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Poulsen, Finn Willy

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AN INTRODUCTION TO PROTON CONDUCTION IN SOLIDS

Finn Willy Poulsen

Abstract. Proton conducting solids have been studied intensively
in recent years due to their potential use as ion conducting
separators in efficient fuel cells for electricity generation.

This report describes fuel cell - and other possible applications
of solid proton conductors. The best performing materials known
today are listed. Typical synthetic routes and some models for
proton transport in solids are discussed. Hints to future re-
search are given.

The literature collected for this report covers mainly the
period 1974 - 1980.

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1. DEFINITIONS AND GENERAL CONSIDERATIONS

1.1. A solid proton conductor is a solid material, crystalline
or amorphous, which allows the passage of electrical current
through the bulk material exclusively by movement of protons,
H^+. When the material is placed between two noble metal/hydrogen
electrodes, H_2 can be transferred electrochemically from one
electrode to the other by applying a potential difference to the
two electrodes: H_2 will be converted to H^+ at the anode, H^+ then
moves through the proton conducting electrolyte driven by the
electrical field and arrives at the cathode, - where it in turn
will be reconverted to H_2.

Solids, that conduct electricity by means of migration of polyatomic
protonic species, such as H_3O^+, OH^- or NH_4^+, are in contemporary
literature included in the group of proton conducting solids.
These materials can in principle be used as electrolytes in a
fuel cell (see 1.2), although the anticipated conductivity for
conduction in solids by polyatomic ions is low (see 4.6).

Impure and doped ice is the classical proton conductor, studied
by physicists for almost a century. Ice and most other proton
conducting materials studied until now, probably less than a
thousand materials, have extremely low specific conductivities
$10^{-9} - 10^{-12}$ $(ohm \cdot cm)^{-1}$, and they usually decompose on heating
with loss of conductivity (Glasser, 1975).

1.2. A fuel cell is an electrochemical device, essentially composed
by an anode, an electrolyte and a cathode, in which chemical energy
is converted to electrical energy. The fuel gasses (H_2 and O_2 in
the simplest case) are continously fed to their respective elec-
trodes, and the reaction product(s) (e.g. H_2O), which normally
form at one electrode only, is likewise removed continously. The
overall process taking place in a fuel cell is often referred to
as a wet or electrochemical combustion of the two fuel gasses.

The voltage developed in the fuel cell is of the order $1 \pm 0,5$ volt per cell, and it depends on nature and pressure of the reacting species, as well as on temperature and the current drained from the cell. Current densities should be higher than 100 mA/cm^2 electrode area to make the fuel cell economically attractive. Current density is limited by both the electrolyte resistance and the catalytic efficiency of the electrode materials.

The overall efficiency of the fuel cell is however not limited by the Carnot principle, since the process ideally can proceed under thermodynamical equilibrium conditions. The fuel cell concept thus potentially offers pollution free, non-mechanical and efficient energy conversion.

The materials problems of the electrodes and the electrolytes are still enormous (Behret et al., 1979). 25 years of successes and failures in fuel cell research have been reviewed by Kordesch (1978).

The renewed interest in fuel cells has been stimulated by the American space programme, the energy crisis, and the belief that hydrogen in the future will replace oil and natural gas as energy vector. Fuel cells operating on the natural oxygen and glucose content of human blood are now being considered as power sources for implanted pacemakers and alike.

1.3. Many types of electrolytes have been suggested and tested in fuel cells on pilot plant - or laboratory scale (Kordesch, 1978). These include aqueous sulphuric acid, phosphoric acid, alkaline solutions, molten carbonates (500-700° C), polymeric films soaked with water (Nafion), and oxide ion conducting ceramics of the CaO-ZrO$_2$ type for high temperature use (700-1000° C). A proton conducting solid electrolyte with high conductivity would make possible the construction of a fuel cell with negligible corrosion problems as compared to the electrolyte types mentioned above. The demands to the optimal solid state proton conductor are listed in section 2.1.

1.4. Aim of this report: Essential literature in this rapidly
expanding field has been collected, with emphasis on the period
from 1974 to 1980. The state of art including the year 1974
has been thoroughly reviewed by Bruinink (1972) and by Glasser
in 1975 (566 references). These authors also cite important
experimental methods for characterization of proton conduction
in solids.

2. POTENTIAL USES OF SOLID STATE PROTON CONDUCTORS

Four future application areas can be foreseen with the advent
of a good proton conductor. The two most important ones are in
energy conversion: fuel gas + oxygen -> energy in the fuel cell,
and water + energy -> hydrogen + oxygen in the electrolyzer.

2.1. The requirements to a proton conductor for application as
the electrolyte in a fuel cell are numerous: 1) A conductivity
higher or equal to $0,1$ $(ohm \cdot cm)^{-1}$ at the working temperature is
mandative to minimize internal ohmic losses. 2) The conduction
should be selective to protons. 3) The electrolyte must be an
electronical insulator to prevent internal short circuit of the
cell. 4) The electrolyte must be stable with respect to thermal
and electrochemical decomposition $(25-300^\circ \text{ C})$, and stable in
the partical water vapour pressure range in the working cell.
5) Easy and cheap fabrication. 6) The proton conductor must have
suitable mechanical and thermal properties, e.g. thermal
expansion coefficient, that match properties of electrodes and
other construction elements of the fuel cell.

None of the materials listed in section 3 fulfil more than a
few of these requirements.

2.2. An electrolyzer for hydrogen production is used when H_2-gas

is needed in industry or when excess electric energy is available. In the last case the produced H_2-gas can be stored, converted to metalhydrides etc., for subsequent use in a fuel cell, when electricity is needed again. In principle an electrolyzer is a fuel cell operated in the reverse direction: water is feed to one electrode and an externally applied potential difference then decomposes water into H_2- and O_2 gas. The materials requirements are similar to those for fuel cell applications (Libowitz, 1979).

2.3. A proton conductor can furthermore in theory be used as the ion specific membrane in sensing devices: for pH-measurements in liquids (Lundsgaard and Brook, 1973), and for partial pressure measurement of H_2 in gasses (Jensen and McGeehin, 1979) and (Bruinink and Kosmeijer, 1973).

Finally, proton conductors have been used as electrolytes in electrochromic optical displays (Mohapatra et al., 1979). A high protonic conductivity is not necessary for the last two application areas.

3. THE BEST PROTON CONDUCTORS

Several ways (Glasser, 1975) have been given to classify proton conducting solids on various bases: type of crystal structure, presence/absence of hydrogen bonds, ion exchange properties, deviation from stoichiometry and so on. Nothing unexpected or usefully can be deducted from such classification schemes, in as much as the best proton conductors found so far belong to highly different "types" of materials. The maximum proton conductivity has never been estimated (lack of models), but it would probably not exceed the conductivity of aqueous acid solutions (of the order $\sim$ 1-5 $ohm^{-1} \cdot cm^{-1}$).

Huggins (1980) reviewed the situation late 1979, and no break-

through has been reported since. Table I summarizes the best
materials found till now.

Two features should be noticed from Table I: i) several materials
exhibit conductivities in the range 10^{-3} to 10^{-1} ohm^{-1}cm^{-1} at
25° C, which make them technologically interesting; but ii)
most materials contain crystal water/and or hydrated protons,
H_3O^+ ions, and will therefore loose water and conductivity on
heating to 100-300° C, where the fuel cell electrodes start
functioning properly. Several other drawbacks connected with
the individual materials are listed in the original papers.

Determination of conductivity of hydrated materials is problematic
due to the possible presence of excess water/electrolyte solution
absorbed and adsorbed by the solid in cracks, grain boundaries
and on the surface. A high conductivity observed for such ma-
terials may often be caused by surface conduction in liquid
like layers between the otherwise poorly conducting bulk particles.
Howe and Shilton (1979) have advised one method to overcome
this problem.

None of the materials listed are anywhere near the ideal for fuel
cell application, although several outhors have made small lab-
oratory scale fuel cells demonstrating the "usefulness" of their
particular proton conductor. Further examples of fuel cells
with solid electrolytes are given by Takahashi et al. (1979).

The column "Possible proton conduction mechanism" will be referred
to in section 4.5 and 4.6.

4. MODELS FOR PROTON CONDUCTION IN SOLIDS

4.1. Formal oxidation number of H in compounds

Hydrogen forms an exorbitant number of compounds with almost all

Table 1. The best solid proton conductors. Specific conductivity measured at room temperature.

Type of material	Compound	Specific conductivity $(\text{ohm} \cdot \text{cm})^{-1}$	Possible proton conduction mechanism	Reference
Hydrated acids	$H_3PMo_{12}O_{40} \cdot 29\ H_2O$	1.8×10^{-1}	liquid-like transport of H^+	Nakamura et al., 1979
	$H_3PW_{12}O_{40} \cdot 29\ H_2O$	1.7×10^{-1}		Nakamura et al., 1979
	$HUO_2PO_4 \cdot 4H_2O$	4×10^{-3}	$H_3\overset{+}{O}/H_2O$ jump	Howe and Shilton, 1979
	$HUO_2AsO_4 \cdot 4\ H_2O$	6×10^{-3}	$H_3\overset{+}{O}/H_2O$ jump	Shilton and Howe, 1979a
	$H_8UO_2(IO_6)_2 \cdot 4\ H_2O$	7×10^{-3}	$H_3\overset{+}{O}/H_2O$ jump	Shilton and Howe, 1979b
	H_3OClO_4	3×10^{-4}	H_3O^+ migration or impurity conduction	Potier and Rousselet, 1973
Amphoteric oxide hydrates	$Sb_2O_5 \cdot 4\ H_2O$	3×10^{-4}	H_3O^+/H_2O jump	
	$SnO_2 \cdot 3\ H_2O$	2×10^{-4}	liquid-like transport of H^+)	England et al., 1979
	$ZrO_2 \cdot 2.3\ H_2O$	3×10^{-5}	liquid-like transport of H^+)	
Clays	H^+ - Montmorillonite	$1\text{-}4 \times 10^{-4}$	liquid-like transport of H^+	Sheffield and Howe, 1979
	H-Aℓ-Montmorillonite	$10^{-4} - 10^{-2}$	liquid-like transport of H^+	Sheffield and Howe, 1979
Ion exchanged ceramics	Hydrated hydronium ß" alumina	5×10^{-3}	H_3O^+/H_2O jump, H_3O^+ migration	Farrington and Briant, 1978
	NH_4^+ - ß alumina	$\sim 10^{-3}$ (a)	NH_4^+ migration	Farrington and Briant, 1979

(a) At 300°

elements of the periodic table except the noble gases. One can
assign a formal oxidation number equal to +1, 0 or -1 to hydrogen
in these compounds; i.e.:

| Formal oxidation number	Radius (Å)	Typical Compound	Possible diffusing species
+1	$1,5 \cdot 10^{-5}$ for H^+	ICE $HUO_2PO_4, 4H_2O$ NH_4+beta alumina H_3O^+beta alumina	H^+ H^+ NH_4^+ H_3O^+ and H^+
0	Bohr-radius 0,529 for H	transition metal hydrides: PdH_x $LaNi_5H_x$	(H^+, e^-) or H^+?
-1	Pauling: 1,54 Goldschmidt 2.08 for H^-	ionic hydrides: LiH, CaH_2	H^-

Table II: Formal oxidation number of hydrogen in chemical compounds.

The assignment of oxidation number equal for zero to H in tran-
sition metal hydrides is debatable.

For obvious reasons, (see below), only compounds with hydrogen
in oxidation number +1 will function as an ion conducting menbrane
in fuel cells. Ionic hydrides (-1) react with O_2 for example -
and transition metal hydrides are often electronic conductors.

4.2. Hydrogen bonds

As a result of the small radius of the free proton, "naked"
H^+ ions are not found in solids under equilibrium conditions, -
"H^+" is always covalently bonded to some electronegative atom/
ion in the structure. Typical covalent bond lengths are around
1Å for C-H, N-H and O-H bonds. It is well known, that protons
can be shared between two electronegative atoms, e.g. O-H----O,
the socalled hydrogen bond. Typical hydrogen bond lengths, the
distance between X and X' in X-H----X', amount to 2.55, 2.76 and
3.0 Å for F-H---F bonds, O-H---O bonds and N-H----N bonds,
respectively. The bond is usually linear. The amount of literature
on hydrogen bonding is overwhelming (Bell, 1973). The nature
of the hydrogen bond is responsible for most of the dielectric/
ferroelectric properties of "H^+" containing compounds. The
presence of hydrogen bonds is easily revealed by vibrational
spectroscopy (Zundel, 1976). Furthermore, the oscillation of H
from one side to the other in a hydrogen bond:

$$O-H----O \rightleftharpoons O----H-O$$
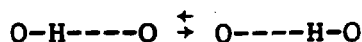
corresponds to a net transport of change, and is therefore one
of the essential steps in the proton conduction mechanism. Recent
literature on hydrated protons, H_3O^+, $H_9O_4^+$ etc- has been given
by Mata- Segreda (1980) and Raffenetti et al. (1977).

4.3. Proton transfer reactions

Quantum mechanical descriptions of proton transfer reactions for
liquid phase reactions have been discussed by many authors:
Stillinger (1978), Brüniche-Olsen and Ulstrup (1979), and Zim-
merman (1964).

Descriptions of proton transfer in solids (other than ice) are
very few in number; - see Azizyan and Klinger (1978).

The possibility of cooperative proton transfer (Groothuus type
conductivity) has been discussed by Wirtz (1950) and Onsager (1968).

Proton transfer rates in solution are extremely fast. The rate
determining steps are often 1) the diffusion of the reacting
species towards each other, and 2) the time necessary for the
species to orientate properly for reaction to take place. When
these two conditions are fulfilled reaction is "almost" instan-
taneous. An example, acceptable by lay-man, has been given by
Eigen and DeMaeyer (1958): If 1 l of a 1 Molar strong base and
1 l of a 1 Molar strong acid could be mixed instantaneously then
the neutralisation reaction: $H^+(aq) + OH^-(aq) \rightarrow H_2O$ would be
completed in less than 10^{-11} sec.

The average lifetime of an individual H_3O^+ ion in aqueous solution
is of the order $2.4 \cdot 10^{-13}$ sec. (Conway, 1964). This time corre-
sponds approximately to 24 vibrational periods of the OH bonds
in H_3O^+.

4.4. Acid-base analogue to proton conduction processes

It is useful to make an analogy between the general acid-base
concept and the movement of protons from one position in a crys-
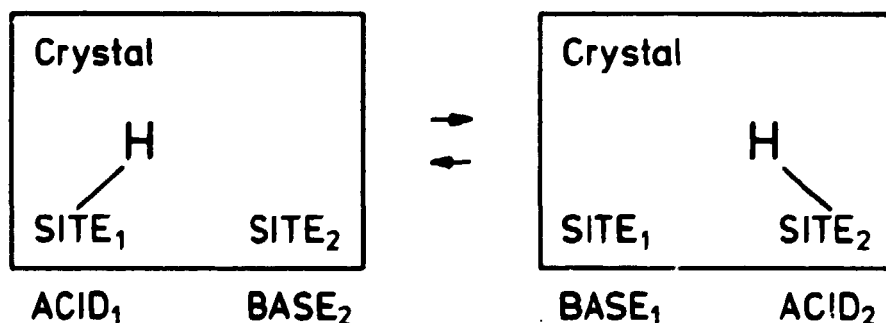tal to the next available site:

Figure 1. Acid-base analogy to proton conduction in solids.

The site, $Site_1-H$, can be viewed upon as an acidic group or part
of the lattice, whereas $Site_2$, before the acceptance of the proton,
is a basic group. The transference of one proton from 1 to 2 is
thus similar to an internal acid-base reaction. Proton transfer
will be energetically costfree when the two sites are chemically
identical (apart from the mobile proton).

Site$_1$-H/Site$_2$ will in this case be a corresponding acid/base system, or stated with a neologism: a topotactical acid-base couple.

In the case where the initial and final states are chemically different, an extra amount of energy has to be spent to transfer the proton, thereby making the conduction process unfavourable, if not impossible. This would be the case for the transfer of a proton from an R-NH$_3^+$ group to R^1-COO$^-$ or from HCO$_3^-$ to H$_2$O.

4.5. The reorientation problem

The nature of proton conduction in solids differs in two important aspects completely from ion conduction by Na$^+$, K$^+$, Ag$^+$ ions etc. in "normal" solid electrolytes: 1) the hydrogen bond is covalent and directional in character, whereas metal ions in ionic solids experience coulomb forces more or less from all sides. 2) as a consequence of this proton conduction involves at least two different steps as opposed to one for metal ion conduction.

The necessity of molecular reorientation during proton conduction can be illustrated by the proton conduction in hydrogen uranyl phosphate tetrahydrate (HUP): HUO$_2$PO$_4$,4H$_2$O (Howe and Shilton, 1979). This structure contains alternating layers of UO$_2^+$ + PO$_4^{-3}$ ions, and layers of H$_2$O + H$_3$O$^+$ ions. The ratio of H$_3$O$^+$ to H$_2$O is 1 to 3. In the H$_3$O$^+$ + H$_2$O layers hydrogen bonding is dominating. A sequence of H-hops can proceed as follows:
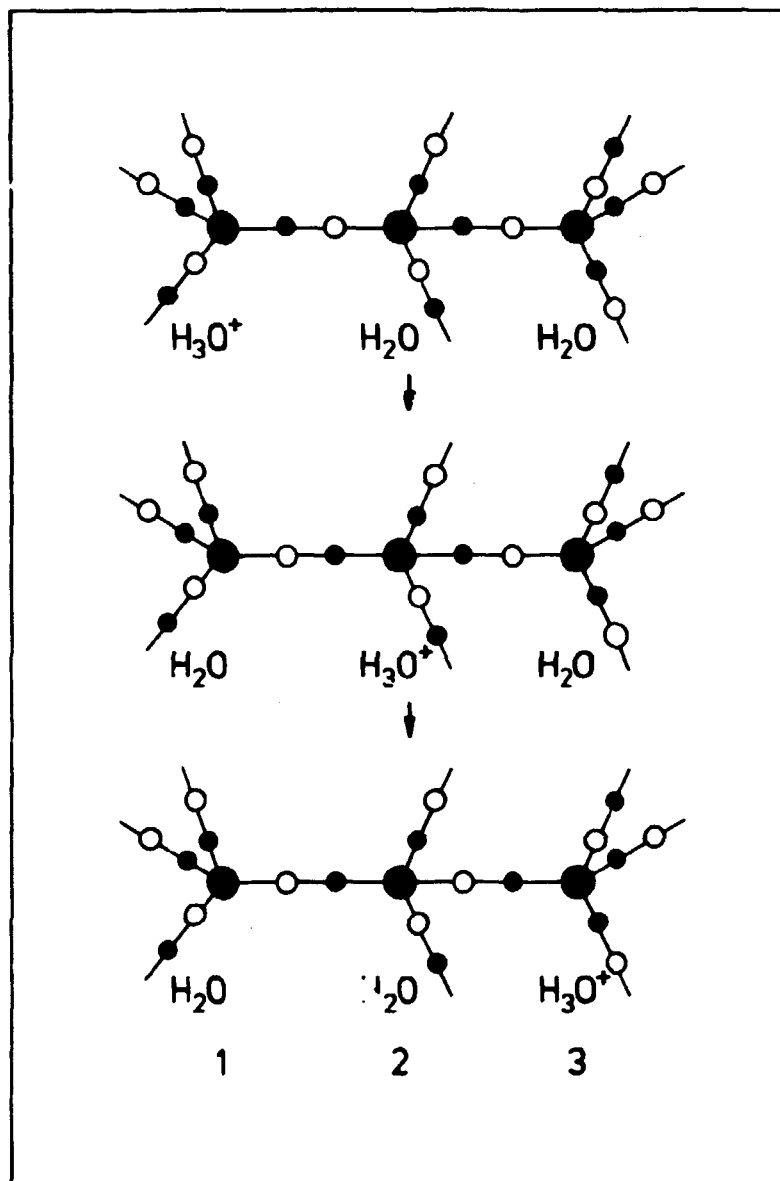
Figure 2 . Proton hopping in $HUO_2PO_4,4H_2O$. Large filled circles are Oxygen, small circles: filled are occupied by proton, open circles are potential but vacant positions for protons.

The net result of the two proton jumps within their respective hydrogen bonds is a transport of charge from 1 to 3. The configuration around position 1 and 2 are however, such that further transport in the field direction is impossible before the water molecule at 2 has reoriented itself. Reorientation and not the proton jump will be the rate determining step. For aqueous solutions this is evident since the activation energy

for proton conduction, ~ 11 kJ/mole, allmost equals the estimated reorientation energy, ~ 10 kJ/mole, for a water-molecule (in water). Reorientation of H_2O, OH^- or other groups in a solid naturally demands higher energies. The activation energy for proton conduction in HUP is 31 (Howe and Shilton, 1979), in ice 34 (Franks, 1972), and in KH_2PO_4 73 kJ/mole, (Sharon and Kalia, 1977), respectively.

4.6. Three proton conduction mechanisms

Three different transport mechanisms for proton conducting has been indicated in Table 1: liquid like transport, H_3O^+ migration, and H_3O^+/H_2O transfer.

Liquid-like transport is possible in materials which contains waterlayers included in the crystal structure i.e. clays (Sheffield and Howe, 1979) or polycrystalline materials composed by charged crystallites held together by a electrolyte solution i.e. $SnO_2, 3H_2O$ (England et al., 1979). The conduction in such materials is not specific to protons and is extremely sensitive to variations in the water content.

Polyatomic ions such as H_3O^+, OH^- or NH_4^+ can migrate as entities through the bulk material. The activation energy would be expected to be very high for such a process unless the structure contains wide internal cavities, channels or alike of suitable size. Materials of the zeolite type and organic polymers may be taylored to meet this requirement. Diffusion of polyatomic ions has been suggested by Farrington and Briant (1978) to account for some of the conductivity of proton exchanged beta alumina, "H_3O^+ beta Al_2O_3. NH_4^+ diffusion has been suggested for the analogue material NH_4^+ beta alumina.

This type of conduction will have to prevail in compounds, where the corresponding acid/base partner is not present, i.e. H_3O^+ without excess H_2O, OH^- without $[O^{--}]$ or H_2O, and NH_4^+ without NH_3 being present in the material.

Proton jumps followed by reorientation of donating and/or accepting groups have been discussed in section 4.5. The proton jump is possible by tunnelling in hydrogen bonds, - the activation barrier possibly lies entirely in the reorientation step.

This mechamism will function with the following acid-base couples, properly located at alternating positions:

H_3O^+/H_2O NH_4^+/NH_3 $RCOOH/RCOO^-$

H_2O/OH^- RNH_3^+/RNH_2 RSO_3H/RSO_3^-

$OH^-/[O^{--}]$
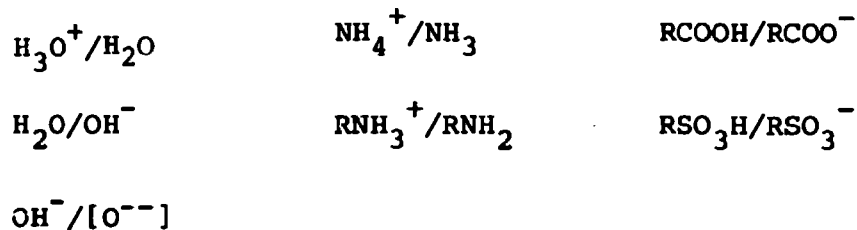
It is at present a matter of pure guessing, to predict the optimal acid-base couple for this type of conduction.

From the point of view of minimizing the reorientation energy one could suggest transfer of H^+ from OH^- to a neighboring oxide ion $[O^{--}]$ to be optimal since it involves reorientation of the smallest possible group, - the OH^- ion. AlOOH and NiOOH are such types of materials. The former is a very poor proton conductor (Arjona and Fripiat, 1967). The diffusion of protons in NiOOH is responsible for the success of the Ni-electrode in secondary Ni-Cd batteries (Briggs, 1974), however, this material also conducts electrons.

5. SYNTHETIC ROUTES TO PROTON CONDUCTORS

The following is a short list of ways of synthesizing proton conductors. The ideologies underlying the respective methods are sometimes given in the original papers.

Precipitation from aqueous solution at controlled pH

$HUO_2PO_4 \cdot 4H_2O$ (Howe and Shilton, 1979)

$ZrO_2 \cdot nH_2O$ and $SnO_2 \cdot nH_2O$ (England et al., 1979)

Ion exchange methods

$Zr(MPO_4)_2$ (M=Li,Na,K) (Yamanaka, 1980)

H_3O^+- beta alumina (Farrington and Briant, 1978)

$HSb(OH)_6 \cdot nH_2O$ (England et al., 1979)

General reference: (Amphlett, 1964)

Decomposition of NH_4^+-compounds

H^+ beta alumina (Collongues, 1978)

Reaction of noble metal compound with H_2/D_2

D^+ beta alumina (England et al., 1976)

Design of ionic polymers

General reference (Eisenberg and King, 1977).

6. FUTURE RESEARCH

The problem of finding new solid state proton conductors bears similarities to the search for organic superconductors and other materials with unexpected or atypical materials properties.

The optimal material may be found by ingenuity, systematic work or by simple luck. Unfortunately none of these ways are easy to promote by human will.

The following subjects should at least be considered in future research in the area:

i) Screening of all available proton containing solids by methods that are sensitive to mobile protons, such as PMR, ac-impedance measurements, electrolysis between H_2-electrodes.

ii) Ion exchange in acid of known metal ion solid electrolytes.

iii) Doping experiments on well established (but poor) proton conductors.

iv) Built new compounds based on chemical analogy, intuition or theoretical predictions.

The suggestion of using solid proton conductors in fuel cells involves three problems which can be summarized as follows:
i) do highly conducting solid proton conductors exist at all?
ii) if so, - can they be fabricated in suitable form? iii) if this is also the case, - are they stable and reliable under the actual working conditions of the fuel cell?

7. Acknowledgements

REFERENCES

ARJONA, A.M., and FRIPIAT, J.J. (1967). Proton Mobility in
    Solids. Part 2. Dielectric and diffusion Measurements in
    Boehmite. Trans. Faraday Soc. 63, 2936-44.

AMPHLETT, C.B. (1964). Inorganic Ion Exchangers. (Elsevier,
    Amsterdam) 141 p.

AZIZYAN, A., and KLINGER, M.I. (1978). Quantum theory of the
    conductivity of crystals with hydrogen bonds and proton
    conductivity. Dokl. Akad. Nauk SSSR 242, 1046-9.

BEHRET, H., BINDER, H., and SANDSTEDE, G. (1979). Development
    of Fuel cells - A materials problem. In: Materials science
    in energy technology. Editors: G.G. Libowitz and M.S.
    Whittingham. (Academic Press, New York) 381-426.

BELL, R.P. (1973). The proton in Chemistry (Cornell University
    Press, Ithaca, New York) 310 p.

BRIGGS, G.W.D. (1974). Nickel hydroxide and related electrodes.
    Electrochemistry 4, 33-54.

BRUININK, J. (1972). Proton migration in solids. J. Appl.
    Electrochem. 2, 239-49.

BRUININK, J., and KOSMEIJER, B. (1973). Mixed ionic conduction
    in solid KHF_2. J. Phys. Chem. Solids 34, 897-903.

BRÜNICHE-OLSEN, N., and ULSTRUP, J. (1979). Quantum theory of
    kinetic Isotope effects in Proton transfer Reactions. J.
    Chem. Soc. Faraday Transactions I, 75, 205-226.

COLLONGUES, R. (1978). Stoichiometry, Phase transition and
    conductivity in beta Al_2O_3. Mat. Res. Bull. 13, 1281-85.

CONWAY, B.E. (1964). Proton Solvation and proton transfer in
    solution. In: Modern Aspects of Electrochemistry. Vol. 3.
    (Butterworths, London). Editors: J. Prockris and B.E. Conway)
    43-148.

EIGEN, M., and DE MAEYER, L. (1958). Self-dissociation and
    protonic charge transport in water and ice. Proc. R. Soc.
    (London). Ser. A247, 505-533.

EISENBERG, A., and KING, M. (1977). Ion containing Polymers,
    Physical Properties and Structures. (Academic Press, New
    York). 287 p.

ENGLAND, W.A., CROSS, M.G., HAMNETT, A., WISEMAN, P.J., and

GOODENOUGH, J.B. (1979). Fast proton conduction in inorganic ion-exchange compounds. Presented at Faraday Division Electrochemistry Group Meeting, Oxford, March.

ENGLAND, W.A., JACOBSON, A.J., and TOFIELD, B.C. (1976). Neutron diffraction Determination of the structures of Deuterium beta-alumina at 4.5 and 823 K. J. Chem. Soc. Chem. Commun. 21, 895-896.

FARRINGTON, G.C., and BRIANT, J.L. (1979). Chemistry and conductivity of protonic beta Alumina. Proceeding of International Conference on Fast Ion transport in Solids (Elsevier North-Holland).

FARRINGTON, G.C., and BRIANT, J.L. (1978). Hydronium Beta alumina: a fast proton conductor. Mater. Res. Bull. 13, 763-73.

FRANKS, F. (1972). Water, a Comprehensive treatise (Plenum, New York).

GLASSER, L., (1975). Proton conduction and injection in solids. Chem. Rev. 75, 21-65.

GOURIER, D., and SAPOVAL, B. (1979). Jump diffusion and rotational tunneling of ammomium in beta-alumina by NMR. J. Phys. C. 12, 3587-90.

HOWE, A.T., and SHILTON, M.G. (1979). Studies of Layered Uranium (VI) Compounds. I. High proton conductivity in Poly crystalline Hydrogen Uranyl Phosphate tetrahydrate. J. Solid State Chem. 28, 345-61.

HUGGINS, R.A. (1980). Solid Electrolytes. In: Nato advanced Study Institute on "Materials for advanced batteries". Editor J. Broadhead (Plenum, New York).

JENSEN, J., and MCGEEHIN , P. (1979). The Properties of Hydrogen Exchanged Beta-Alumina and their Use on Gaseous Concentration Cells. Silicates Industriels A27/78, 1-8.

KORDESCH, K.V. (1978). 25 years of fuel cell Development (1951-1976). J. Electrochem. Soc. 125, 77C-91C.

LIBOWITZ, G.G. (1979). The role of Materials Science in the development of Hydrogen Energy systems. In Materials science in energy technology. Editors: G.G. Libowitz and M.S. Whittingham. (Academic Press, New York). 427-452.

LUNDSGAARD, J.S. and BROOK, R.J. (1973). Mixed Conductivity of Beta-Alumina Electrolyte in Aqueous Concentration Cells. J. Mat. Sci. 8, 1519-21.

MATA-SEGREDA, J.E. (1980). Proton inventory of the transition
state for ionic migration of the aqueous hydrogen ion.
J. Phys. Chem. 84, 446-8.

MOHAPATRA, S., BOYD. K., STORZ, G.D., WAGNER, S., and WUDL, F.
(1979). Application of solid proton conductors to tungsten
oxide electrochromic displays. J. Electrochem. Soc. 126,
805-8.

NAKAMURA, O., KODANA, T., OGINO, I., and MIYAKE, Y. (1979).
High-conductivity solid proton conductors: Dodecamolybdophos-
phoric acid and dodecatungstphosphoric acid crystals. Chem.
Lett. 1, 17-18.

ONSAGER, L. (1968). Physics of ice. Proceedings of the Inter-
national Symposium, Munich 1968. (Plenum Press, New York,
1969). 363-8. Editor: N. Riehl.

POTIER, A., and ROUSSELET, D. (1973). Conductivité électrique
et diffusion du proton dans le perchlorate d'oxonium
J. Chem. Phys. 70, 873-78.

RAFFENETTI, R.C., PRESTON, H.J. T., and KAUFMAN, J.J. (1977).
Ab-initio configuration interaction calculations of hydronium
ion exited states. Chem. Phys. Lett. 46, 513-18.

SHARON, M., and KALIA, A.K. (1977). Electrical conduction and
diffusion studies in ammonium dihydrogen phosphate and
potassium dihydrogen phosphate single crystals. J. Solid
State Chem. 21, 171-83.

SHEFFIELD, S.H., and HOWE, A.T. (1979). High proton conductivity
in pressed pellets of proton-montmorillonite, proton-aluminum-
montmorillonite and proton-aluminum-iron-montmorillonite
Clays. Mater. Res. Bull. 14, 929-35.

SHILTON, M.G., and HOWE, A.T. (1979a). Hydrogenbond ordering
in the proton conductors hydrogen uranyl phosphate and
arserate tetra hydrates. J. Chem. Soc., Chem. Commun. 79,
194-6.

SHILTON, M.G., and HOWE, A.T. (1979b). Evidence for Proton Con-
ductivity in compounds in the hydrogen-Uranyl-Periodate-
Water System. Proceedings of the International conference
on Fast Ion Transport in Solids (Elsevier North-Holland).

STILLINGER, F.H. (1978). Proton transfer Reactions and kinetics
in Water. Theoretical Chemistry. Adv. and Perspectives 3,
177-234.

TAKAHASHI, T., TANASE, S., YAMAMOTO, O., YAMAUCHI, S., and
   KABEYA, H. (1979). Proton conduction in some solids and the
   fuel cell with a proton conducting electrolyte. Int. J.

   Hydrogen Energy 4, 327-38.

WIRTZ, K. (1950). Conduction effects in Hydrogen-bridge Systems.
   Z. Elektrochem. 54, 47-51.

ZIMMERMANN, H. (1964). Protonenzustände in der Chemie. Angew.
   Chem. 76, 1-9.

ZUNDEL, G. (1976). Easily polarizable hydrogen bonds - their
   interaction with the environment - IR continuum and anomalous
   large proton conductivity. In: Hydrogen Bond. Recent devel-
   opment in theory and Experiment. II. Structure and spectro-
   scopy. 683-766. (North-Holland, Amsterdam. Editor: P. Schuster,
   G. Zundel and C. Sandorfy).

YAMANAKA, S. (1980). Ionic conductivity in anhydrous crystalline
   zirconium phosphates, $Zr(MPO_4)_2$ (M = Li,Na,K), with layered
   structures. J. inorg. nucl. Chem. 42, 717-20.

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Abstract

Proton conducting solids have been studied intensively in recent years due to their potential use as ion conducting separators in efficient fuel cells for electricity generation.

This report describes fuel cell - and other possible applications of solid proton conductors. The best performing materials known today are listed. Typical synthetic routes and some models for proton transport in solids are discussed. Hints to future research are given.

The literature collected for this report covers mainly the period 1974 - 1980.

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