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978-0-521-38317-2 - Proton Conductors: Solids, Membranes and Gels-Materials and Devices

Edited by Philippe Colombar

Frontmatter

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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.

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Chemistry of Solid State Materials

Proton conductors

Solids, membranes and gels – materials and devices

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Chemistry of Solid State Materials

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Proton conductors

Solids, membranes and gels – materials and devices

Edited by

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Contents

List of contributors	xvii
Preface	xxi
Symbols	xxviii
I. HYDROGEN BOND AND PROTONIC SPECIES 1	
1 The hydrogen bond and chemical parameters favouring proton mobility in solids 1	
<i>A. Potier</i>	
1.1 From ionic to protonic conduction 1	
1.2 The lone proton migration mechanism (translocation) 2	
1.3 Proton-carrying mechanisms (the vehicle mechanism or V-mechanism) 6	
1.4 Structural effects 7	
1.5 Chemical ‘equilibrium’ and the ‘ionic defect’: towards a chemical classification 10	
1.6 References 15	
2 Protonic species and their structures 18	
<i>D. J. Jones and J. Rozière</i>	
2.1 General introduction 18	
2.2 Proton hydrates 19	
2.3 Nitrogenous protonic species 24	
2.4 References 32	
3 Proton conductors: classification and conductivity 38	
<i>Ph. Colombe and A. Novak</i>	
3.1 Introduction 38	
3.2 Classification of protonic conductors 42	
3.3 References 56	

Contents

4	Defects, non-stoichiometry and phase transitions	61
	<i>Ph. Colombe and A. Novak</i>	
4.1	Introduction	61
4.2	Ionic mobility and conductivity	62
4.3	Electronic conduction and non-stoichiometry	64
4.4	Water vapour pressure	69
4.5	References	75
5	Structural studies of proton conductors	79
	<i>J. O. Thomas</i>	
5.1	The structural situation	79
5.2	Proton jumps	80
5.3	Proton jumps and molecular reorientations	81
5.4	Short hydrogen bonds	85
5.5	Ordered and disordered networks	86
5.6	References	89
6	Hydrogen in metals: structure, diffusion and tunnelling	90
	<i>I. Svare</i>	
6.1	Introduction	90
6.2	Hydrogen absorption in metals	90
6.3	Hydrogen diffusion and tunnelling	93
6.4	A model of tunnelling	95
6.5	Other theories of tunnelling	98
6.6	References	99
II.	MATERIALS: PREPARATION, STRUCTURES AND PROPERTIES	101
7	Structure and characterization of hydrogen insertion compounds of metal oxides	101
	<i>P. G. Dickens and A. M. Chippindale</i>	
7.1	Introduction	101
7.2	Preparations	104
7.3	Thermodynamic aspects of hydrogen insertion	105
7.4	Location of hydrogen in H_xMO_n	109
7.5	Conclusions	118
7.6	References	119
8	High temperature proton conductors based on perovskite-type oxides	122
	<i>H. Iwahara</i>	
8.1	Introduction	122

Contents

8.2	Proton conducting solids at high temperature	122
8.3	Preparation and properties of ceramics	123
8.4	Verification of protonic conduction	124
8.5	Conduction properties	128
8.6	Proton formation in oxides	129
8.7	Migration of protons	133
8.8	References	136
 9	 Highly ionic hydroxides: unexpected proton conductivity in Mg(OH) ₂ and homologues	 138
	<i>F. Freund</i>	
9.1	Introduction	138
9.2	Non-hydrogen bonded systems	138
9.3	Potential energy curve of the O–H oscillator	140
9.4	Direct current proton conductivity measurements	144
9.5	Proton conductivity results	147
9.6	Proton carrier density on the conduction band	151
9.7	Summary	155
9.8	References	156
 10	 Ice	 158
	<i>I. A. Ryzhkin</i>	
10.1	Introduction	158
10.2	Structure of ordinary ice	158
10.3	Defects and conduction mechanism	159
10.4	Electrical properties of doped ice	163
10.5	Conclusion	163
10.6	References	164
 11	 Anhydrous materials: oxonium perchlorate, acid phosphates, arsenates, sulphates and selenates	 165
	<i>Ph. Colombe and A. Novak</i>	
11.1	Oxonium perchlorate	165
11.2	Dihydrogen phosphates and arsenates, MH ₂ XO ₄	169
11.3	Hydrogen sulphates and selenates	170
11.4	References	179
 12	 Hydrogen behaviour in graphite–nitric acid intercalation compounds	 183
	<i>H. Fuzellier and J. Conard</i>	
12.1	Graphite intercalation compounds	183

Contents

12.2	Crystal structure of GNCs	184
12.3	H mobility	185
12.4	Conclusion	188
12.5	References	188
A	Inorganic ion exchangers	190
13	Proton-containing β - and β'' -alumina structure type compounds <i>H. Ikawa</i>	190
13.1	Synthesis	190
13.2	Crystal structure and structural characteristics	191
13.3	Thermal transformations	196
13.4	Conductivity	201
13.5	Applications	204
13.6	References	205
14	Proton conduction in zeolites <i>E. Krogh Andersen, I. G. Krogh Andersen and E. Skou</i>	210
14.1	Introduction	210
14.2	Materials and materials modification	212
14.3	Protonic conduction in alkali metal zeolites	213
14.4	Protonic conduction in ammonium zeolites and in hydrogen zeolites	216
14.5	Protonic conduction in tin zeolites	220
14.6	Summary	222
14.7	References	223
15	Proton containing NASICON phases <i>A. Clearfield</i>	224
15.1	Triphosphate phases	224
15.2	Silicophosphate phases	231
15.3	Structural considerations	234
15.4	Conclusions	235
15.5	References	235
B	Layer hydrates	238
16	Phosphates and phosphonates of tetravalent metals as protonic conductors <i>G. Alberti and M. Casciola</i>	238
16.1	Introduction	238

Contents

16.2	Layered α -zirconium phosphate and its modified and intercalated phases	239
16.3	Other phosphates and phosphonates of tetravalent metals	248
16.4	Applications and future perspectives	251
16.5	References	251
17	Hydrogen uranyl phosphate, $H_3O\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (HUP), and related materials <i>Ph. Colombe and A. Novak</i>	254
17.1	Introduction	254
17.2	Preparation and chemistry	255
17.3	Thermal and chemical stability	258
17.4	Structure and phase transitions	261
17.5	Electrical properties	264
17.6	Related materials	267
17.7	References	269
18	From crystalline to amorphous (particle) hydrates: inorganic polymers, glasses, clays, gels and porous media <i>Ph. Colombe and A. Novak</i>	272
18.1	Hydrous heteropolytungstic (molybdic, silicic) acids	275
18.2	Water layers in 2D frameworks	278
18.3	Hydrous oxides	282
18.4	References	289
19	Perfluorinated membranes <i>G. Pourcelly and C. Gavach</i>	294
19.1	Historical background and development	294
19.2	Synthesis of perfluorinated membranes	295
19.3	Structure of perfluorinated membranes	296
19.4	Proton transport in perfluorosulphonic membranes	300
19.5	Perfluorinated membranes and related materials	307
19.6	Conclusions	308
19.7	References	308
20	Mixed inorganic–organic systems: the acid/polymer blends <i>J. C. Lassègues</i>	311
20.1	Introduction	311
20.2	Preparation	314

Contents

20.3	Classification of the acid/polymer blends	314
20.4	Temperature dependence of the conductivity	323
20.5	Conclusion	325
20.6	References	326
III.	PROTON DYNAMICS AND CHARGE TRANSPORT	329
21	Incoherent neutron scattering studies of proton conductors: from the anhydrous solid state to aqueous solutions <i>J. C. Lassègues</i>	329
21.1	Introduction	329
21.2	Anhydrous solid protonic conductors	334
21.3	Hydrated solid protonic conductors	338
21.4	Acidic aqueous solutions	342
21.5	Conclusion	345
21.6	References	346
22	NMR studies of local motions in fast protonic conductors <i>S. V. Bhat</i>	350
22.1	Introduction	350
22.2	NMR as a probe of structure and dynamics	351
22.3	High resolution NMR study of ammonium ferrocyanide hydrate (AFC)	353
22.4	High pressure NMR studies of AFC	359
22.5	Relaxation time studies of AFC	360
22.6	Effect of low dimensionality	361
22.7	Conclusion	362
22.8	References	363
23	Vibrational spectroscopy of proton conductors <i>Ph. Colomban and A. Novak</i>	367
23.1	Introduction	367
23.2	Hydrogen bonding	368
23.3	Relationship between OH stretching frequencies and O...O distances	369
23.4	Isotopic dilution method	369
23.5	Structure determination	370
23.6	Disordered crystals	371
23.7	Potential barrier and conductivity	374
23.8	Phase transitions	375
23.9	References	375

Contents

24	Raman spectroscopic studies of proton conductors <i>R. Frech</i>	377
24.1	Introduction	377
24.2	The Raman effect	377
24.3	Applications of Raman spectroscopy to the study of proton conductors	379
24.4	References	387
25	Frequency dependent conductivity, microwave dielectric relaxation and proton dynamics <i>Ph. Colomban and J. C. Badot</i>	389
25.1	Definitions	389
25.2	Dielectric relaxation	392
25.3	Relaxation assignment in protonic conductors	397
25.4	Phase transitions, ferroelectricity and collective motions	402
25.5	References	406
26	Measuring the true proton conductivity <i>K.-D. Kreuer</i>	409
26.1	The sample	409
26.2	H^+ -conductivity measurement by a.c.-impedance spectroscopy	410
26.3	$^1H^+$ -diffusion coefficient measurement by PFG-NMR	412
26.4	References	416
27	D.c. techniques and a.c./d.c. combination techniques <i>E. Skou, I. G. Krogh Andersen and E. Krogh Andersen</i>	418
27.1	Introduction	418
27.2	E.m.f. methods	419
27.3	D.c. methods	420
27.4	A.c./d.c. combination techniques	425
27.5	Conclusion	430
27.6	References	430
28	NMR in gels and porous media <i>J. P. Korb and F. Devreux</i>	432
28.1	Introduction	432
28.2	Nuclear relaxation of solvent imbibed in porous materials	432
28.3	Pulsed field gradient experiments	437
28.4	Nuclear relaxation in fractal aerogels	439
28.5	NMR imaging and microscopy	442
28.6	Conclusion	442
28.7	References	443

Contents

IV.	PROTON DIFFUSION MECHANISMS	444
29	Mobility in hydrogen-containing oxide bronzes: the atomic-level detail <i>R. C. T. Slade</i>	444
29.1	Applicable techniques	444
29.2	Results of atomic-level investigations	446
29.3	References	455
30	Conductivity mechanisms and models in anhydrous protonic conductors <i>Ph. Colombe and A. Novak</i>	457
30.1	Theoretical interpretations of superionic conduction	457
30.2	Proton tunnelling	467
30.3	Superionic protonic conductivity	468
30.4	References	470
31	Conduction mechanisms in materials with volatile molecules <i>K.-D. Kreuer</i>	474
31.1	Proton conduction mechanism in dilute acidic aqueous solutions	475
31.2	Proton conduction mechanism in concentrated acidic aqueous solutions	481
31.3	Proton conduction mechanism in <i>n</i> solid acidic hydrates	481
31.4	References	484
V.	DEVICES	487
A.	Energy storage and production	487
32	Applications of perfluorinated proton conductors (Nafions) <i>C. Gavach and G. Pourcelly</i>	487
32.1	Introduction	487
32.2	Solid polymer electrolyte (SPE) technology	488
32.3	Fuel cells and electrochemically regenerative cells	491
32.4	Electrolysers	493
32.5	Separation techniques	495
32.6	Catalysis	495
32.7	Coated electrodes	496
32.8	Conclusions	496
32.9	References	496

Contents

33	Synthesis of polycrystalline H_3O^+ and NH_4^+ - $\beta''/\beta\text{-Al}_2\text{O}_3$ <i>P. S. Nicholson</i>	499
33.1	Introduction	499
33.2	Ion conducting structure of β'' - and β -aluminas	499
33.3	Synthesis of precursor ceramics	500
33.4	Alkali-ion exchange	502
33.5	Oxonium and ammonium ion-exchange	503
33.6	Electrolyte characteristics and preliminary steam-electrolysis/ fuel-cell calculations and performance	506
33.7	Summary	508
33.8	References	509
34	Fuel-cells, steam-electrolysis for hydrogen production and hydrogen separation using high temperature protonic conductors <i>H. Iwahara</i>	511
34.1	Introduction	511
34.2	Fuel-cells	511
34.3	Steam-electrolysis for hydrogen production	516
34.4	Hydrogen separation	519
34.5	Other applications	520
34.6	References	522
B.	Small components and microionic devices	523
35	Ice-based devices <i>I. A. Ryzhkin</i>	523
35.1	Introduction	523
35.2	Screening effects and capacitance devices	523
35.3	Devices based on memory effects	525
35.4	Field transistors	525
35.5	Sensors	525
35.6	References	526
36	Solid-state gas sensors operating at room temperature <i>N. Miura and N. Yamazoe</i>	527
36.1	Introduction	527
36.2	Principle of potentiometric sensors	530
36.3	New sensing modes	532
36.4	Simplification of sensor elements	534
36.5	Extension of proton conductor sensors	536
36.6	References	537

Contents

37	All solid-state protonic batteries <i>J. Guittion, C. Poinsignon and J. Y. Sanchez</i>	539
37.1	A solid-state battery with a proton conducting electrolyte	539
37.2	Advantages and problems of batteries with a liquid proton conducting electrolyte	539
37.3	Characteristics of an ideal all solid-state battery	541
37.4	The first attempts	542
37.5	Recent improvements	543
37.6	References	550
38	Applications of proton conductors in electrochromic devices (ECDs) <i>O. Bohnke</i>	551
38.1	Introduction	551
38.2	Structure of electrochromic devices	552
38.3	Mixed conductors as electrochromic materials	554
38.4	Proton conductors as electrolytes in ECD devices	557
38.5	ECD performances	560
38.6	Conclusions	563
38.7	References	564
39	Supercapacitors and interfacial charge accumulation devices <i>Ph. Colombe and M. Pham-Thi</i>	567
39.1	Introduction	567
39.2	Device fabrication	568
39.3	Electrical properties	570
39.4	Giant accumulation layer at the Si–HUP interface	570
39.5	References	572
	Index	573

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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 H₃OUO₂PO₄.3H₂O, α-Zr(HPO₄)₂.nH₂O and β"-aluminas and is linked to the prominent role

Preface

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 $10^{-10} \Omega^{-1} \text{ cm}^{-1}$ 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 $10^{-6} \Omega^{-1} \text{ cm}^{-1}$.
- (iii) ‘Superionic’ conductors with a conductivity higher than $10^{-5} \Omega^{-1} \text{ cm}^{-1}$ and usually between 10^{-4} and $10^{-2} \Omega^{-1} \text{ cm}^{-1}$. 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

Preface

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 ($\sigma_{300\text{ K}} \approx 5 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$) 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

Preface

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

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Edited by Philippe Colombe

Frontmatter

[More information](#)*Preface*

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 ‘Grothuss’ 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. Colombe

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Frontmatter

[More information](#)

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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
$\alpha_{\rho\sigma}^{jm}$	$\rho\sigma$ 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
$\nu(X)$	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
J	current density
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
$\text{tg}\delta$	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	$[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$
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
$S_{\text{inc}}(Q, \omega)$	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 ($D_{\text{Al}^+}/D_{\text{H}_2\text{O}}$)
a	jump distance