This book aims to give a comprehensive survey of the chemical and physical parameters governing proton conduction. It includes descriptions of the preparation, structures and properties of typical materials (glasses, crystals, ceramics, metals, organic and inorganic polymers) and of devices.

Chemistry of Solid State Materials

Proton conductors

Solids, membranes and gels – materials and devices

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Preface

Since the discovery of ice conductivity more than one hundred years ago in Japan, proton transport in solids has aroused considerable interest. Currently, proton conductors appear interesting because of protonic transport in biophysical processes, and – as with many other ionic conductors – since they can be used in numerous electrochemical devices such as batteries, fuel cells, chemical sensors, electrochromic displays and supercapacitors. Furthermore, energy systems based on hydrogen are a possible answer to prevent earth pollution. The number of materials, crystalline or amorphous, organic or inorganic, solids and gels, where proton transport is known to play an important role, has increased during the last few years. At the same time, a better understanding of proton transfer mechanism seems to have been reached. Recently, the debate on cold fusion has made most scientists aware of the proton peculiarity.

It is hardly an exaggeration to say that everything about hydrogen is unique. Mendeleev could not find a place for this element in the Periodic Table. The hydrogen ion 'H^+' is an ion without an electron, a bare proton and so, protons are usually solvated. The literature about proton transport is also unique and must be read with caution. For instance, early measurements on ice by Eigen, de Maeyer & Spatz showed a measurable ionic conductivity which was explained in proton defect terms, protons diffusing by quantum-mechanical tunnelling, and the carrier concentration could be adjusted by doping. In 1973, Von Hippel, Runch & Westphal showed that conductivity measurements were perturbed by surface and interfacial phenomena. More recently Petrenko and co-workers showed that the defect concentration close to the surface of ice crystals is higher than in the interior. This can be compared with oxide ceramics where a layer a few micrometres thick near the surface is always different from the bulk, because of a diffusion gradient. Controversy exists also in the cases of the fast proton conductors such as $H_3OUO_2PO_4 . 3H_2O$, α $Zr(HPO_4)_2 . nH_2O$ and β''-aluminas and is linked to the prominent role

of surfaces for protonic materials and the influence of water partial pressure on thermal stability. As recently as 1983 Ernsberger cast doubt on the existence of true fast protonic conduction. Nevertheless, most of the reviews on ionic diffusion do not mention protons.

This book aims to give a survey of the chemical and physical parameters concerning (fast) proton conduction, the preparation, structures and properties of typical materials, the dynamics of charge transport and some examples of devices using proton transport.

The distinction between 'conductors' and 'insulators' depends on the conductivity which can vary by more than ten orders of magnitude. The charge carriers can be either electrons (or holes) or ions (or vacancies). Ionic conductivity implies a diffusion of matter inside the solid (gel) and/or at its surface; and thus most ionic conductors are also very good ion-exchangers. Materials (oxides, nitrides, halides or polymers) can be divided into four groups according to their electrical properties.

(i) 'Insulators' with a residual conductivity lower than $10^{-10}\ \Omega^{-1}\ cm^{-1}$ where the electronic conduction is generally also of the same order of magnitude.
(ii) 'Ionic' conductors in which the presence of structural defects leads to an ionic conductivity between 10^{-9} and $10^{-6}\ \Omega^{-1}\ cm^{-1}$.
(iii) 'Superionic' conductors with a conductivity higher than $10^{-5}\ \Omega^{-1}\ cm^{-1}$ and usually between 10^{-4} and $10^{-2}\ \Omega^{-1}\ cm^{-1}$. The main difference between superionic and ionic conductors concerns the activation energy (E_a) of the ionic conductivity: for the former, which are also called fast ionic conductors or solid electrolytes, E_a is lower than 0.4 eV while values varying between 0.6 and 1 eV are usually observed for 'normal' ionic conductors. A low activation energy implies that good electrical properties are present far from the melting point. In the latter two types of materials, the electronic conductivity is usually low.
(iv) Finally, there are also mixed conductors exhibiting both good ionic and electronic (metallic or semi-conductor) conductivity. These materials are used as non-blocking electrodes.

Protonic conduction is a particular case of ionic conduction; however, the small dimension of the proton implies that there may be some similarities with electronic conduction. The existence of a bare proton is restricted to very special cases (e.g. in a plasma, solar wind, or synchrotron-ring). In condensed matter, however, the proton reacts strongly with the

environment because of the absence of electron shells to shield the nucleus. In metals, the proton interacts with a conduction electron and proton transport is correlated with some elastic and inelastic displacements (polarization) of electrons and can be assisted by phonons. In electronic insulators and semi-conductors, in which the Debye length is larger than the interatomic distances, the proton penetrates the valence electron shell and directional (covalent) bonds occur: tunnelling can be expected, but fast proton diffusion is generally not possible. The proton can also interact with certain molecules (e.g. solvation by oxygen, water or ammonia) in the liquid state and multinuclear protonic species are formed, leading to 'classical' ions such as OH^-, H_3O^+ or NH_4^+. Two main mechanisms of proton transfer have been recognized: the 'vehicle mechanism', where the proton is supported by the solvated species, and the Grotthuss mechanism which involves a correlated jump of the bare proton between host molecules and correlated reorientation of the latter.

Much in the same way that the beginning of the investigation into fast ionic conduction in solids is usually ascribed to the discovery of Na^+ ion conductivity in Na β-alumina ceramics by Ford Motor Research Group, so research into fast proton conductors was initiated with the Du Pont patent on Nafion© perfluorocarbon sulphonic acid polymer ($\sigma_{300K} \approx 5 \times 10^{-2}\ \Omega^{-1}\,cm^{-1}$) in 1972, in connection with the Gemini fuel-cell program, and by Potier's group who showed proton conductivity in oxonium perchlorate in 1973. Large-scale studies with the possible applications to low-temperature fuel-cells (EEC Research Program initiated by J. Jensen) and microionic devices with the work on hydrogen uranyl phosphate, HUP (by the Leeds group) began after 1980. These investigations were followed by the discovery of high conductivity above 150 °C in stable acid sulphates by Russian groups and more recently by an increased interest in gels which are nearly always good proton conductors. Finally, earlier works and the role of mineralogists in the understanding of proton mobility in solids should be mentioned. For instance, the first notion of a 'quasi-liquid state' of ions in a solid (HUP) is due to Beintema in 1938 ('these ions may thus be considered as true vagabond ions') while Wilkins described many structures containing mobile water and oxonium ions in 1974.

Unlike metals or semi-conductors for which the concept of the surface is well-defined, the analogous concept in protonic materials corresponds to a much thicker 'layer' similar to that in ceramics: it is a zone where the atmospheric pressure in contact with the solid induces a high

concentration gradient and thus important diffusion phenomena which are accelerated at temperatures close to the melting or decomposition point. In proton conductors, it is usually not possible to have both a high conductivity and thermal stability. The latter is usually low because of the weakness of hydrogen bonds. The presence of defects in the surface layers facilitates 'absorption' of various molecular entities until a liquid phase is formed. The versatility of hydrogen bonds which can be 'stretched' from strong to weak ones helps to obtain a quasi-continuous passage from the solid to liquid state via intermediate states such as particles with covered surface or soaked porous materials.

Progress in the understanding of superionic conduction is due to the use of various advanced techniques (X-ray (neutron) diffuse scattering, Raman spectroscopy and a.c.-impedance spectroscopy) and – in the particular case of protons – neutron scattering, nuclear magnetic resonance, infrared spectroscopy and microwave dielectric relaxation appear to be the most powerful methods. A number of books about solid electrolytes published since 1976 hardly mention proton conductors and relatively few review papers, limited in scope, have appeared on this subject. Proton transfer across biological membranes has received considerable attention but is not considered here (see references for more details).

The present book contains many contributions covering very different aspects and is organized as follows.

The first part describes chemical and physical parameters necessary for fast proton conduction and proposes a classification of different kinds of proton conductors. The methods used to determine the protonic nature of the charge carriers are given. The importance of partial water pressure, the role of defects and surface phenomena are discussed.

The second part treats the chemistry, structures and electrical properties of typical materials, from hydrogen bronzes to polymers via ice, hydroxides, acid sulphates, layer hydrates, inorganic ion exchangers, gels, porous media and mixed inorganic–organic polymers. These materials are compared with liquid and molten salt conductors, intercalated graphites and metal hydrides and have been chosen in order to illustrate the different behaviour of the proton: it has 'electron-like' properties in some oxides and hydrides, ion-like behaviour in some other oxides or liquid-state behaviour such as encountered in solution covered particles or pores of a gel.

The third part discusses the approaches leading to an understanding

of proton dynamics and the methods used to study the motions on a short-range (local), long-range and macroscopic scale are given.

The fourth part concerns interpretation of three main conductivity mechanisms: the 'electron-like' type, the proton jump in statically or dynamically disordered solids and the 'quasi-liquid' state in hydrated materials giving rise to either vehicle or 'Grotthuss' mechanism.

Finally, the last part deals with applications, in particular with high-current electrochemical systems for energy production or storage, (micro)-ionic components using insertion or blocking electrodes and the devices such as MnO_2, PbO_2 batteries where the role of protons has been neglected for a long time.

ONERA, January 1992 Ph. Colomban

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Symbols

Chapter 3

V	vacancy
D	diffusion coefficient
C	concentration
e	charge
σ	conductivity
E	enthalpy

Chapter 4

C	concentration
D	diffusion coefficient
e	charge
σ	conductivity
E	enthalpy
f	correlation (or Haven) factor
B	mobility
σ_0	prefactor
σ_i	ionic conductivity
σ_e	electronic conductivity
t_i	ionic transport number

Chapter 20

A	pre-exponential factor
E_a	activation energy
k	Boltzmann constant
pKa	ionization constant of acids
pK	ionization constant of polymers
pK_0	ionization constant of polymers at $\alpha = 0$
T	absolute temperature
T_0	ideal glass transition temperature
T_g	glass transition temperature

Symbols

x	number of acid moles per polymer repeat unit
α	degree of ionization
σ	specific conductivity
ν	stretching vibrational frequency

Chapter 21

D_t	self-diffusion coefficient
D^+	abnormal proton self-diffusion coefficient
D_r	rotational diffusion constant
σ	specific conductivity
τ	residence time

Chapter 22

γ	nuclear gyromagnetic ratio
$\hbar$	$1/2\pi$ Planck's constant
I	nuclear spin
H_0	static field
H_1	amplitude of the r.f. field
ω	frequency of the r.f. field
$\tilde{\sigma}$	chemical shift tensor
$\tilde{J}$	indirect spin–spin coupling tensor
Q	electric quadrupole moment of the nucleus
V	electric field gradient
$\tilde{C}$	spin rotation tensor
T_1	spin–lattice relaxation time in the Zeeman field
$T_{1\rho}$	spin–lattice relaxation time in the rotating frame
T_2	spin–spin relaxation time
τ_C	correlation time
$\nu = 1/\tau_{CO}$	attempt frequency
E_a	potential barrier

Chapter 24

$I_{\rho\sigma}{}^{jk}$	intensity of scattered light polarized in the σ direction due to a transition from state j to state k induced by incident light polarized in the ρ direction
$\alpha_{\rho\sigma}{}^{jk}$	$\rho\sigma$ component of the Raman polarizability tensor originating in a transition from state j to state k
$\alpha_{\rho\sigma}{}^{m}$	$\rho\sigma$ component of the Raman polarizability tensor originating in a fundamental vibrational transition of normal mode m in the electronic ground state
P_σ	σ component of the electric moment operator
ν(X)	vibrational frequency of species X
M(X)	molecular mass of species X

Symbols

$I(X)$	moment of inertia of species X
V_0	barrier height for motion from one site to an adjacent site
d	separation between adjacent sites
Γ	bandwidth (full width at half maximum intensity)
Γ_{vib}	vibrational contribution to the bandwidth
τ_c	correlation time for a vibrational mode coupled to a disordering process
ΔU	activation energy for a disordering process which is coupled to a vibrational mode
E_a	activation energy for thermally activated reorientational motion
D	diffusion coefficient

Chapter 25

σ^*	complex conductivity
σ'	real conductivity
σ''	imaginary conductivity
$\boldsymbol{J}$	current density
$\boldsymbol{E}$	electric field
ε_0	vacuum permittivity
ε'	real permittivity
ε''	imaginary permittivity
ε^*	complex permittivity
ε_∞	optical permittivity
ε_s	static permittivity
n^*	complex refractive index
n^B	Bose–Einstein occupation number
$\mathrm{tg}\delta$	tangent loss
I	Raman scattered intensity
$\alpha(\omega)$	infrared absorption
J_0, J_1	Bessel functions
c	light velocity
α	Debye deviation parameter
τ	Debye relaxation time (collective)
τ'	Debye relaxation time (individual)
f_c	loss peak frequency
μ	dipole moment
C	Currie constant
k	Boltzmann constant
T	Curie–Weiss temperature

Chapter 26

B_0	magnetic field
D	self-diffusion coefficient
G	magnetic field gradient
M	magnetization

Symbols

n	$[H_3O^+]/[H_2O]$
R	resistance
T_1	longitudinal spin relaxation time
T_2	transversal spin relaxation time
γ	gyromagnetic ratio
σ	specific conductivity

Chapter 28

$R_z(t)$	normalized longitudinal magnetization time decay
$R_{xy}(t)$	normalized transverse magnetization time decay
$1/T_1$	longitudinal or spin–lattice relaxation rate
$1/T_2$	transverse or spin–spin relaxation rate
W_n	distribution of pore sizes
D	diffusion coefficient
D_f	fractal dimension
$A(G)/A(0)$	attenuation of the spin–echo signal
G	intensity of the pulsed gradient field
k	permeability
Φ	tortuosity

Chapter 30

τ	relaxation time
τ_0	residential time
τ_1	time of flight
$P(\omega)$	Fourier transform of the autocorrelation function of particle velocities
$S_{inc}(Q,\omega)$	spectral density
Q	momentum transfer
$\sigma(\omega)$	frequency dependent conductivity
E_0	activation energy
η	viscosity
r_1	radius of mobile species
k	Boltzmann constant
e	charge
T_0	equilibrium glass transition temperature
R_τ	electrical relaxation time
m_i	effective mass of mobile species
V_{eff}	effective potential
γ	damping

Chapter 31

A	amplification factor $(D_{\Lambda_H^+}/D_{H_2O})$
a	jump distance