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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 research are given.

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

INIS-descriptors: ELECTROLYTES, FUEL CELLS, IONIC CONDUCTIVITY, PROTON TRANSPORT, PROTONS, REVIEWS, SOLIDS, USES.

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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 $10^{-9} - 10^{-12} \text{ (ohm}\cdot\text{cm)}^{-1}$, 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 continuously fed to their respective electrodes, and the reaction product(s) (e.g. H_2O), which normally form at one electrode only, is likewise removed continuously. 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 ($500\text{-}700^\circ \text{C}$), polymeric films soaked with water (Nafion), and oxide ion conducting ceramics of the CaO-ZrO_2 type for high temperature use ($700\text{-}1000^\circ \text{C}$). 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 \rightarrow energy in the fuel cell, and water + energy \rightarrow 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 $0,1 \text{ (ohm}\cdot\text{cm)}^{-1}$ 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 electrical insulator to prevent internal short circuit of the cell. 4) The electrolyte must be stable with respect to thermal and electrochemical decomposition ($25\text{-}300^{\circ}\text{C}$), and stable in the partial 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 $\sim 1-5 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$).

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} $\text{ohm}^{-1}\text{cm}^{-1}$ 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 $100\text{-}300^{\circ}\text{C}$, 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 materials 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 laboratory 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 (ohm · cm) ⁻¹	Possible proton conduction mechanism	Reference
Hydrated acids	H ₃ PMO ₁₂ O ₄₀ · 29 H ₂ O	1.8 x 10 ⁻¹	liquid-like transport of H ⁺	Nakamura et al., 1979
	H ₃ PW ₁₂ O ₄₀ · 29 H ₂ O	1.7 x 10 ⁻¹		Nakamura et al., 1979
	H ₂ UO ₂ PO ₄ · 4H ₂ O	4 x 10 ⁻³	H ₃ O ⁺ /H ₂ O jump	Howe and Shilton, 1979
	H ₂ UO ₂ AsO ₄ · 4 H ₂ O	6 x 10 ⁻³	H ₃ O ⁺ /H ₂ O jump	Shilton and Howe, 1979a
	H ₈ UO ₂ (IO ₆) ₂ · 4 H ₂ O	7 x 10 ⁻³	H ₃ O ⁺ /H ₂ O jump	Shilton and Howe, 1979b
	H ₃ OCrO ₄	3 x 10 ⁻⁴	H ₃ O ⁺ migration or impurity conduction	Potier and Rousselet, 1973
Amphoteric oxide hydrates	Sb ₂ O ₅ · 4 H ₂ O	3 x 10 ⁻⁴	H ₃ O ⁺ /H ₂ O jump	England et al., 1979
	SnO ₂ · 3 H ₂ O	2 x 10 ⁻⁴	liquid-like transport of H ⁺	
	ZrO ₂ · 2.3 H ₂ O	3 x 10 ⁻⁵	liquid-like transport of H ⁺	
Clays	H ⁺ - Montmorillonite	1-4 x 10 ⁻⁴	liquid-like transport of H ⁺	Sheffield and Howe, 1979
	H-A ₂ -Montmorillonite	10 ⁻⁴ - 10 ⁻²	liquid-like transport of H ⁺	Sheffield and Howe, 1979
Ion exchanged ceramics	Hydrated hydronium β" alumina	5 x 10 ⁻³	H ₃ O ⁺ /H ₂ O jump, H ₃ O ⁺ migration	Farrington and Briant, 1978
	NH ₄ ⁺ - β alumina	~ 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	H^+
		$H_2O_2, PO_4, 4H_2O$	H^+
		NH_4^+ beta alumina H_3O^+ beta alumina	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^-

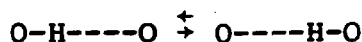
Table II: Formal oxidation number of hydrogen in chemical compounds.

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

For obvious reasons, (see below), only compounds with hydrogen in oxidation number +1 will function as an ion conducting membrane 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 so-called 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:



corresponds to a net transport of charge, 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 Raffanetti 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 Zimmerman (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 (Groothuis 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" instantaneous. 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 corresponds 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 crystal to the next available site:

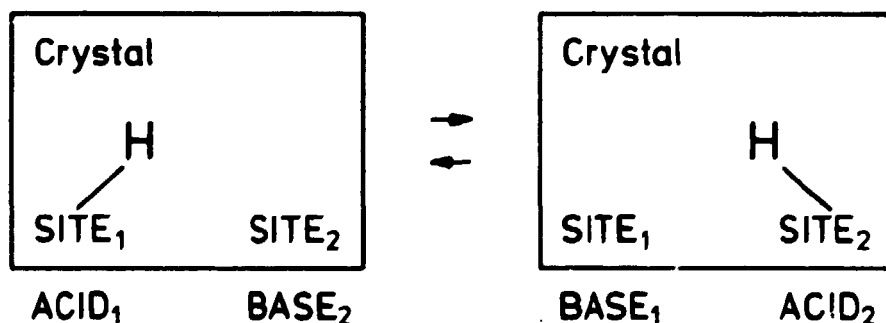


Figure 1. Acid-base analogy to proton conduction in solids.

The site, Site₁-H, can be viewed upon as an acidic group or part of the lattice, whereas Site₂, 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).

Site₁-H/Site₂ 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-NH₃⁺ group to R¹-COO⁻ or from HCO₃⁻ to H₂O.

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): HUO₂PO₄·4H₂O (Howe and Shilton, 1979). This structure contains alternating layers of UO₂⁺ + PO₄⁻³ ions, and layers of H₂O + H₃O⁺ ions. The ratio of H₃O⁺ to H₂O is 1 to 3. In the H₃O⁺ + H₂O layers hydrogen bonding is dominating. A sequence of H-hops can proceed as follows:

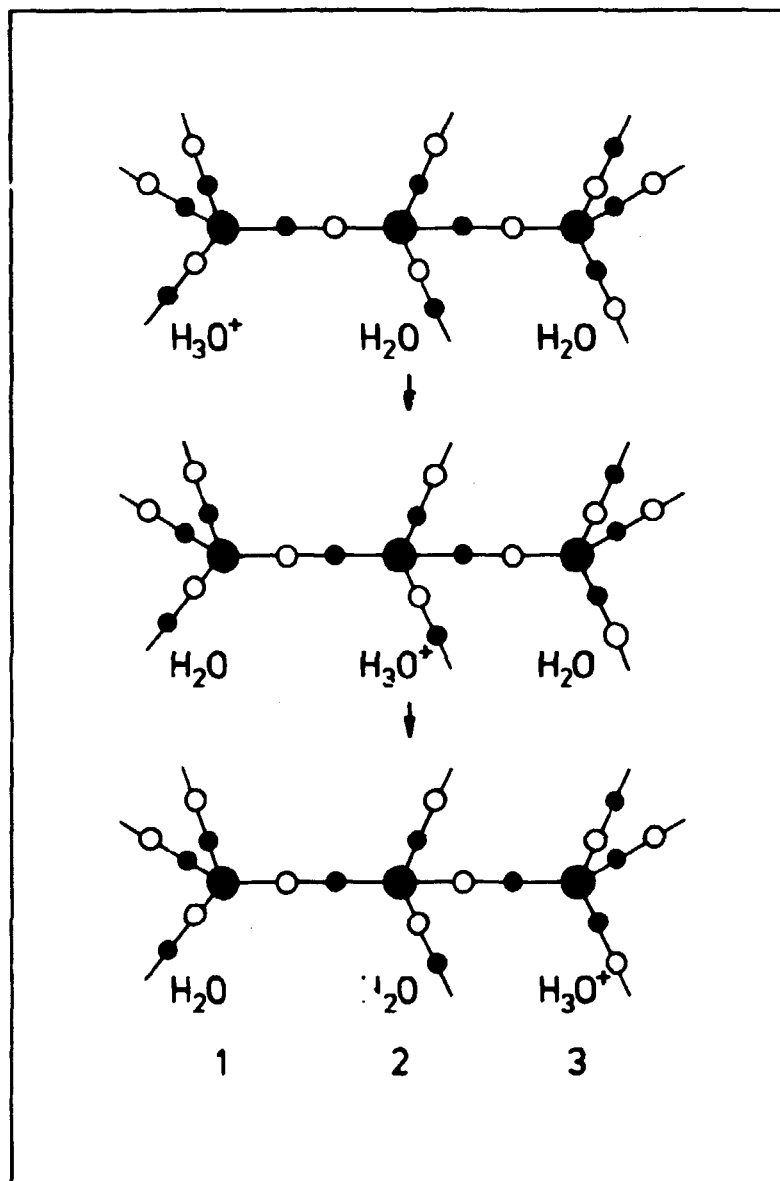


Figure 2. Proton hopping in $H_2O_2PO_4 \cdot 4H_2O$. Large filled circles are Oxygen, small circles: filled are occupied by proton, open circles are potential but vacant positions for protons.

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, almost 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 $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ transfer.

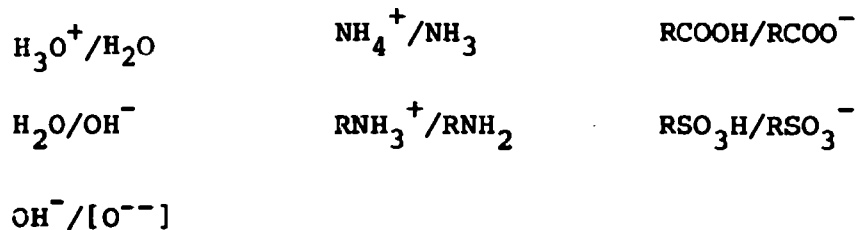
Liquid-like transport is possible in materials which contains waterlayers included in the crystal structure i.e. clays (Sheffield and Howe, 1979) or polycrystalline materials composed by charged crystallites held together by a electrolyte solution i.e. $\text{SnO}_2 \cdot 3\text{H}_2\text{O}$ (England 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 tailored 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 $[\text{O}^{--}]$ 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 mechanism will function with the following acid-base couples, properly located at alternating positions:



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 $[\text{O}^{--}]$ 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

$\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (Howe and Shilton, 1979)

$\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ (England et al., 1979)

Ion exchange methods

$\text{Zr}(\text{MPO}_4)_2$ (M=Li,Na,K) (Yamanaka, 1980)

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

$\text{HSb}(\text{OH})_6 \cdot n\text{H}_2\text{O}$ (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?

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<p>Title and author(s)</p> <p>AN INTRODUCTION TO PROTON CONDUCTION IN SOLIDS</p> <p>Finn Willy Poulsen</p>	<p>Date September 1980</p> <p>Department or group Metallurgy Department</p> <p>Group's own registration number(s)</p>
<p>23 pages + tables + illustrations</p>	
<p>Abstract</p> <p>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.</p> <p>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.</p> <p>The literature collected for this report covers mainly the period 1974 - 1980.</p> <p>Available on request from Risø Library, Risø National Laboratory (Risø Bibliotek), Forsøgslæg Risø), DK-4000 Roskilde, Denmark Telephone: (03) 37 12 12, ext. 2262. Telex: 43116</p>	<p>Copies to</p>