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Proton conductors and their applications: A tentative historical overview of the early researches

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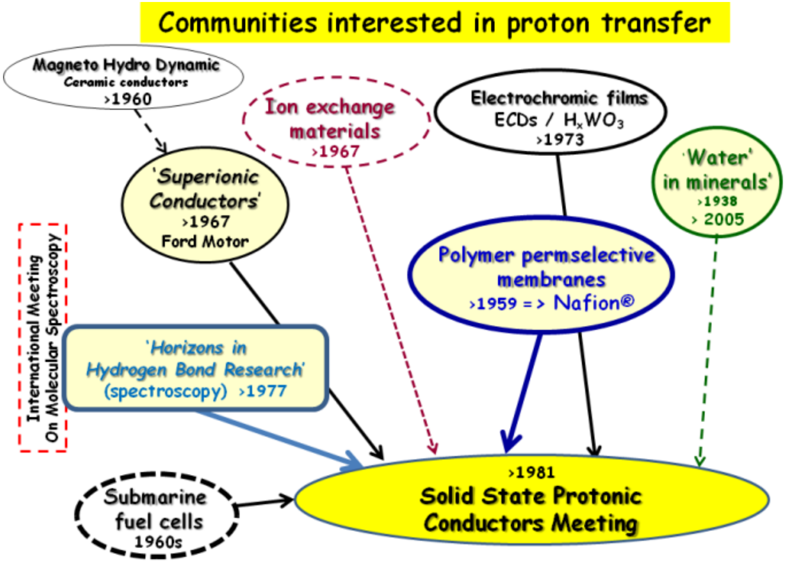
Abstract

We present here an historical overview of the early researches on proton conductor solids for materials such as fuel cell, battery, electrolyser or H_2-sensor. Unexpectedly, the early researches and developments (1960s Gemini orbiter US program, 1967 Ford patent and papers on solid electrolyte battery for electric cars) happened to be a few years before the 1972 'The Club of Rome' report, the first oil crisis in 1973 and certainly the ecological concerns related to global warming. A renewal of research activity then took place in relation with the global warming issues after 1995 and search for the decarbonated energy sources and storage. We discuss here the history of proton conductor research in terms of the communities involved (ion exchange materials, superionic conductors, hydrogen-bonded compounds, electrochromic films, polymer membranes, geology) and the first studied materials, with a comparison between the researches leading to commercial applications and the ones remaining under study. Special attention is paid to the methods of analysis well adapted for the understanding of the space- and time-scale dynamics of proton conductors, namely neutron scattering, frequency dependent conductivity/relaxation and modelling. Some unsolved questions are formalised.

Keywords: hydrogen, conductivity, history, fuel cell, electrolyser, sensors

Graphical Abstract



Highlights:

Research on electric cars starts much before ecological concerns

Proton conduction modelling is highly related to the first communities involved in proton transfer and diffusion.

A historical view on space- and time-scale proton dynamics is given.

1. Introduction

We aim to present here a brief historical overview of the first studies conducted on proton conductors with low (electrolyte) or high electron conductivity (Mixed Ion Electron Conductor electrode or MIEC). Proton conductors can be used as solid electrolytes in electrochemical devices of energy storage and production such as fuel cells, electrolysers and CO_2 converters. These devices are very important for the development of an ecological and sustainable way of life based on hydrogen as pollutant-free energy vector. They can be associated to an electronic conductor to form a cermet/composite (porous) electrode. If they display sufficient electronic conductivity, they can be used as an electrode. These materials can also be the active layer of H_2 or H^+ sensor.[1] Figure 1 gives an overview of the research activities in this field deduced from Web-of-Science^{TM} database. First studies date from the 1960s and the number of researchers has expanded only after 2000 with the second oil crisis, the global warming issue and the associated funding. The interest on this topic, measured as the sum of times cited per year, has significantly increased after 1980 and drastically after 1995. The huge difference between the efforts devoted for the development of fuel cells is obvious and the effort on the production of hydrogen by water electrolysis has remained very little for a long time. In fact, the effort has significantly increased only after the 2000s, although the need of new low-cost production tools of hydrogen with high degree of purity is required for fuel cells.

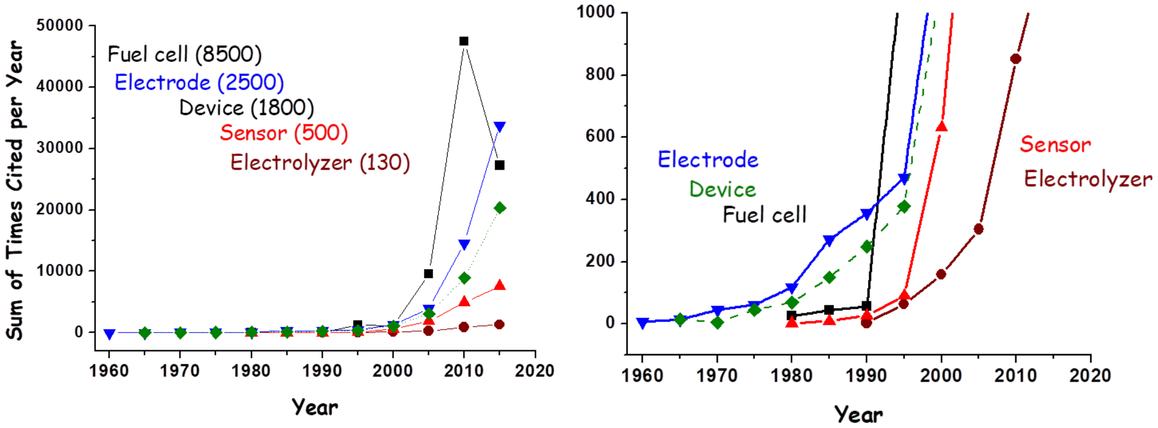


Fig. 1: Comparison of citation reports per year in Web-of-Science^{TM} database (Clarivate Analytics) for results with fuel cell, electrode, device, sensor and electrolyser (with the topics of proton and conductivity to be representative) as keywords; the number of papers is given in parentheses; a zoom is given on the right side.

1.1. Fast ion/proton conductors

As noted in the first book devoted to this topic entitled as *Proton Conductors - Materials and Devices*[1] in 1992, the first reviews published in peer review journals with a focus on the understanding of proton conductors in solids are dated to 1972[2] and 1975[3]. Table 1 lists the milestones regarding proton conductors and devices based on these materials. It can be expected that the development of an academic community devoted to ion- and proton-conductivity in the solid state has started with the first oil crisis (end of 1973) with the special funding given for the search of new (solid) electrolytes and electrodes for advanced energy conversion devices and associated sensors. We can see that the search of new energy production and storage devices by industrial research laboratories has anticipated the political demand for decades (Table 1).

The first international conference on fast ion conductors was held at Belgirate, Lake Maggiore close to Ispra JRC Centre (Italy) in September 1972[4,5] with the initiative of W. Van Gool from Utrecht University in the form of a NATO Advanced Study Institute on '*Fast Ion Transport in Solids, Solid State Batteries and Devices*'. The proceedings of this conference were published in 1973.[5] Actually, the birth of a "large" academic and industrial attention to advanced batteries based on solid electrolyte membrane dates from the patent applied by Dzieciuch and Weber from Ford Motor Co a few years before, in 1967[6] which is associated to the paper of Yao and Kummer[7], also from Ford Motor Labs, demonstrating the ion exchange properties and high conductivity of beta alumina ceramics and the possibility to build Na(Li)/beta alumina/Na(Li)S_x battery: alkali metal and sulphide liquid electrodes (liquid electrodes hinder detrimental polarisation effects) promote very high density and volume energy, making it possible the electric powered vehicle.

It is important to note that the objective of developing an electric car at Ford Motor Labs has started a few years before the asking of 'The Club of Rome' to Massachusetts Institute of Technology (MIT) to study the energy saving at the earth scale and "*The Predicament of Mankind*" which is a work popularized by the publication of the famous report "*The limits to growth*" in 1972.[8]

The publications of Ford had a great impact in electrochemists, materials scientists and communities of car industry and gave rise to a huge activity regarding Superionic Conductors (SIC), also called as Fast Ion Conductors (FIC). Very rapidly, a second conference was held in the United States, namely at Schenectady General Electric (GE) Research Laboratory in 1976.[9] The organisers, Roth (GE) and Mahan (Indiana University) then published a book both covering the theoretical and technological facets based on physics, chemistry and electrochemistry.[9] Lake Geneva[10] and Gatlinburg[11] meetings also led up to the series of Solid State Ionics Conferences which have remained active until today.[12] These meetings attracted researchers from different academic and industrial communities. A few books were also published then.[13-16] The journal *Solid State Ionics* was founded in 1980 by Whittingham (Exxon), Huggins (Stanford University) and Steele (Imperial College, London) but attention to proton conductors was at those times very limited.

1.2. Beta alumina and the first devices based on Proton Conductor Solid Electrolyte

The first two papers on proton conductors published in the 1980 and 1981 issues of *Solid State Ionics* dealt with potassium hydroxide (KOH) by Stephen and Howe[17] as well as with β alumina single crystal conductivity by Baffier, Badot and Colomban.[18] "Beta alumina" is actually not a variety of alumina but an aluminate of sodium, potassium or lithium with a non-stoichiometric composition: 11 Al_2O_3 1.3 to 1.6 M_2O.[18-21] However, there was confusion at the time of the discovery of the variety of transition alumina phases (γ, δ, etc.). It should be noted that many of the latter phases are actually water aluminates and exhibit proton conductivity.[1] In the book of Hagenmuller and Van Gool published in 1978[16], only two pages in Takahashi's chapter on "Organic Ion Conductors" (conductivity of $C_6H_{12}N_4$-H_2SO_4) and two pages in Whitingham and Silbernagel's chapter (H_xWO_3 bronze and $LaNi_5O_6$ hydride) address the H diffusion/conductivity among 545 pages.

The β alumina framework is very open and conducting ions (M^+) diffuse almost freely in loosely packed planes located in between dense spinel blocks.[19-21] The conducting ion sub-lattice melts between ~50 and 300 K, as a function of the stoichiometry and nature of the cation although the whole compound melts at a temperature of ~2300 K.[21-23] Today's electricity storage units of 8, 12 or 34 MW have been commercialized by NGK since the 2000s with more than 500 MW total capacity works in the world.[24]

In 1967, Yao and Kummer[7] from Ford Motor Labs also demonstrated the possibility to exchange monovalent alkali ions by many others, monovalent or bivalent, including NH_4^+ and H_3O^+. In 1973, Lundsgaard and Brook (AERE, UK and Odense University, Danmark) also demonstrated the possibility to measure Na^+ but also H^+ and H_2 concentration in water[25] and in gas[26] using β alumina pellets. The conductivity of full protonated beta alumina pellets was measured on H_3O^+ β alumina ceramics in 1977 by Roth GE group[27] as well as on H_3O^+, $H^+(H_2O)_n$ and NH_4^+ single crystals by Colomban et al.[28] Furthermore, Farrington and Briant (GE) measured exceptional conductivity on beta" alumina form but the values were never reproduced (and the paper was not signed by Roth as the group leader).[29] Afterwards, Jensen and Mc Geehin continued the work of Lundsgaard and Brook.[30] Conductivities of beta and beta" alumina with different non-stoichiometry and cations were also measured on single crystals and ceramics.[18,28,31,32] Activation energies of 0.15 eV for the beta alumina phase and 0.20 eV for the beta" one, below 673 and 573 K respectively, were measured for (hydro)oxonium aluminate; a higher activation energy (0.3 eV) was measured for ammonium beta alumina due to the larger size of the ammonium cation and the room-temperature conductivity reaches ~2.10^{-3} S cm^{-1} at ambient temperature. The low activation energy thus proved the superconductivity.

The first (end of 1973) and second (1979) oil crisis occurred at the right time to justify research on new solid electrolytes and MIEC. Attention was focalised on sodium, lithium and silver ion conductors. Lithium was considered because of its light weight and high electrochemical window whereas sodium was selected due to its good compromise (nowadays, a great attention is given again to sodium batteries to replace lithium ones because of the larger availability of the element sodium and rather similar electrochemical characteristics) and its size well adapted to the diameter of conducting pathway in open frameworks. After all, AgI as the first fast ion conductor has been known since the beginning of the 20th century (see [4] and Table 1). Silver-based electrolytes were first used for high density miniaturised battery (e.g. for pacemaker). Proton conductors also could lead to high density/kg production and storage systems. There is also a big interest in developing H_2-sensors for on- or at-line automatic control in oil refineries.[32]

1.3. The foundation of Solid State Protonic Conductors Conference Series.

The first workshop on '*Solid State Protonic Conductors*' initiated by late Professor Johs Jensen from Odense University was organised by myself in Paris from 8th to 11th December 1981 with financial support from French-Danish Society for Research and Scientific Exchanges, Thomson-CSF and Air Liquide French Companies.[33] The photograph of the attendees at the first meeting is available upon request. Second and third editions were organized in Denmark (Hindsgavl Castle, 6th-10th September 1982) and France (La Grande Motte, 15th-18th May 1984). All the proceedings were edited by Odense University Press.[33-35] The series then continued at Exeter (UK, 12th-15th September 1988), Assisi (5th in Italy, 16th – 20th September 1990), Villard de Lans (6th in France, 6th – 11th September 1992), Schwäbisch Gemünd (7th in Germany, 29th August- 1st September 1994), Gol (8th in Norway, 18th- 23th August 1996), Bled (9th in Slovenia, 17th – 21th August 1998), Montpellier (10th in France, 24th - 28th September 2000), Guilford (11th in Great-Britain, 27th - 30th August 2002), Uppsala (12th in Sweden, 15th – 19th August 2004), St Andrews (13th in Scotland, 4th - 6th September 2006), Kyoto (14th in Japan, 7th – 11th September 2008), Santa-Barbara (15th in the USA, 15th – 18th August 2010), Grenoble (16th in France, 10th - 14th September 2012), Seoul (17th in Korea, 14th - 19th 2014), Oslo (18th in Sweden, 18th to 23rd September 2016) and recently for the second time at the USA in Stowe the 19th SSPC Meeting (16th-21th September 2018). All proceedings were published in *Solid State Ionics*.[36]

Table 1: Milestones regarding proton conductors and devices based on these materials. Important economical/political events regarding energy cost, greenhouse gas and global warming are also noted. Most stringent dates are in bold.

Date	Actor	Materials	Concept	Refs
1806	C.T.J. Grotthuss	water	Conductivity mechanism (jump)	37
1839	W. Grove	water	H_2/O_2 fuel cell	38
1889		Pt	Porous electrode	39
1897	W. Nernst	ZrO_2	Lamp	40
1905	B. Tijmstra et al.	water	H^+ diffusion in water	41
1914	C. Tubandt	AgI	Solid electrolyte	4,42,43
1938	J. Beintema	HUP/HUAs	Vagabond ions	44
1950	S.E. Rogers & A.R. Ubbelhode	Acid sulphates	1st Review paper "Proton conduction in solids"	45
1959	G. Grubb	Polymer membrane	Fuel cell (Gemini orbiter)	46-48
1959	D. Hadzi	Hydrogen bonding	book	49
1964	F. Faurat et al.	Perovskite ($LaAlO_3$)	Fuel cell based on a ceramic membrane	50
1967	**M.A. Dzieciuch & N. Weber**	**Na β alumina**	**US Patent: battery with liquid electrodes (Na/NaS_x)**	6
1967	**L.T. Yao & J. Kummer**	**Ion exchange of β aluminas (NH_4^+, $H^+(H_2O)_n$)**	**Publication**	7
1968	W.R. Wolfe	Sulfonate polymer membrane	Patent	77
1969	A. Clearfield	Ion exchange materials	book	51
1972	J. Bruinink	Imidazole, acid salts, hydrates	Review paper "Proton migration in solids"	2
1972	D.A. Shores & R.A. Rapp	ThO_2	Proton Conductor	52
1972	**The Club of Rome 'The limits of Growth' report**			**8**
1973	D. Rousselet & A. Potier	H_3OClO_4	Fast proton diffusion in solid state	53
1974	J. Lundsgaard & R. Brook	Na/H_3O β alumina ceramic	H^+ & H_2 sensors	25,26
1974	A. Novak	H-bonded compounds	Structure-bonding relationship	54
1974	R.W.T. Wilkins et al.	Water in minerals	Review paper	55
1974	**Kippour War and 1st Oil Crisis (barrel: 14$)**			
1975	L. Glasser	Oxides, perchlorates, acid salts, hydrates, synthetic and natural polymers (cellulose, collagene, keratine,etc.)	Comprehensive review paper	3
1977	P. Schuster, C. Zundell, C. Sandorfy	The Hydrogen bond – Recent developments in Theory and Experiment	Book	56
1978	P. Hangenmuller & W. Van Gool (Eds)		4 pages deal with proton conduction in a 545 pages book on Superionic Conductors	16
1979	**2nd Oil Crisis (barrel : 40$)**			
1980	T. Takahashi & H. Iwahara	perovskites	Stable proton conductors	57
1981	**Ph. Colomban & J. Jensen**		**1st SSPC Meeting (Paris)**	**33**
1983	Ballard Co.	Nafion© PEM	FC for truck and bus	58
1983	J. Ensberger		*"Much is doubtful"* The non-conformist ion	59
1981-1984	Ph. Colomban & Coll.	Na and D^+ β alumina thin film (300 nm) prepared by ion implantation, thermal diffusion and plasma exchange	Microionics Microprotonics (micro H_2 sensor)	60,61
1986	Ballard	Nafion© PEM	Pressurized air stack	58
1987	M. Yoshimura, S. Somiya & coll.	Stabilized Zirconia	Water corrosion	62
1987	R. Lascar & S. Chandra (Eds)		First book with a chapter devoted to Proton Conductors	63
1989	NASA	Nafion© PEM	FC for Lunar Apollo landing	48
1992	Ph. Colomban (Ed.)	Proton conductors – Solids, Membranes and Gels – Materials and Devices	Book	1
1992	**United Nations Framework Convention on Climate Change (UNFCCC)**			
1994	D. Scanu & Ph. Colomban	aluminosilicates	Water, proton insertion and stability of H-containing silicates	64-66

1997		**Kyoto Protocol**		
1998	Ballard	Nafion© Fuel Cell vehicles	Chicago Transit Authority and BC Transit (Vancouver) each deploy three Ballard-powered fuel cell buses	58
2005-2008	**Finance Crisis (barrel: 140 $)**			
>~2005		Nafion©, Aquivion©, Dow©, Flemion©, …	Fuel Cell Electric vehicles commercially available	48,67-70
2005	Ballard	Nafion© Fuel Cell vehicles	The fleet of 33 Ballard-powered fuel cell buses operating in Europe, Iceland and Australia surpass one million kilometers	58
2010	AREVA	Ba and Sr Zirconates	Pressurized electrolyser and CO_2 converter	71,72
2012	Ph. Knauth & M.L. Di Vona	Solid State Proton Conductors	book	79
2010	**Arabic Spring (barrel: 120$)**			
2015	**Shale oil development (barrel: 40$)**			
2015		Toyota Mirai	Fuel Cell Electric vehicle commercially available	80
2016	M. Marrony	Proton Conducting Ceramics. From fundamental to applications	Book	78
2018		PEM	Fuel Cell Electric train (Alstom)	73

The design, testing or use of electrochemical devices based on a solid electrolyte or a proton conductor is much older as mentioned at the beginning of this introduction ([37-43], see Table 1 [1,37-73]). Tubandt used AgI for electrochemical experiments in the first part of the 20th century ([42,43], see also the very complete historical review paper of Funke [4]). Polymer membrane-based fuel cells were developed in 1955 at GE by Grubb[46,47] using polystyrene-divinylbenzene sulfonic acid cross-linked with an inert fluorocarbon film and Pt electrodes for the U.S. Gemini Space Vehicle which ran around the planet in 1962 (see the historical review of Perry and Fuller in ref. [48]). At the same time, a perovskite $AlLaO_3$ ceramic membrane-based H_2/O_2 fuel cell was tested in 1964 in France by Forrat et al.[50], probably with the intention of submarine military applications.

Ballard Power Systems Inc. (Canada) then started to develop fuel cells for trucks and transit buses based on a sulfonated tetrafluoroethylene based fluoropolymer-copolymer in 1983[58], called as Nafion® developed by E.I. DuPont de Nemours & Company, primarily as a perm selective separator in chlor-alkali electrolysers.[48,74-77] One advantage of the Nafion® fuel cell technology was its higher potential to make vehicles ready-to-start in cold environment.[58]

Takahashi and Iwahara have conducted the first systematic investigation of ionic conduction in perovskite ceramics, following the work of Forrat et al.[50] They published their original paper on proton conductivity of lanthanum–yttrium oxide and strontium zirconate in a French journal devoted specifically to solid state chemistry, entitled as *La Revue de Chimie Minérale* in 1980[57] which was recently qualified in Marrony 's book by Coors as an '*obscure journal*'.[78]

We now see that the perfluorosulfonic acid polymers [46-48,74-77] constitute the core of commercially available Polymer-Electrolyte Fuel Cell (PEFC) for automotive applications: about 6500 hydrogen fuel cell cars were sold at the end of 2017 [39,40,67-70], based on a variety of Nafion® homolog membranes (Table 1). PEMFC has also started to be tested in September 2018 for commuter trains. [73] Electrolysers based on Nafion® membrane are also available.[66,67] On the other hand, some prototypes of electrolysers based on (oxygen vacancy conductor) stabilized zirconia membrane are manufactured although earlier works have demonstrated the slow corrosion of zirconia by water[62], as experimented with the decay of hip prosthesis.[85] Yet, their development is still in continuation.[81-85] At the same time, pressurized electrolyser and industrial prototypes of fuel cells in association with many stacks are in development.[66,67] Conversion of CO_2 by reaction with nascent and highly reactive hydrogen is also tested.[67]

In the case of common electrochemical applications, liquid or gelled electrolytes are used. However, solid state devices are at the origin of electrochemistry: Tubandt and Lorenz discovered the huge conductivity of AgI above 422 K (the first known superionic conductor)[4,42,43] and spoke of '*molten state of the cationic partial lattice*' already in 1920. Decades before, the Nernst lamp based on ZrO_2 oxygen ion conductor was invented in 1897 and produced after 1901 by Westinghouse.[40] Proton conduction was suggested by Rogers and Ubbelhode[45] for solid acid sulphates in 1950 after Beintema[44] discovered the mobility of protons in uranyl phosphate hydrate in 1936 and said "*these ions may thus be considered as true vagabond ions*".

Obviously, this overview will be partially subjective for it is written by an actor of this adventure. After addressing the origin of interest on this very special class of compounds and the communities involved, we will mainly address the materials under study in the 1990s that have retained attention up to the present time; the first use of specific methods of analysis of H-containing materials, even in tiny amounts (nominally anhydrous oxides). Neutron scattering and frequency dependent conductivity and relaxation will particularly be discussed and the link between the afore-mentioned communities and the mechanisms of conductivity considered will be displayed. The importance of the vapour pressure, gradient and microstructures will be highlighted and some perspectives will be discussed. The variety of studied compounds by first researchers should have initiated new studies. The attention is focused on the period before 2000, but some recent/review papers are also added to represent some links with the last developments.[81-85]

2. Sources of interest on proton conduction: The different communities involved in proton transfer studies

Different communities of scientists have taken attention in the study of protons in solid phase, namely in oxides. Figure 2 shows the different communities working on proton-containing compounds, proton transfer in solid state and associated applications and their links.

2.1. Space Orbiter Fuel Cell

The development of hydro-carbon based polymer membrane for H_2/O_2 fuel cell for Gemini program at the end of the 1950s assembled the first group of researchers and engineers, taking advantage of the development of new polymer permselective membranes for the production of Cl_2.[46-48] A major improvement has been made with the development of fluorinated membranes (as Nafion ®) that do not suffer from rapid degradation in a fuel cell since C-F bonds are more stable than C-H bonds. The material consists of a PTFE (polytetrafluoroethylene) backbone with perfluorinated-vinyl-polyether side chains terminated by a sulfonate group. Actually, the number of academic publications was limited (Fig. 3, see in refs [48,74,75]), even after the Wolfe Patent of Pt-free electrode in 1968 opening ways to avoid the need of expansive catalysts.[77] This membrane joins the thermal and chemical stability of fluoromembrane backbone (similar to that of well-known PTFE Teflon©) and the combination of hydrophobic (fluor) and hydrophilic (acid sulphate) branches: the acidic water is retained in the porous network formed by the macromolecules and a high mobility of water is obtained.

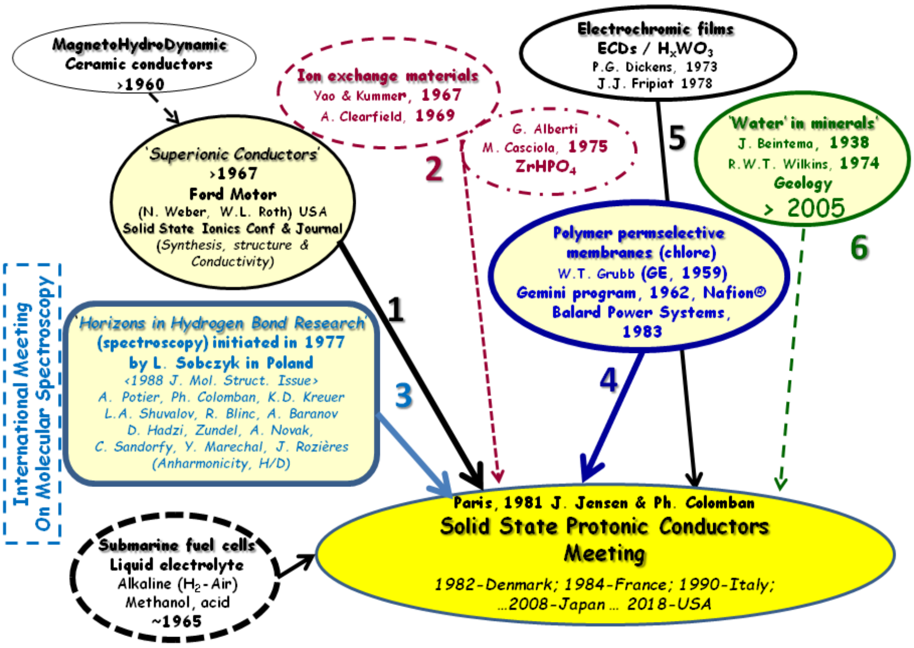


Fig. 2: Communities addressing ion/proton transfer/conductivity, hydrogen containing solids and their applications.

2.2. Hydrogen-bonded compounds

The oldest group studying proton transfer in solid state is certainly that of scholars interested in hydrogen bonding, especially in relation with the biological compounds: polyamide, cellulose, keratin, collagen, etc. (Table 1). References can be found in Hadzi's book and papers[49,86], in Glasser's review[3] and in the book "Proton Conductors".[1] This academic community created the always active series of conferences as '*Horizons in Hydrogen Bond Research*', initiated in 1977 by

Sobczyk in Poland.[87] For instance, the proceedings published as a 1988 special issue of *Journal of Molecular Structure* should be considered. [88] Novak, Orville-Thomas and Ratajczak were the editors of this journal and were very active in the study of hydrogen bonding together with Maréchal[89], Zundell and Sandorfy.[56] The 1988 special issue offered two important review papers on proton conductors: one by Kreuer from Max Planck Institute[90] and a second one by Colomban and Novak from CNRS.[89] In the later paper, the first classification of proton conductors was proposed and more than a hundred compounds listed with their conductivity and activation energy were compared to the twenty compounds listed by Bruinink in his review paper twenty years ago.[2] This has demonstrated that the community was rapidly enlarged (see further). A significant study to be noted regarding the proton conduction in H-bonded frameworks was that of Potier and Rousselet in 1973. This work quantitatively demonstrated a superionic phase transition for a solid protonic conductor, H_3OClO_4 (Table 1) with an important conductivity jump at 249 K to reach 4.9 10^2 S cm^{-1} at 321 K.[53] Thus, for the first time the measurement of T and ^{18}O diffusion showed the proton conduction unambiguously (D_H = 2.19 10^9 cm^2s^{-1} at 304 K).

2.3. H-containing minerals

The third group interested in structure hosting (mobile) proton has brought the mineralogists together. A good example is the 1974 review paper of Wilkins et al.[55] with the Infrared spectroscopy (IR) and Nuclear Magnetic Resonance (NMR) signatures of H_3O^+ (oxonium) ion in the minerals. The rotational and translational diffusion of water and oxonium in hydrogen uranospinite [$H_3O(UO_2AsO_4).3H_2O$] (HUAs: Hydrogen Uranyl Arsenate)[92-94] already detected by Beintema[44] in 1938 was demonstrated. Similar properties were found in some alunites and jarosites[1,55] as well as in clays.[1,95] The easy exchange between the protonic species (the Grotthuss mechanisms) were pointed out.[37]

$H_3O^+ + OH^- \Leftrightarrow H_2O + H_2O$.

Similar features are observed for other compounds by Infrared spectroscopy.[96,97] The existence of higher hydrates such as $H_5O_2^+$ was already well established in the space/atmosphere. Curiously, Wilkins et al. ignored the work of Beintema.[44] However, the bibliography as well as the exchange of knowledge between the communities was indeed limited at that time. Synthetic phosphate homologues of HUAs such as HUP: $H_3O(UO_2PO_4).3\ H_2O$ exhibit the best bulk proton conductivity, thus comprehensive characterizations were conducted in the 1980s.[92-94] Giant accumulation of electrons at the HUP-electrolyte/C-electrode interface was further studied[98] and used to make the first all solid supercapacitors[99](supercapacitors are now associated to the battery of electric car to recover and deliver instant energy). The interest of geologists on proton conductors started again in the 2000s with a discovery that a large amount of 'water' may be stored in deep mantle and could be at the origin of ocean water.[100-104] The earth's mantle is made of perovskite (a 'nominally anhydrous compound' but hosting 'water traces'). These 'water traces' strongly influence the mechanics of the earth's mantle.

2.4. Water corrosion resistant ceramics

Ceramists as well as experts in corrosion/protection of metals also paid great attention to the diffusion of protonic species in oxides. Many studies have been conducted on metal corrosion, in particular by water or hydrogen[105-109], whereas studies on corrosion of oxides by water or hydrogen are rare[64-66], whatever the active corrosion of metal actually implies the corrosion of oxide(s) formed at the metal surface.[108] Attempts to use a material with very low or even null thermal expansion in turbine ceramic parts made of lithium aluminosilicate (LAS) were first made in the 1970s.[110] Low thermal expansion would prevent the deleterious effect of thermal shock in ceramics. However, lithium ion can easily be exchanged by protons[64,66,111,112] that led to variation of the unit-cell in the form of cracks and crumbling. This was well known by the experts of lithium ore treatments[113,114] although the experts in mechanics did not take care and tried to develop SiC or C fibre-reinforced LAS matrix composites (Ceramic Matrix Composites: CMCs) in the 1990s.[115] These materials exhibit very good mechanical properties but are rapidly corroded by exhaust fume from aeroengines.[116]

The Orton lecture on '*The nonconformist ion*' presented at the 85th Annual Meeting of The American Ceramic Society by F.M. Ernsberger in 1983[59] should be emphasized, not only for being the first comprehensive discussion about proton transport models in solids at a significant conference, but for its alerting to the fact that the literature in this field must be read with caution: "*Much of is doubtful, and some, alas is wrong*". I believe that this remark has unfortunately remained valid up to now. He begins by recalling that the hydrogen atom can gain one electron (the hydride ion) or can lose its only electron, forming the proton: "*This is the only ion of chemical significance that has no electrons. It is this unique characteristic that underlies the extraordinary nature of the hydrogen ion"*. At this point, I will add: 'its quantitative detection is difficult and the question of how protons are present in the compound formula is rarely solved'.[117] This is because the proton has series of peculiarities: i) the size of the proton, H^+ is intermediate between that of the electron and that of Li^+ as the smallest ion, ii) when proton enters the electronic cloud of an acceptor, the size of the acceptor decreases (OH^- vs. O^{2-}; H_3O^+ vs. H_2O; OH^- vs. H_2O), iii) its localization by X-ray and even neutron diffraction is difficult or impossible when protons are diffusing ((very) low amount, poor signature, high anharmonicity). Ernsberger also questions the proton transfer in silicates, usually described with the following reaction:

$H_3O^+ + SiO^- \Leftrightarrow SiOH + H_2O$

This was put forward in particular to explain the lixiviation-degradation mechanisms of glasses (potassium and oxonium ions are easily exchanged because of their very similar ionic radius[32,118]). Substitution of lithium or sodium ions is much more detrimental to the material's mechanical properties since the size mismatch generates stress and cracks. However, the IR spectra are more complex than those expected for 'simple' SiOH species. Ernsberger furthermore proposed a second mechanism:

$H_3O^+ + SiOSi \Leftrightarrow Si[OH]^+Si + H_2O$

where a species more complex is formed when bridging oxygen atoms are considered. Methods capable of detecting protons are numerous, either directly (neutron scattering, NMR, nuclear reactions, vibrational spectroscopy of protonic species, gas chromatography) or indirectly (thermogravimetry, vibrational spectroscopy of the host framework perturbations provoked by proton) but many of them requiring some hypothesis about the formed/evolved species.[118]

The cradle of preparation and studies on ion (and proton) conductors can be searched in the attempt to build a magnetohydrodynamic generator (MHD) conducted at the end of the 1960s.[119,120] Basically, it would operate by the motion of an electric conductor in the presence of a magnetic field by inserting electrodes in the fluid stream where direct electric current can be generated at high voltage. This requires materials, either stable at high temperature such as an insulator or exhibiting a high conductivity. Stabilized zirconia was identified as electrode whereas alumina, magnesia and pure zirconia as insulators.[120] Titanium oxide, thoria and silica were also studied and proton mobility was evidenced in these phases.[52] Actually, the conditions were too severe for the stability of these materials; for instance, amorphous, cubic and tetragonal zirconias host protons (but not monoclinic ones) that induce crumbling on heating.[121,122] A few decades after the work of Yoshimura et al.[62], limited stability of stabilized zirconia in human body (10 to 15 years) generated major problems.[83,123-125] The prescription of hip prosthesis to rather young patients led to imperative replacement due to degradation of the material surface, although its poor stability was established long time ago.[62] Degradation of lithium aluminosilicate-based composites by protons was also neglected by engineer's developing materials for aerospace[115] despite the corrosion by water had been known for many years (in 1977,[110]) as explained in reference [116].

2.5. Passive corrosion films

Materials developed for nuclear plant turbine also provided interesting information about the stability of oxides versus water at high temperature. Nuclear plants are based on heating of pressurized water by heat produced by nuclear reaction. In BWR (Boiling Water-cooled Reactor) and PWR (Pressurized Water–cooled Reactor) water is respectively at 70 bar at 558 K and 150 bar at 594 K while in the next generation SCWR (Super Critical Water-cooled Reactor) 250 bar and 723 K will be achieved.[126] This has led to studies of a variety of (passive) phases formed at the surface of metallic alloys exhibiting convenient stability and mechanical strength (e.g. ferritic and austenite steels and nickel-based alloys). Hence, the observed phases stable in the presence of hot pressurized water has received interest ; thus, silicates, in particular with apatite structure, were studied, first as oxygen ion conductors, then as proton conductors.[127-129] It should be noted that a window of hotest oxide corrosion is observed between 523 and 673 K since the corrosion activity of water strongly decreases above these values due to the non-polar character of water at higher temperature. This point is actually not considered for the selection/improvement of proton conductors. It is also important to note that economic reasons imposing fuel cell and electrolysers would be pressurized, but tests at a high water pressure have remained rare.[70,71,130-138]

2.6. Ion exchange materials

So far, we have pointed out the important role of the outstanding ion exchange properties of beta alumina in the early development of superionic and proton conductors. Yet, the importance of another group of ion exchangers should be considered. Zirconium phosphates and phosphonates in their amorphous or crystalline forms[139] have been known for a long time for their exceptional exchange properties and thus are used in nuclear chemistry and medicine; detailed information can be found in Clearfield and Alberti groups' publications.[1,51,140-144] The great interest of these compounds is for their various states, from crystals to gels. Exceptional conduction of Sn derivative was also recently demonstrated.[145] The behaviour of clays is rather similar.[95] Silica and aluminosilicate porous structures, in particular those prepared by hydrolysis-polycondensation of metal alkoxides (the so-called sol-gel route), 'pure' or hosting hydrates exhibiting high proton conductivity received attention in order to mimic polymeric membranes such as Nafion with inorganic gels. Rather good conductivity was achieved in these materials at room temperature.[146-149]

2.7. Mixed Ion-Electron Conductors

Compounds exhibiting both ionic and electronic conductivity (also called MIEC) have been searched as well for the electrodes since the beginning.[1,4,5,9-11] Potassium ferrite, a compound with a structure similar to those of β alumina[32,150-152] and 'hydrogen bronzes' (H_xMO_n or $H_xMM'O_n$) have been studied since the 1970s.[1, 153-170] Hydrogen containing tungsten bronzes and homologues have received much attention in relation with their electrochromic properties to be used in display devices.[158] Today's portholes of modern aircrafts use electrochromic films to replace moving shutter and save weight.[171,172] Cobaltites, ferrites, nickelates and mixed compounds have also received great attention for a decade (see e.g. [135,136]).

It is worth mentioning that not only electron-insulator polymer membranes can exhibit proton conduction. Very high proton conductivity was also discovered in 1971 by Doriomedoff et al. in a conducting polymer: emeraldine polyaniline (acid) salt.[173] Polyaniline (PANI), as an important member in the family of (electron) conducting polymers, has been studied extensively because of its unique electrochemical behaviour and environmental stability[174-183] but very little attention was paid to its proton conductivity. The emeraldine polymer backbone consists of equal numbers of reduced (-B-NH-B-NH) and oxidized (-BN=Q=N-) repeating units (B and Q denote a -C_6H_4-phenyl ring in the benzenoid and quinoid forms). The emeraldine salt (chloride) is first synthesized; the emeraldine base is obtained by immersion in aqueous base (de-protonation) and drying; reversible treatment with HCl, H_2SO_4, H_3PO_4, camphor sulfonic acid, etc. restores the acid form; upon exposure to protonic acids, the -N-- sites of the emeraldine base are (re)protonated and anions of the acid are intercalated. The resulting emeraldine salt exhibits many properties characteristic of a (semi)metallic state, although the (electronic and ionic) conductivity was found to be activated up to 0.5 Scm^{-1} at room temperature, especially under pressure.[177] These polymers (PANI base) and polymeric salts (PANI salt) form powder, fibres, sponge and gels.[180] Free (delocalized) proton was evidenced in these conducting polymers by neutron inelastic scattering (see further).[182,183] Similar properties were also found/expected in other aromatic cycles-based compounds: carbons, coals, graphene, etc.[184-192] However, intercalation materials often exhibit both proton and electronic conductivity: graphite can host different acids[184,189-192], and carbons now receive a great attention, in particular to develop advanced capacitors with graphene[193] with a very high surface area per mass unit being achieved. However, the electrode/electrolyte interface generates a large charge accumulation.[98,99] Some other ‘famous’ compounds such as YBaCuO and similar structures can host hydrogen but this has retained almost no attention.[193-196]

3. From laboratory prototype to application

Obviously, development of devices can precede academic studies which provide a good understanding of the material structure and properties. We will present a few examples regarding this. Among the first commercial application based on ceramic proton conductors, we can cite the TYK Corp hydrogen sensor.[197] Coors in the preface of Marrony’s book explains the story of this sensor sold under the trade name “Notorp” produced by Protonetics International Inc. after 2000.[197-199] Stability requirements are less for an electrolyte used in a sensor than in a (pressurized) fuel cell or an electrolyser due to the less critical working parameters. The material used was yttrium-doped barium cerate (BCY), but when it became apparent that this type of perovskite was chemically unstable under the operating conditions, the production has eventually stopped. Confirmation of the low stability of Ce-based compounds (as In-based) was carried out by accelerate ageing under high temperature and high water pressure.[200,201] This example shows that materials exhibiting top conducting properties should also have a very good chemical stability and many other characteristics such as high mechanical properties. This is actually well known by ceramic engineers: for instance, α alumina is used in many thermal applications because of its high chemical stability, good mechanical strength, white colour and low cost in spite of its high thermal expansion and high sensitivity to thermal shock.

Another example of the difficulty to transform a good result at the laboratory scale into a success in the production can be given by the first microsensors. Following the experience gained with O_2 micro-sensor based on zirconia and Na β alumina thin films[61,202], first microionic proton-conductor thin film (300 nm) sensors were prepared using tools of the microprocessor industry (Mg^{2+} ion implantation in a sapphire wafer, thermal treatment in Na aluminate powder to transform the amorphised surface into β alumina, Na^+/D^+ exchange in D-plasma) in 1983 at Thomson-CSF Central Laboratory (Figure 3) in which proton diffusion coefficient of 10^{-7} $cm^2.s^{-1}$ was measured at RT.[60] This was carried out by the preparation of O_2 μ-sensor and λ-control probe, the first example of a microionic and microprotonic device. H_2-sensors based on macroscopic polycrystalline ceramic pellets[29,30] suffer the degradation of mechanical properties after ion exchange (degradation limited by starting from potassium beta alumina ceramic[32]). Grain boundary also decreases the electrical conductivity. Thus, efforts to prepare oriented ceramics, especially using microwave sintering have been made in the very early times.[203] The layer structure of the thinfilm sensor offers many advantages by decreasing the thickness of the solid electrolyte and hence its electrical resistance. Thus, many characteristics are improved such as the response time (presence of cracks is not detrimental, etc). However, except some attempts made by Motorola with the development of methanol/air fuel cell for cellular phones in the 2000s[204,205], no production of miniaturised devices succeeded at that time.

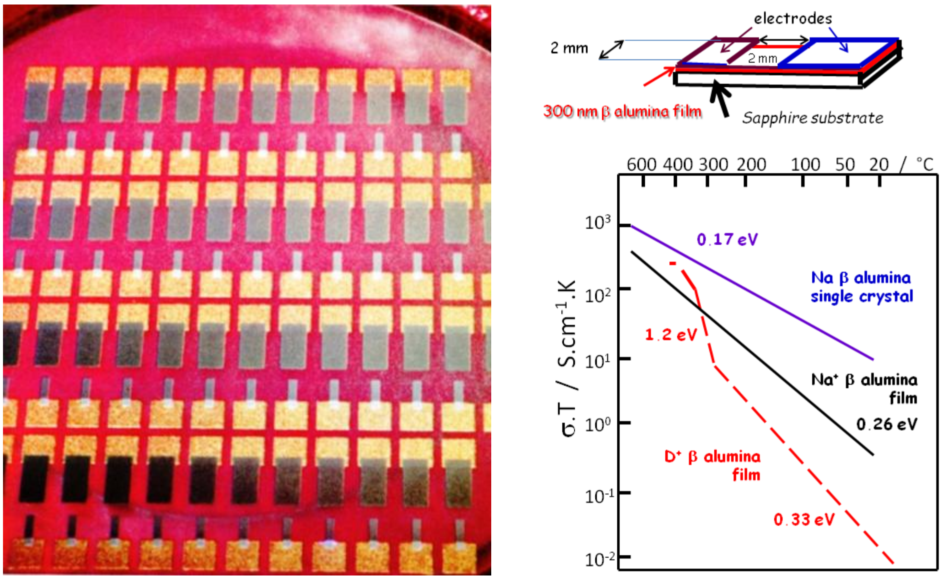


Fig. 3: Sapphire wafer covered by microsensors prepared using micro-electronic processes: ion implantation, screen printing, thermal treatments and exposition to plasma; on the right conductivity values (see refs[60,61,202] for details).

4. Representative materials

Table 2 lists the proton conductors among the most studied in the 1990s, selected both for their good properties and representativeness from the point of view of proton conduction history. Although Nafion® Dupont de Nemours polymer was patented in 1968, the academics' attention to this material has actually developed after 2000 (see refs [48,74] for a review of the early works). Early attention was paid to hydroxides, perchlorates, hydrates and gels, i.e. to materials which preparation is easy.[1] Many of these compounds have a layer structure or develop a interconnected porosity at the very short scale (so-called open framework). Ionic exchange is generally possible. The thermal stability depends on the nature of the protonic species and the strength of their interaction with the host framework, for a given water/proton partial pressure.[1] Consequently, materials are often not in equilibrium with the environment (partial pressure of water is very variable in air) and poor attention was paid to precisely determine the H content and furthermore to its gradient in the compound. Very soon after, scholars have understood that the framework hosting of the protonic species should have a sufficient interaction with the species to offer a certain thermal stability, but the interaction should be limited to allow the easy diffusion of these species (see Potier's chapter[206] in ref [1]). In non-equilibrium condition, the H content (and crystallinity) will depend on the sample size which explains the difficulty to study some of the hydrates. Dispersion of the proton conductor in a porous host retains the water kinetically and hinders the water loss.[207] It should also be noted that in spite of the outstanding properties of HUP, studies have stopped due to the uranium content. Beta alumina remains a reference material. Acid sulphates, phosphates and their mixtures (spreading out the transition to the superionic phase[207-210]) still continue to receive attention.[211] These compounds reach the superprotonic state when the free-rotation of HXO_4 ions takes place, in a similar way as the melting of the sublattice of conducting ions in superionic sodium and silver beta alumina or in AgI. Among new materials receiving attention, we can cite lanthane-based compounds such as apatite or perovskites.[127-135,137,138,212-219] Perovskites have received an increasing attention since the works of Forrat et al. and then Iwahara et al.[1,50,57,213-225] Most of the recent works deal with technological issues (preparation, sintering, compatibility with substrate, electrodes, stability/ageing, etc.) and tests (fuel cells and steam electrolysis but also methane dehydroaromatization, methane reforming, coal steam gasification, H_2 separation and compression of devices based on zirconates and cerates).[70,71,226-230] Ba-Zr-Ce solid solution has attracted the most interest because of its high conductivity and relative easiness to sinter but Sr-Zr homologues are preferred for their higher chemical stability by other groups.[70,71,30-135] The challenge is the combination of antagonist criteria: high conductivity, high (electro)chemical stability versus (pressurized) H_2 and H_2O but also CO_2, H_2S, CH_4, etc. and associated compounds (electrodes, current collectors, etc.), high mechanical properties for the temperature window required by the device, similar thermal expansion, etc.

Table 2: Proton conductors representative of the different classes studied; most of them since 1980 (see ref [1] for a more complete list); compounds in bold, in bold capital and italics and in bold underlined capital represent the different states of under study; in development or usage in commercially available devices, respectively.

Compounds	**Formula**	**Temperature range (K)**	**Typical (maximal) conductivity (S/cm)**	**Activation Energy (eV)**	**Water pressure sensitivity**
Hydroxides	CsOH (0 to 1) H_2O	360-400		0.4 - 0.7	Huge
	KOH (0 to 1)H_2O	300-420	10^{-2}		
Hydrates	$H_3O(UO_2PO_4)$ 3 H_2O Keggins' ions hydrates	250-400	5 10^{-3}	0.3	High
Gels	$Zr(HPO_4)$ nH_2O	300-480	10^{-3} to 10^{-8}	0.3 to 0.5	High
	$Sn(HPO_4)$ nH_2O				
	$SiO_{2-x}(OH)x$ mH_2O				
	aluminosilicate				
β/ β'' alumina	11 Al_2O_3 1.3 M_2O (M= H_3O^+, NH_4^+ …)	300-600	10^{-2}	0.2-0.4	Very low
Perchlorates	H_3OClO_4, NH_4ClO_4	200-320	10^{-2}	0.4	Huge
Acid sulphates, acid phosphates	$CsHSO_4$ KH_2PO_4	420-450	10^{-2}	0.3	Medium
	$Cs_{1-x}M_xHSO_4$	300-450	5 10^{-3}	0.3-0.5	
PEROVSKITES	$Sr/BaZr_{1-x}M_xO_{3-\delta}$	300-800	10^{-2}-10^{-3}	0.6-0.9	Very low
	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	300-800	10^{2}		
βFerrite	$M_{1+\delta}Fe_{11}O_{17}$	300-600	10^{-2}	0.3	
Polyaniline	$[(C_6H_4)\text{-}NH\text{-}(C_6H_4)\text{-}NH\text{-}]_m$ nH_2O	300-500	1		High
<u>NAFION© and homologues</u>	$[(CF_2\text{-}CF_2)_n\text{-}CF\text{-}CF_2]_m$ $(O\text{-}CF_2\text{-}CF\text{-}CF3)_z$ $(O\text{-}CF_2\text{-}CF_2\text{-}HSO_3H)$ xH_2O	300-350	5 10^{-2}	0.2	High
$PEO\text{-}HSO_4$		300-350	2 10^{-4}		Medium

5. Proton conduction mechanisms

Direct conductivity requires the displacement of the charge, from one side to the other one of the electrolyte in a battery, of the lone proton, or of the proton-bearing species, the so-called vehicle mechanism. Alternating current doesn't require long distant diffusion and the length explored by the charge depends on the frequency. At femtosecond scale, the charge displacement takes place at the atomic bond scale. Describing and modelling the conductivity and ion/proton dynamics is thus a complex feature in the space-time domains. Simplified modelling considers only the energy point of view, i.e. the potential well from which the ion/proton should escape to jump/diffuse, height of the potential well being the activation energy of conductivity and/or diffusion phenomenon. Three models are commonly considered (Fig. 4): i) the ion jump or hoping model, a model issue from the study of oxides with defects (Kröger defect, Schottky defect, interstitial, etc. described with Kröger-Vink notation)[231,232], ii) the two-level potential well issued of Hydrogen-bond studies[1,49,56,233-242] also called Grothuss model and iii) models developed specifically for superionic conductors, 'free', dynamic or gas-like diffusing ions, the species being in the continuum over the potential well.[242-252] More recently, some models consider the coupling between the diffusing species and associated defect (polaron).[253-255] Models linked to the quantum entangling of proton (i.e. strong correlated particles) have also been proposed for the low temperature behaviour of H-bonded compounds.[254-256]

5.1. Time-scale and space dynamics

Figure 4 compares the sketch of the frequency distribution function P(ω), a function that can be measured by neutron incoherent scattering[242,259,260] for an ideal solid (Einstein solid where ions are isolated oscillators), for a solid made of interacting particles (a Debye chain (1D solid) with a distribution of vibrational excitations) and an ideal liquid (Brownian motion) where each species is diffusing continuously: any residence site can be identified whatever the time scale considered. Actually, for real liquids having a viscosity at convenient time scale, some species are diffusing while some others experiment local motion and for the latter, a mean position can be measured. Mobile ions belonging to superionic conductor molten sublattice are rather similar to those belonging to a viscous liquid: some species are diffusing ('free'/ballistic/dynamic particles) whereas some others are in the bottom of the potential well: residence time, flying time, jump distance, etc. can be considered.

Glasses and polymer electrolytes are not solids in a certain sense. They can be considered as a supercooled liquid. Above their glass transition temperature(Tg), the structural disorder is dynamic and at the same time static. These materials appear macroscopically as solids because of their very high viscosity. Their conductivity doesn't follow the Arrhenius law (the conductivity x temperature data plotted versus inverse temperature exhibit a linear behaviour: σ T=σ_o exp(-E_o/kT)) but Vogel-

Tamman Fulscher law (VTF) is observed for polymer and glass: $\sigma = \sigma_o \exp(-B/k(T-T_o))$.[1] A more complex law, the Williams-Landel-Ferry (WLF) law will better describe the conductivity vs. temperature behaviour.[261,262] To differentiate polymers and glassy materials, C.A. Angell has defined a decoupling index, Rt as the ratio of mechanical (viscosity η) and electrical relaxation time: $R\tau = \tau(\eta)/T(\sigma)$. The classification has also been extended to liquids.[263-265] Strong systems show a quasi Arrhenius behaviour over a wide temperature range, whereas 'fragile' ones show an increasing activation energy when the temperature approaches Tg. WLF relationship implies strong correlations between electrical and mechanical relaxations. All the models mentioned above (except entanglement model) ignore interactions between moving species. Measurement of the Haven ratio by comparing diffusion and conductivity measurements gives evidence of correlated diffusion in some of the superionic conductors. Haven ratio or correlation factor varies between 1 (no correlation) and 0.[232,266,267] Little attention has been given to this point for proton conductors.

An understanding of the conductivity mechanism is not possible from the 'simple' measurement of conductivity and corresponding activation energy and a more complete view in the space (occupied site and amount of proton in each site, distribution, 'jump' distance) and time/dynamics (residence time, fly time, anharmonicity, coupling) is required. As explained in reference [131], high quality structure refinement should be performed on single crystal or dense ceramic, especially after deuteration for neutron diffraction. To get a good identification of the site/area where hydrogen atoms are distributed, anharmonical thermal parameters should be used in the refinement of the structure that increases very much the number of parameters to be refined and the number of Bragg peaks to be collected. X-ray Rietveld procedure on powders rarely provides the requested information, especially if water is absorbed at the grain surface that increases the background and limits the number of Bragg peaks measured. For further understanding of the superprotonic conductivity, measurements should be made at the temperature where protons diffuse and conductivity is maximal. Furthermore, the view given by diffraction is completely static. Because of the huge incoherent cross section of hydrogen atom (80 barn, i.e. about 100 times or more than those of other elements), neutron scattering offers a dual space and time view of the matter.[268] This will be discussed in the next paragraph.

The time/frequency behaviour can also be determined by measuring the conductivity and its relaxation, in other terms the complex permittivity or conductivity over a broad frequency range; the imaginary part is the displacement current and the real part is the loss (heating). The dielectric constant is a measure of electrical polarizability, i.e. ability of the charges and dipoles to respond to the electric field. Infrared (and near-infrared from one side and far-infrared now called THz absorption) coefficient is directly related to conductivity : $\alpha(\omega) = 4\pi\sigma(\omega)/nc$ where n is the refractive index and c is the velocity of light in free space; the formula linking the Raman scattering spectrum to conductivity is a little more complex but both methods give access to frequency dependent conductivity.[1]

5.2. Proton transfer mechanisms

Frequency dependent conductivity and vibrational spectroscopy contribute to achieve a description of proton dynamics at different scales. Figure 4c shows the evolution of the number of publications on proton conductors identified on Web-of-Science database with keywords related to the mechanisms of conductivity. However, the mechanism is not really discussed in most of the cases. Proton transfer/ Grotthuss mechanism is the most popular one.

Proton transfer and conductivity mechanisms proposed can be linked to the ambivalent character of the proton due to its size intermediate between the electron and Li cation.[1] In liquid water, proton transfer is associated to the two-minima potential as a well characteristic of the H-bond (Fig. 4b); the charge transfer is supported both by the Brownian motion and the low viscosity of the liquid and by the proton jump from an H_3O^+ ion to a water molecule, the so-called Grotthuss mechanisms. Mechanisms involving such proton jump/Grotthuss mechanism was proposed for ice by N. Bjerrum a long time ago[234,235] and is consistent with oxygen and deuteron/tritium diffusion coefficients measured in compounds like H_3OClO_4 [53] and in many other hydrates.[269-273] A variety of this two-level potential well mechanism was proposed for acid salts like $CsHSO_4$, $Rb_3H(SO_4)_2$, NH_4HSeO_4, etc.[275-277] The huge rotational disorder of HSO_4 ion (and of H_2PO_4 ion in phosphate) above the superionic transition, a few tens K before the decomposition-melting of the whole structure allows the H transfer from one sulphate ion to the next one. The picture of a quasi-liquid state for the H_nXO_4 sublattice is also used, as for Ag^+, Na^+, etc. superionic conductors. However, comprehensive quasi and inelastic neutron scattering studies of various acids and aqueous salt solutions as well as comparative studies with pure water show a more complex picture: the relaxation of water molecules surrounding the hydronium ions prior any proton transfer appears as a critical parameter. Addition of a strong acid such as H_2SO_4 or HNO_3 to water provokes a marked slowing down of the mean translational diffusive motion measured by quasielastic neutron scattering and, to a lesser extent, of the rotational ones. An additional QNS component which is not present in pure water is observed. But, presence of the latter component in concentrated salt solutions eliminates the hypothesis of a fast proton transport process (Grotthuss mechanism) previously proposed and indicates that some kind of relaxation process of the ionic environment (charge effect) could be involved.[278-282] A possible search of relationship with Angell’ glass description would be interesting.

Grotthuss mechanism has been proposed for perovskite[281,282], a class of compounds where the H-content is (very) low, usually called nominally anhydrous compounds. The rocking of oxygen ion between two positions gives rise to the possibility of proton bonded to oxygen atom as OH species to approach an adjacent oxygen atom and inverse the H-bond (jump) in the same way as Grotthuss mechanism in the liquid state.[283] This model was based on the observation of broad OH features on some samples, features assigned to intrinsic bulk OH bonds.[284] This assignment has actually been contested very early.[285] Many years after, it was pointed out that these Infrared fingerprints arise from species located at the sample surface.[286] Consequently, new modelling has been put forward to describe the proton conductivity[253-255] in better agreement with previous neutron and vibrational spectroscopic investigations.[255,286,287]

5.3. Activation Energy and liquid/gas behaviour

Superionic conductors (by comparison with ion conductors) should actually be defined not primarily by their high conductivity but by their (very) low activation energy. Low activation energy guaranties that conductivity remains high far away from the melting temperature of the compound; the activation energy should typically be less than 0.2 eV, a value characteristic a flat conducting pathway for the moving of the ions in the structure.[1] Figure 4a shows the schematic of a potential well: diffusion and conductivity involve ion jump between the neighbouring open sites and the activation energy (Ea) is determined by the height of the well. The upper levels are occupied with increasing temperature and the diffusing species can raise the continuum (Freund was the first to demonstrate this point in a protonic material[288-290] and proton dynamics in hydroxides received the attention of different groups, in particular for neutron studies[291-293]). Using a temporal description, we will have a transition from rare ion jump events to a liquid or gas state where mobile/ballistic particles are distributed along pathways.[242] The consideration of both the temporal and spatial dynamics is required to have an understanding of the proton conductivity mechanisms.

The $P(\omega)$ formalism established by Egelstaff to analyse Inelastic Neutron Spectra of liquids[259] was first applied by Lassègues and Colomban[260] to proton conductors. $P(\omega)$ function is directly linked to momentum transfer function and to the velocity autocorrelation of proton (it's its Fourier transform) and can be measured easily by incoherent neutron scattering at low to moderate temperatures (the resolution and the sensitivity both decrease rapidly for existing spectrometers when temperature reaches 200-300K). This function has an interesting simple limit: D/π at $\omega=0$[259], D being the self-diffusion coefficient of the diffusing particle. Some typical examples of $P(\omega)$ are represented on Figure 4, centre: Einstein solid, a Dirac peak, a Debye solid (no diffusion is possible in these models of solids), a viscous liquid (some particles are diffusing while some others have a mean residence time at the photo-time scale of the neutron technique) and a Brownian motion where all species are moving. The form of $P(\omega)$ is homogeneous with the $\nu I_{(\nu)}$ formalism currently used in the analysis of low wavenumber Raman spectra[294]: this formalism suppresses the strong Rayleigh wing and emphasizes the low wavenumber excitations characteristic of moving species. This will be discussed in the next paragraph. However, the incoherent cross section of H atom (~x100 higher than those of other elements/isotopes) makes neutron scattering one of the best techniques to study proton conductors and to be able to have arguments to discuss conductivity mechanisms (jump distance at the atomic scale, residence and fly time, etc.). Neutron scattering is able to see all hydrogen atoms, even those not covalently bonded ('free' protons). The best way to analyse the proton transfer is the measurement of conductivity from low to high frequency, i.e. from the relaxations and charge transfer (current) from long scale (electrode/electrolyte interface, grain boundary) to short scale (charge relaxation, ion jump), i.e. from long range charge displacement to atomic vibration.[294-300] Calculations also offer an important source of data. In the beginning, molecular dynamics and Monte-Carlo techniques were used[301-320] and then DFT came forward.[320-326]

The number of publications has significantly increased after 1980. Attention was first paid to diffusion and proton transfer, i.e. general mechanisms not specific to proton conductors, then to Grotthuss model and quantum effect (tunnelling). Papers on 'free' particle and continuum effect remain to be rare.[252-255]

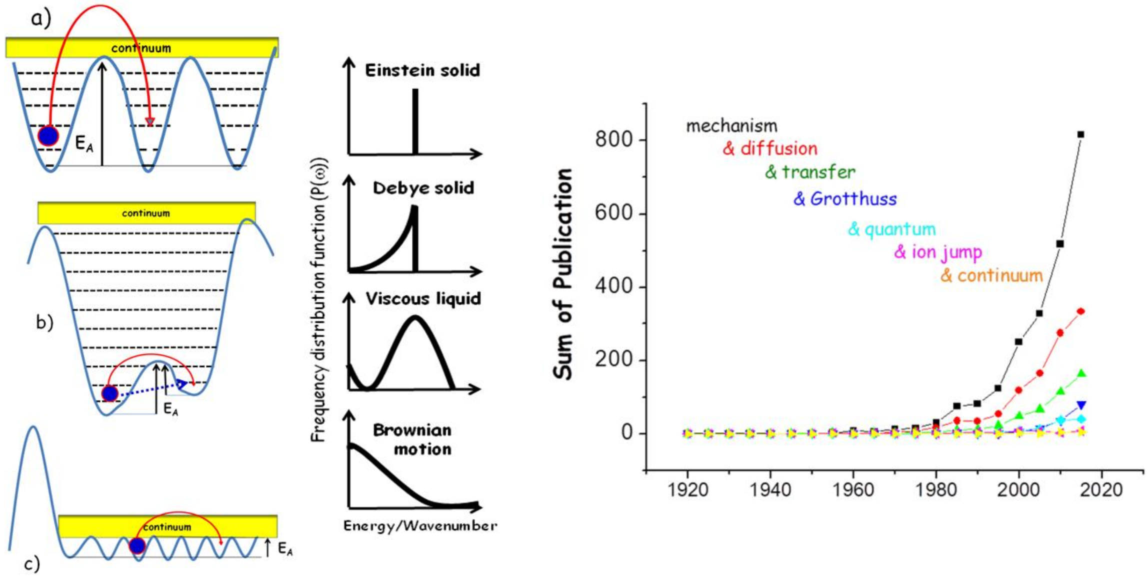


Fig. 4: Schematic view of the different potential wells: a) standard, b) two-level and c) flat potential wells along the conducting pathway in a superionic (open) framework; in the centre, the frequency distribution function (P(w)) is compared for different models of the states of matter. On the right hand, comparison of sum of publications in Web-of-Science database for results with proton conductivity and mechanisms plus diffusion, transfer, Grotthuss, quantum, ion jump and continuum as search criteria.

6. Development of techniques adapted to the study of proton conduction

The highest numbers of papers published since 1940 are observed for NMR (1583), Raman (1016) and Infrared (913) studies. Actually, in comparison to about 10500 papers identified, 85% of them are devoted to conductivity measurements, demonstrating that most of the research concerns technological advancements (preparation of devices, properties measurements) and does not try to get a more complete fundamental understanding of involved mechanisms (comprehensive studies of structure and H diffusion). NMR, neutron scattering, vibrational techniques and frequency dependent conductivity give information on the dynamics of proton at various scales, from micro to picoseconds. 6.1. First NMR and neutron scattering studies

The examination of the Proceedings of the 1st SSPC meeting (1981, Paris) with the contributions of Potier's Group[327] and Arribart[328] as well as those of 3rd SSPC meeting (Montpellier, 1984) with the reviews of Slade[329] and Potier's Group[330] show the efficiency of NMR to understand proton dynamics. Being not an expert in this field, application of the technique to proton conductors is not reviewed here. To get a convenient view of the dynamics, a good picture of the structure and available sites for (potentially) mobile species is required. Tranqui and Anne have already discussed at the first meeting the difficulty to identify the proton distribution; especially at the temperature where the diffusion is important.[331] Deuteration (coherent neutron cross-section of D nucleus is higher than that of H one and its weaker incoherent cross section reduces the background) and measurement at low temperature allow structure refinement with a good reliability but the data at low temperature are rarely pertinent to understand the proton conductor state.[332] Use of single crystal is a great advantage for high quality refinement[333] but powders are currently used because of the difficulty to prepare single crystals and the time to collect a high number of Bragg peaks intensity with a 4-circle diffractometer. Consequently, there is a great temptation to use Rietveld refinement of a X-ray powder pattern where the high resolution of Synchrotron diffraction instrument is an advantage.[334] As discussed in a 2012 review paper[131] in the lack of single crystal, high dense ceramic pieces should be preferred due to the reduction of surface adsorbed water and associated background. Early in 1995, Thomas addressed the refinement strategy in structural studies of proton conductors and all his advice shave still remained valid.[335] The difficulty to localize proton is well considered in 'good' papers (e.g. [336-339]) although some others draw conclusions with poor data. The same problem is present for all superionic conductors but the higher (coherent) cross section of alkali ions or silver ones allows analysing the X-ray diffuse scattering arising from short-range correlation between mobile ions.[21,22,340,341] A special difficulty arises for H-containing compounds measured out of their equilibrium state versus water pressure. The gradient at the sample surface induces non-stoichiometry and loss of crystallinity.

We will consider more specifically neutron scattering and frequency dependent conductivity. The number of papers based on neutron scattering (diffraction: 357; quasielastic: 79 and inelastic: 39) is limited despite the very efficiency of neutron techniques to understand the structure and dynamics of H-containing compounds (see refs[1,94,117,131,137,260,268,278-281] and further references).

The interest on proton conductors in the 1980s was concomitant with the development of high flux neutron facilities (for instance, The Institut Laüe-Langevin at Grenoble started running in December 1971 and many studies have been conducted at ILL since then).

The potential of neutron scattering to understand water dynamics has already been demonstrated.[265,340] The work based on the paper of Chudley and Elliott[343] became the substrate on which other studies were developed. Janik et al. firstly studied the rotational dynamics of NH_4^+ and H_3O^+ in perchlorate in 1965.[344] Figure 5 shows the great information provided by coherent and incoherent neutron scattering.[260,268,345] Coherent Bragg peaks are used for the structure identification and the background level is a direct measure of the H content; evolution of this background as a function of temperature allows controlling the H-content[130-133] with the background level being the summit of the elastic (incoherent) peak. Measurement of the incoherent scattering at different wavenumber/energy is not trivial: different instruments with different resolution and energy window are needed. The common interpretation of neutron scattering postulates that translational diffusion, rotational diffusion and vibration take place at different time scales, typically in the µeV, meV and hundreds of meV ranges. A defined instrument is needed for each range. Time-of-flight or backscattering instruments are the most used. Energy window and resolution should be adapted to the measured phenomena; typically, the resolution should be five times better than the quasielastic broadening to be able to differentiate the elastic peak (its shape is fixed by the instrument) from the Lorentzian component due to the H dynamics. If the resolution is too high, the component disappears in the background. For instance, studies on $H^+(H_2O)$ n beta alumina crystals demonstrated that the expected separation between rotational and translational time scale/energy was not pertinent, and that a large number of energy windows should be studied for the understanding of dynamics. It should be noted that 3-axis diffractometers designed to measure Bragg peaks (i.e. coherent scattering) can also be used to measure the low wavenumber incoherent scattering.[130,131] The spectral window explored by these instruments is weak ($<\sim150$ cm^{-1}) but the resolution is very good even at high temperature. This domain is interesting because the shape of the spectrum ($P_{(\omega)}$, see Fig. 4) differs very much for an Einstein solid (i.e. H_3O^+ stoichiometric beta alumina, poor conductor, Fig. 5), a solid Debye with a distribution of vibrational excitation as observed for $CsHSO_4$, H_3OClO_4 at low temperature and a quasi-liquid superconductor [$CsHSO_4$, H_3OClO_4 and $H^+(H_2O)$n beta alumina in their conducting state].[89] Most representative works on proton conductors carried out before 2000 are given in refs: [130-132,137,164,182-188,255-260,268,279-281,331,332,346-392]. Perchlorates [344,346,365,366], beta aluminas [349-351,373,374], clays[352], Nafion®[353,390,391], HUP[354,359], $CsHsO_4$[350,358,360], $M_3H(SO_4)_2$[368], hydrates[362,363,372,388], hydroxides[367,369], hydrogen-containing metals and hydrides[348, 357], perovskites[130-137,164,375,377,378,379-388] and polyanilines[182,183-186,382] also received attention. An alternative technique such as muon diffusion was also tested.[389] It is interesting to note that QNS measurement on Nafion® presented at 1st SSPC meeting[353] already gave diffusion coefficient of water in the membrane. Certainly, the present description is much more sophisticated[38,388,] in terms of *operando* measurements achieved (i.e. under electric field[391]). On the contrary, measurements made by Anne et al. on beta" alumina powder are poor[351] when compared with those obtained at the same time on single crystals.[349] The lower H content makes the measurement more challenging; furthermore, the two-dimensional character of the cation conductivity and the protonic species adsorbed at the (isotropic) powder surface decrease the efficiency of the measurements. This explains the much better results obtained with a layer of oriented single crystals. [349]

Some species are observed only by inelastic neutron scattering: for instance, the independent oscillator, in other words an interstitial proton located in a large cavity and free of strong covalent bonding is characterized by a single INS peak at ~1000 cm^{-1} as in the cases of dehydrated Keggin salt[370] and MnO_2.[1,185-187] Free protons characterized by a background in INS spectrum have also been observed in many compounds using different instruments.[373,382] The latter species don't give infrared absorption and thus are generally not observed/considered by many scientists. Surprisingly, the symmetry of H_3O^+ ion in beta alumina fits with a Td symmetry indicating a very fast exchange of hydrogen atom on Td position.[373,374]

The number of neutron dynamic studies has decreased for the last few years, most probably due to the increasing difficulties for access to neutron facilities; some instruments have been closed and/or the allocated time to proton conductors was decreased. The interest of the community also moves to technological questions and electrochemistry. However, theoretical approaches have increased (Molecular dynamics: 278; DFT: 65; Monte Carlo: 28), testifying the huge development of such studies. At very early times, the 1999 paper of Paddison et al.[392] gave evidence of the potential of modelling (statistical mechanics based on Liouville equation) to understand the acid water behaviour inside the polymer membrane, as it was made for liquid phosphoric acid which is the substance with the highest intrinsic proton conductivity[278] with *ab initio* molecular dynamic calculations.[319] Nowadays, calculations of molecular dynamics are much more sophisticated.[320]

In any case, calculations and their comparison with measurements should be taken with caution. For instance, the observation of broad bands in the wavenumber range expected for stronglyH-bonded protonic species (2000-3500 cm^{-1}) in partially substituted $BaZrO_3$ perovskite ceramics has attributed to the fingerprint of strongly H-bonded OH group and the mechanism was modelled[283,284] and disputed.[285,286] Other mechanisms were proposed including polaronic proton free of covalent bond and thus without characteristic IR signature, as observed for some other proton conductors[182,183,185-188] and the debate remains open.

6.2. Frequency-dependent conductivity and relaxation (Impedance Spectroscopy)

The huge dipolar character of X-H bond leads to strong absorption in the radio-frequency/microwave to THz range as well as up in the infrared range.[1] Attention to this technique remains very limited though, except the works of Badot and Colomban in the 1990s.[294-300]

Impedance spectroscopy was initially applied to the study of electrode reaction kinetics in aqueous systems by the use of modelling developed by Randles (1947)[393], then Sluyters (1960)[394], Delahaye (1966)[395], De Levy (1969)[396], Bauerle [397] and Epelboin and Keddam (1970).[398] First works on solid-state electrochemical systems date from the end of 1960s: Bauerle in 1969 studied [O_2,Pt/Ytrium stabilized zirconia/Pt,O_2] cell.[397] The main originality of Bauerle's paper was to show that a diagram representing the imaginary part versus the real part of the complex impedance[399] reveals different domains corresponding to different relaxation phenomena, identified as bulk and interfacial relaxations. At that time, the explored frequency range was from a few Hz to a few MHz. The first paper using impedance spectroscopy to study the conductivity of a proton conductor, single crystals of $H^+(H_2O)_n$ β'' and ion-rich β aluminas, was published by Baffier, Badot and Colomban in 1981[18], using a Wheatstone bridge circuit (AC current source, resistances, capacitances and oscilloscope). Measurements were made point-by-point at each frequency to build Cole-Cole diagram at different temperatures. The availability of automatic impedancemeters (such as Solartron® in the 1980s) makes the measurements much easier and faster. Books devoted to these techniques became also available such as Kleitz and Dupuy in 1975[400], Jonscher in 1983[401], Ross Macdonald in 2005 [402] and so on. Measurements in the 500 MHz-50 GHz require the use of many microwave sources, guide/coaxial cables and detectors; each for selected frequency ranges making the measurements time consuming and difficult.[403, 404] With the development of high frequency microelectronic and the research on the stealth of rockets and aircrafts[405,406] in the 1990s, new instruments called Network Analyzers, working up to tens of GHz range made the measurements easier and faster. Nowadays, the link with far-infrared absorption is at the same time possible (also called THz spectroscopy).[1] In the range of 0.5 to hundreds of GHz, localized charge relaxations are observed: rotational and translational jumps, also detected by NMR or neutron scattering. As sketched on Figure 6c, a free proton gives a plateau as a function of the frequency, up to GHz, before the infrared absorption (O-H bond). On the other hand, a slope is observed for a trap proton; corresponding features in complex dielectric representation are shown. For instance, plateaus are observed for very good proton conductors such as HUP and $CsHSO_4$.[295,297]

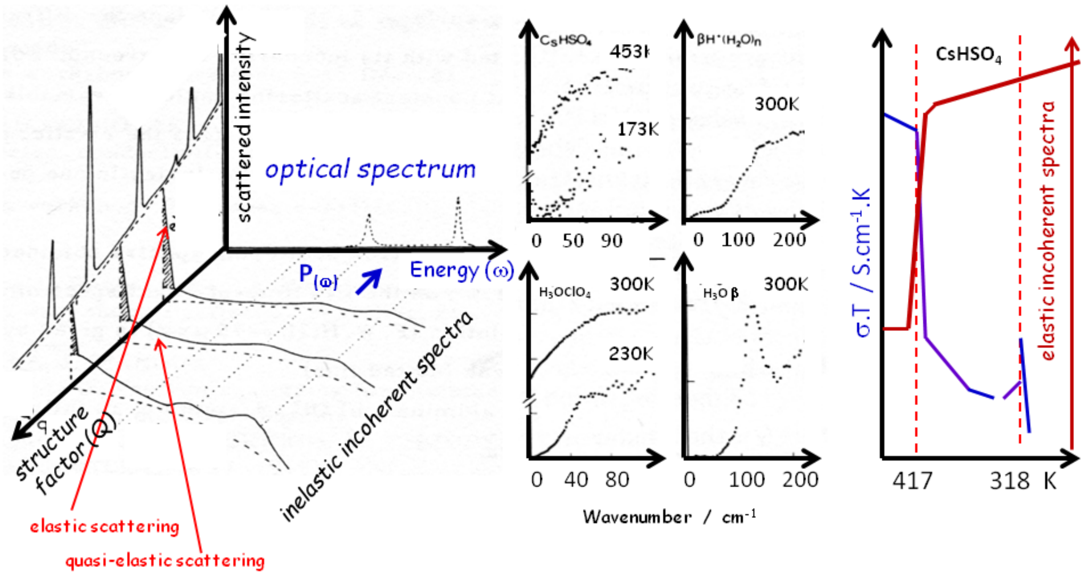


Fig. 5: left) Sketch of the information regarding structure (diffraction, coherent scattering) and energy (wavenumber/incoherent scattering) by neutron scattering; corresponding optical spectra are also given. centre) examples for comparison of low wavenumber spectra of some proton conductors in their low temperature (poor conductor) and high temperature (proton conductor) phases ($CsHSO_4$, H_3OClO_4, H_3O^+ and $H^+(H_2O)_n$ beta alumina): note the convex shape of $P_{(\omega)}$ curve in high temperature (conducting) phase and the concave one at low temperature; a quasi “Dirac” peak is observed for H_3O^+ beta alumina T’ in-plane mode of oxonium cation[20,91]; right) comparison of the evolution of the intensity of the elastic peak (i.e. the intensity of the coherent background) versus (inverse) temperature for $CsHSO_4$ crystal with the conductivity: note that the intensity decreases when the conductivity jumps to a high value.[91]

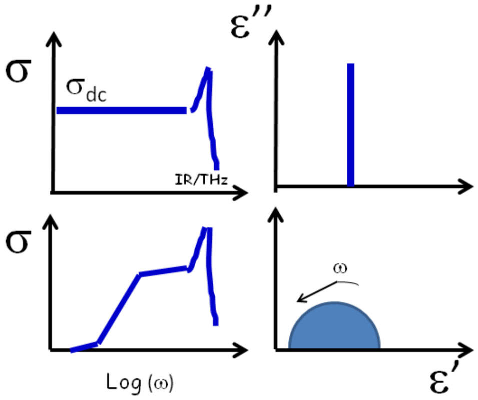


Fig. 6: Sketch showing the correspondence between conductivity and dielectric relaxation for a free (top) and a trap (bottom) proton; the dashed high frequency spectrum corresponds to infrared absorption (after [91]).

7. Unsolved questions and perspectives

Looking at the early studies in the 1970s gives evidence of the big development of some devices and associated technology. At the moment, up to six and more authors is common which show the big changes in the research practice due to the higher technological input in the published works. About fifty years after the first H_2/O_2 fuel cell of Gemini program based on hydrocarbon- membrane, perffluorosulfonic-acid membrane working at ~330-350 K, commercially available cars, trucks, buses and trains started to be mobilized by electric motors powered by fuel cells and the amount of rare platinum metals used as electrode decreased from 100 $mg.cm^{-2}$ to about 0.1 $mg.cm^{-2}$. First fuel cells based on perovskite ceramic were also tested in the 1960s but it is only with the global warming issue that the industrial development had really started; their higher working temperatures (750-1050 K) make all problems more complex. Additionally, technological research on water electrolysers is now active. Attention was mostly paid to technological developments while less attention was paid to fundamental questions: the nature of the proton-environment bonding at the working temperature, the proportion and distribution of diffusing protons by comparison with all protons in the bulk (Hall ratio), the correlation between mobile species (Haven ratio), the nature and behaviour of grain boundary, the change of the material at micro/nanoscale under electric field and after representative operating time, etc. remain open questions for most of the compounds (Table 3).

Table 3: Questions to be addressed.

Materials	**Questions**	**Objectives**
Electrolytes	Long term ageing	Life time/ prediction Failure modelling
	Micro- to nano-structure control	(Gradient) Defect control
	D and T diffusion Comparison with conductivity	Fundamental; Correlated diffusion? Hall/Haven ratio; number of diffusing protons, etc.
	Water pressure dependence	Increase the efficiency and temperature operating range
	Mechanical properties	Failure mechanism understanding & modelling
	Electric field effects	*Operando* behaviour at macro, micro and nanoscale
	New materials	
Interfaces	properties/control	
Electrodes	Long term ageing	
	Micro- to nanostructure control	
Integration	Thermal expansion control Sintering temperature	

Severe conditions experimented by an electrolyte membrane in an electrolyser and the fact that the membrane itself undergoes important water partial pressure gradient require ageing studies under harsh conditions (water pressure, temperature, cycling, etc.). Studies at the microscale are now needed in order to understand the behaviour of each constituent (grain boundary in ceramics, pores in polymers, surface, near-surface and interface, defects, etc.) and their relationship with failure or decrease of the electrochemical characteristics.[407] New compounds (or better new forms) are also at the focus. Fillaux and co-workers pointed out the very special behaviour of proton in carbons.[382] Graphene oxide, a single or a few layer of carbon easily hosts water and exhibits proton conductivity.[408-413] The large community interested in graphene, may increase the number of researchers interested in proton conduction. Theoretical interest on agostic bond (a bond involving a fractional number of electrons, as the H-bond)[414,415] may also offer a way to better understand the chemical bonding of the very specific entity which is the proton.

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Figure and Table Captions

Fig. 1: Comparison of citation reports per year in Web-of-Science^{TM} database (Clarivate Analytics) for results with fuel cell, electrode, device, sensor and electrolyser (with the topics of proton and conductivity to be representative) as keywords; the number of papers is given in parentheses; a zoom is given on the right side.

Fig. 2: Communities addressing ion/proton transfer/conductivity, hydrogen containing solids and their applications.

Fig. 3: Sapphire wafer covered by microsensors prepared using micro-electronic processes: ion implantation, screen printing, thermal treatments and exposition to plasma; on the right conductivity values (see refs[60,61,202] for details).

Fig. 4: Schematic view of the different potential wells: a) standard, b) two-level and c) flat potential wells along the conducting pathway in a superionic (open) framework; in the centre, the frequency distribution function (P(w)) is compared for different models of the states of matter. On the right hand, comparison of sum of publications in Web-of-Science database for results with proton conductivity and mechanisms plus diffusion, transfer, Grotthuss, quantum, ion jump and continuum as search criteria.

Fig. 5: left) Sketch of the information regarding structure (diffraction, coherent scattering) and energy (wavenumber/incoherent scattering) by neutron scattering; corresponding optical spectra are also given. centre) examples for comparison of low wavenumber spectra of some proton conductors in their low temperature (poor conductor) and high temperature (proton conductor) phases ($CsHSO_4$, H_3OClO_4, H_3O^+ and $H^+(H_2O)_n$ beta alumina): note the convex shape of $P_{(\omega)}$ curve in high temperature (conducting) phase and the concave one at low temperature; a quasi "Dirac" peak is observed for H_3O^+ beta alumina T' in-plane mode of oxonium cation[20,91]; right) comparison of the evolution of the intensity of the elastic peak (i.e. the intensity of the coherent background) versus (inverse) temperature for $CsHSO_4$ crystal with the conductivity: note that the intensity decreases when the conductivity jumps to a high value.[91]

Fig. 6: Sketch showing the correspondence between conductivity and dielectric relaxation for a free (top) and a trap (bottom) proton; the dashed high frequency spectrum corresponds to infrared absorption (after [91]).

Table 1: Milestones regarding proton conductors and devices based on these materials. Important economical/political events regarding energy cost, greenhouse gas and global warming are also noted. Most stringent dates are in bold.

Table 2: Proton conductors representative of the different classes studied; most of them since 1980 (see ref [1] for a more complete list); compounds in bold, in bold capital and italics and in bold underlined capital

represent the different states of under study; in development or usage in commercially available devices, respectively.

Table 3: Questions to be addressed.