility) and self-diffusion coefficient of phosphorus for poly(diallyldimethylammonium-dihydrogenphosphate)−phosphoric acid ($(PAMA^{+}H_2PO_4^{-})\cdot nH_3PO_4$), as a function of the phosphoric acid content.[233] Note that the ratio D_σ/D_P remains almost constant (see text).

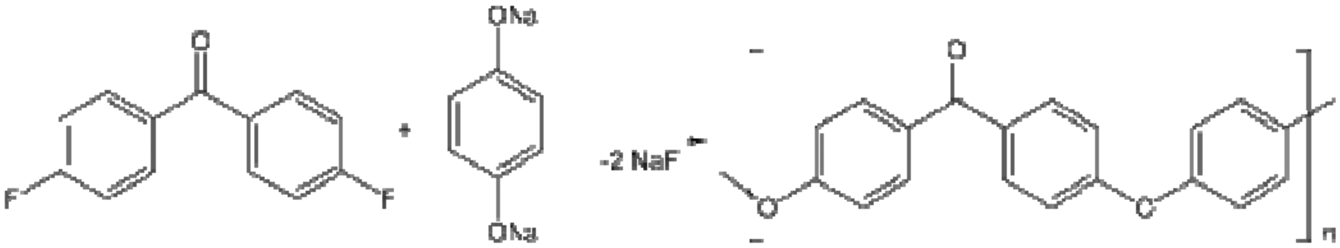
Phosphoric acid can be used as a solvent in polymer membranes as well.
Very little molecular information available—just macroscopic observations.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

Other polymer membanes:

Polyether ether ketone (PEEK)



Sulfonated Polyether ether ketone (s-PEEK)

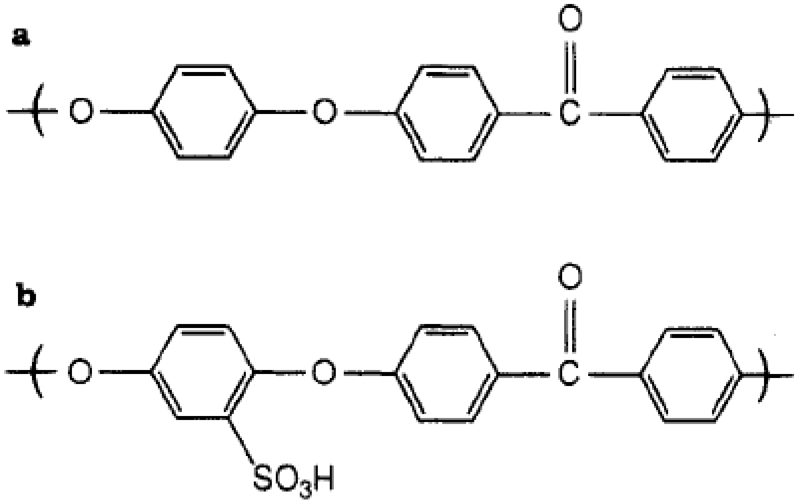
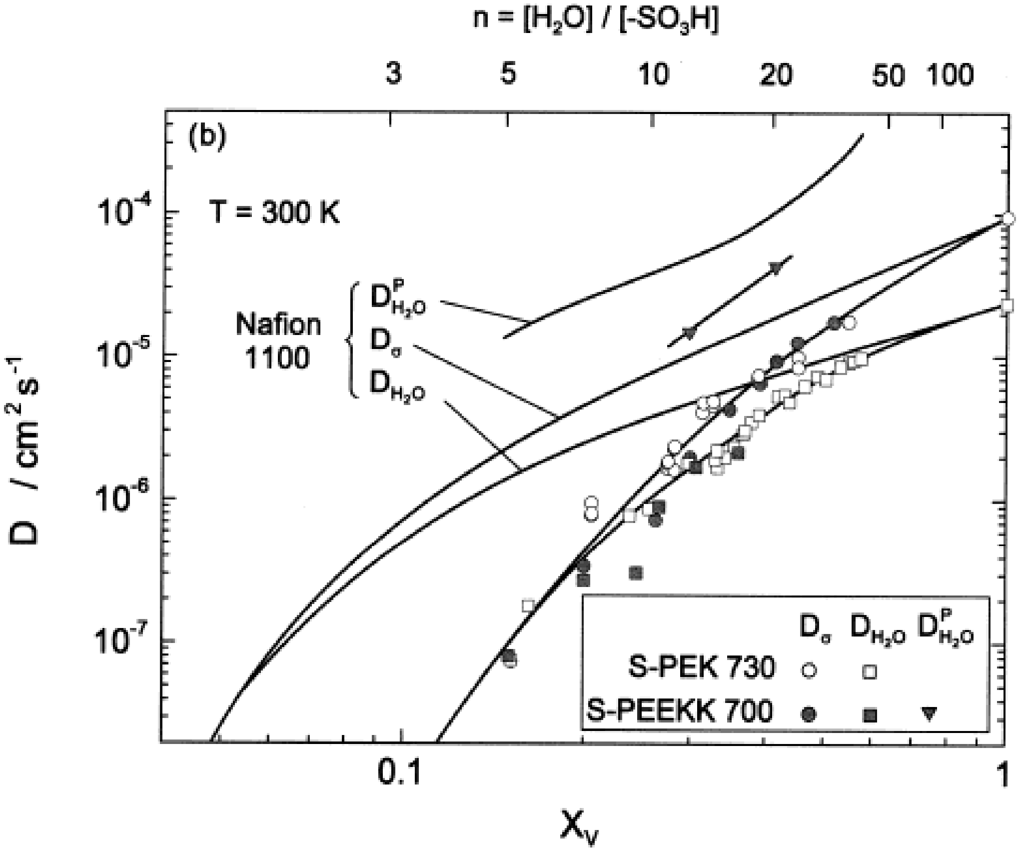


Figure 1. Chemical structure of PEEK (a) and a sulfonated PEEK (b) repeat unit.

Shibuya & Porter, Macromol., 1992.

Membranes: Solvated Polymers



s-PEEK loses conductivity as it dries out as well.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

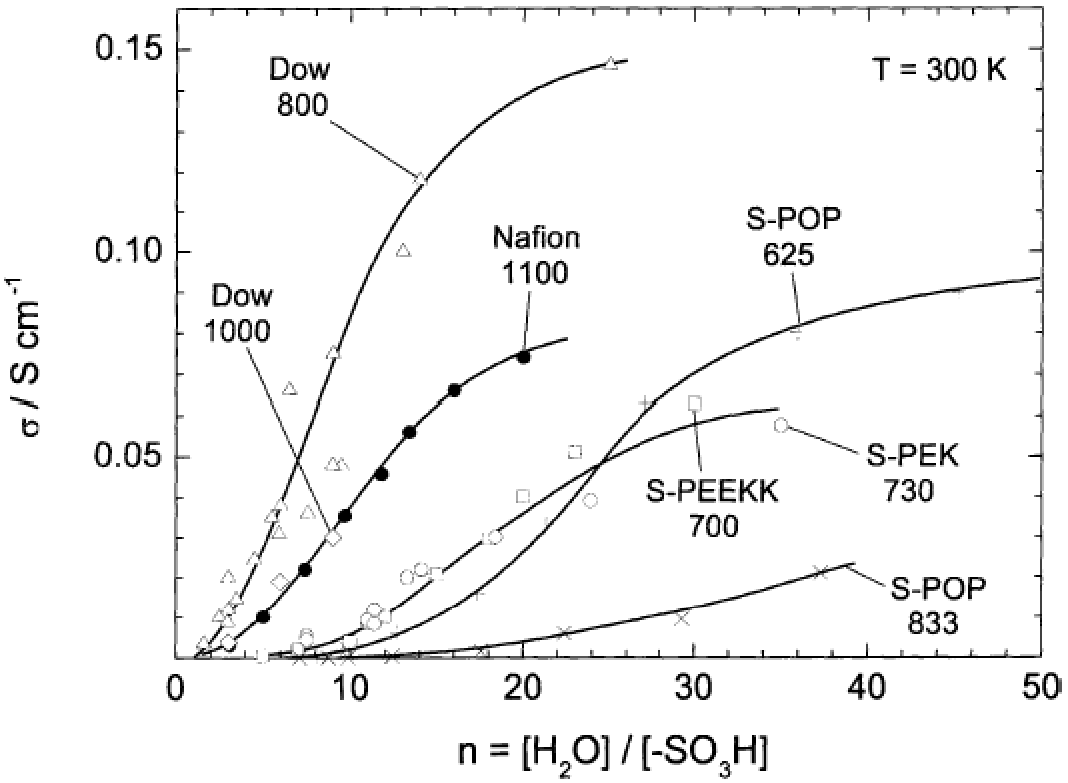


Figure 17. Room-temperature proton conductivity of two Dow membranes[226,255,260] of different EW values, Nafion, two varieties of sulfonated poly(arylene ether ketone)s (S−PEK and S−PEEKK, unpublished data from the laboratory of one of the authors), and sulfonated poly(phenoxyphosphazene)s (S−POPs[301]) of different equivalent weights (685 and 833 g/equiv), as a function of the degree of hydration $n = [H_2O]/[-SO_3H]$ (number below the compound acronym/name indicates the EW value).

Dow = SSC

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

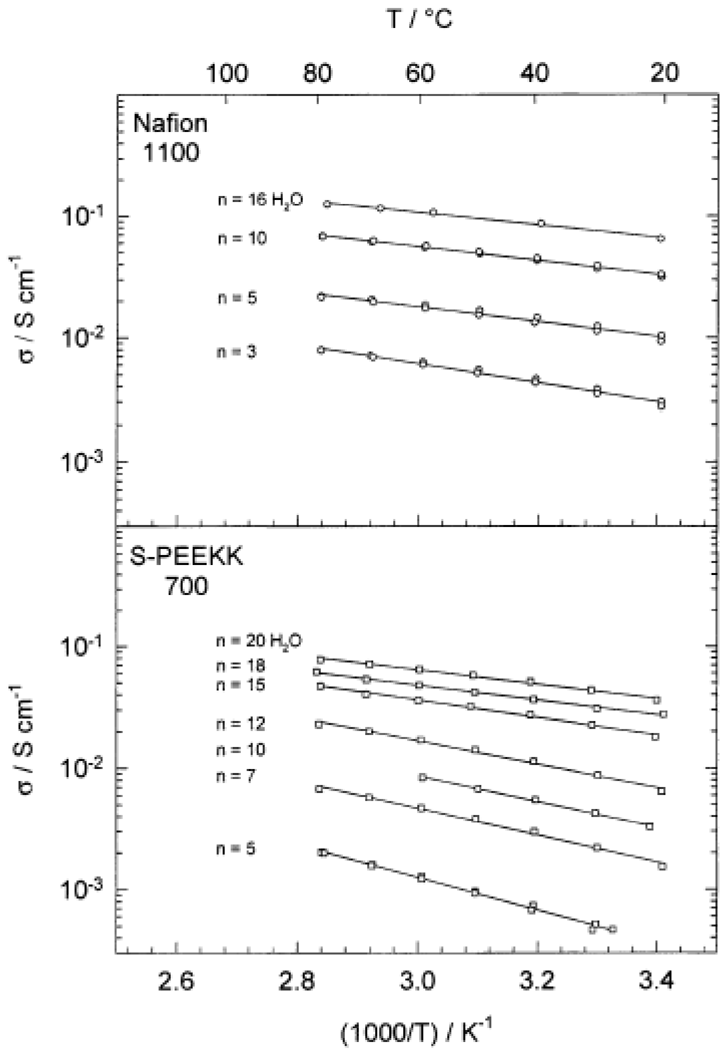


Figure 18. Proton conductivity of (a) Nafion 117 (EW = 1100 g/equiv) and (b) a sulfonated poly(arylene ether ketone), as a function of temperature and degree of hydration ($n = [H_2O]/[-SO_3H]$).[197]

S-PEEK loses conductivity with a decrease in hydration as well.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

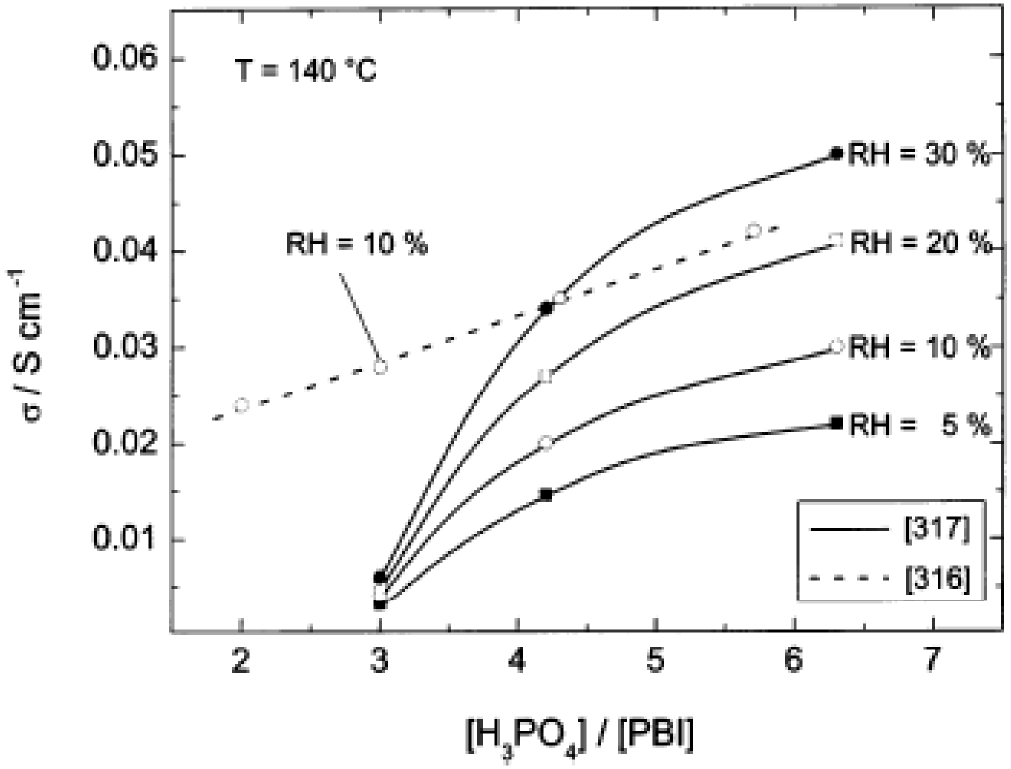


Figure 21. Proton conductivity of PBI·$n$$H_3PO_4$ adducts, as a function of phosphoric acid concentration and relative humidity (RH).[317] Data from another source (denoted by the dashed line)[316] are given for comparison.

Phosphoric acid-based solvated membranes also show a strong dependence on water content.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

YONSEI UNIVERSITY

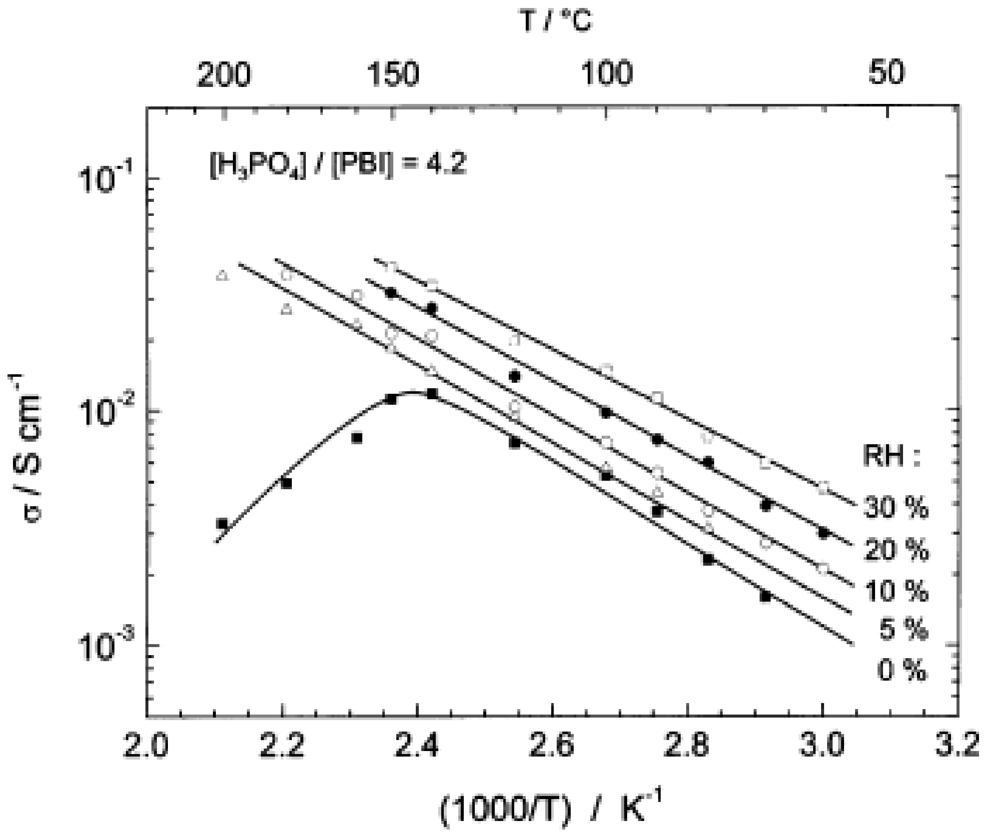


Figure 22. Proton conductivity of PBI·nH$_3$PO$_4$ adducts, as a function of temperature T and relative humidity RH for a given phosphoric acid concentration.[317]

Phosphoric acid-based solvated membranes can function at much higher temperatures.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

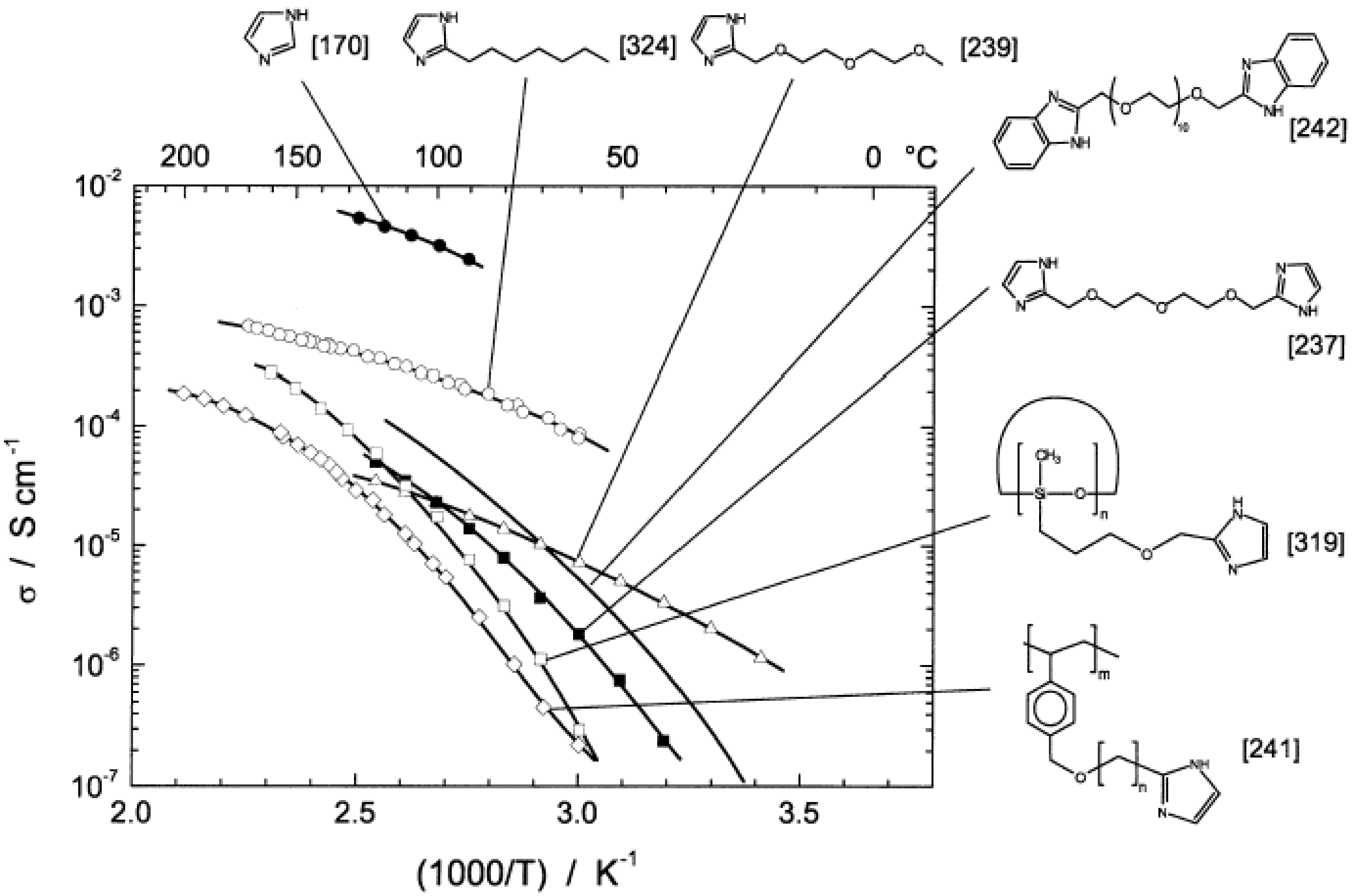


Figure 23. Evolution of proton conductivity of imidazole-based systems with increasing immobilization: from the monomer via oligomers to fully polymeric systems.

Imidazole solvated systems show conductivities below 10^{-2} S/cm.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

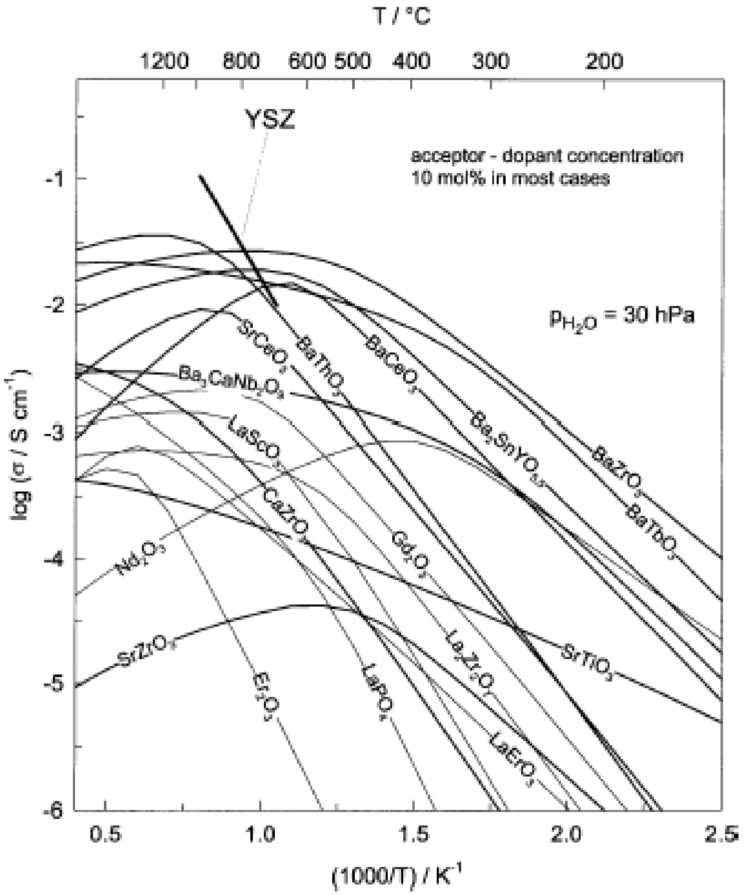


Figure 25. Proton conductivity of various oxides, as calculated from data on proton concentrations and mobilities, according to Norby and Larring (the type of dopant is not indicated; see ref 187 for source data).[186] The conductivity of oxides with a perovskite-type structure are shown by bold lines, and the conductivity of the oxide ion conductor YSZ (yttria-stabilized zirconia) is shown for comparison. (reproduced with the kind permission of *Annual Reviews*, http://www.AnnualReviews.org).

Comparison with solid oxides.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

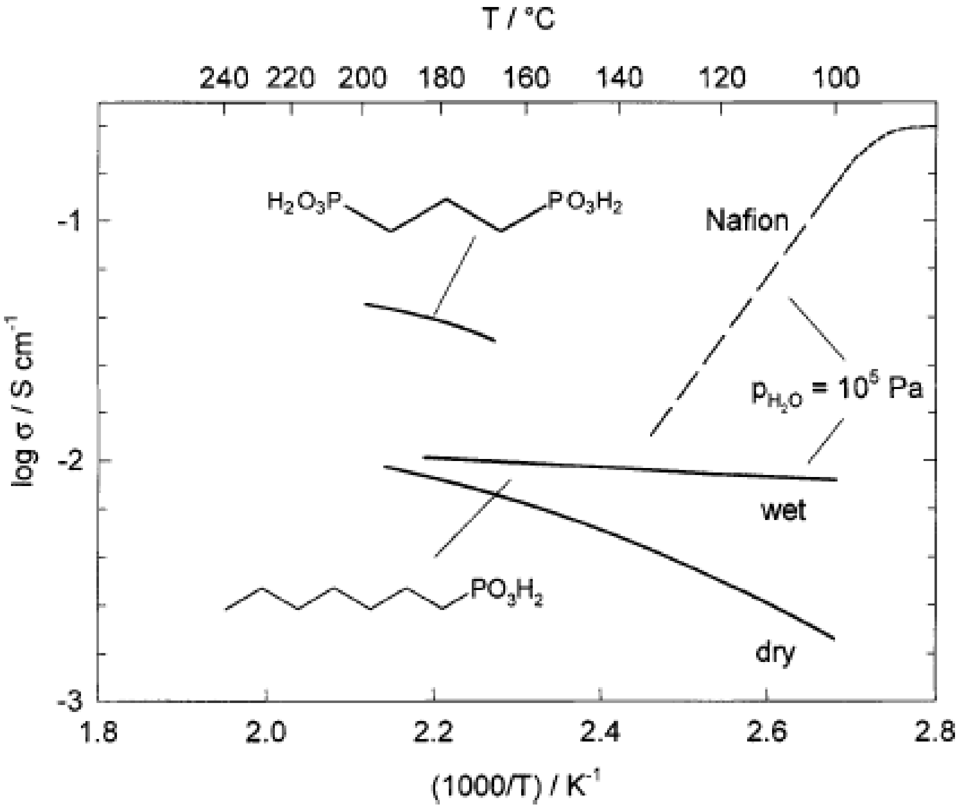


Figure 28. Conductivity of two phosphonic acid-terminated oligomers under dry and wet conditions, compared to the proton conductivity of Nafion at a water partial pressure of $p_{H_2O} = 10^5$ Pa.[324]

New materials may provide performance at intermediate temperatures.

Kreuer et al., Chem. Rev. 2004.

Membranes: Solvated Polymers

Kreuer et al., Chem. Rev. 2004.

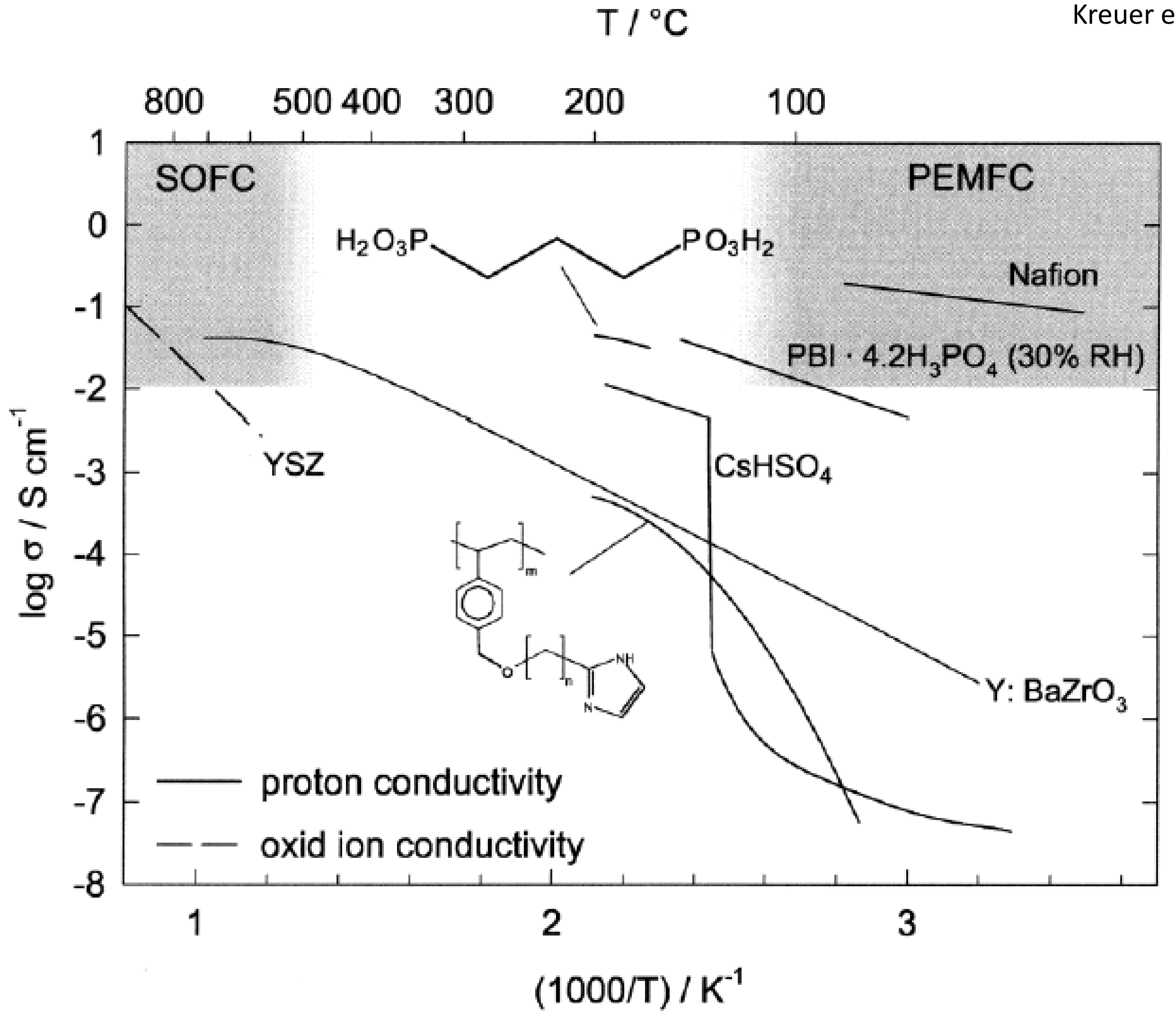


Figure 29. Conductivity of some intermediate-temperature proton conductors, compared to the conductivity of Nafion and the oxide ion conductivity of YSZ (yttria-stabilized zirconia), the standard electrolyte materials for low- and high-temperature fuel cells, proton exchange membrane fuel cells (PEMFCs), and solid oxide fuel cells (SOFCs).

New materials may provide performance at intermediate temperatures.

Conclusions

Hydrated Nafion is hard to beat when fully humidified at room temperature.

However, other PFSA membranes have superior performance at low water contents.

Higher temperature fuel cells could benefit from solvents with much higher vapor pressures, such as phosphoric acid or imidizole. These solvents allow for structural diffusion of protons.

Higher temperature fuel cells may also benefit from other types of polymer membranes, that better retain their morphology at elevated temperatures.