

## Contents

**Foreword** V

**Preface** XV

**List of Contributors** XIX

<b>1</b>	<b>Storage of Hydrogen in the Pure Form</b>	<b>1</b>
	<i>Manfred Kell</i>	
1.1	Introduction	1
1.2	Thermodynamic State and Properties	1
1.2.1	Variables of State	2
1.2.2	T-s-Diagram	4
1.2.2.1	Joule-Thomson Coefficient	5
1.2.3	Properties	5
1.3	Gaseous Storage	8
1.3.1	Compression and Expansion	10
1.3.2	Tank Systems	12
1.3.3	High Pressure Infrastructure	13
1.4	Liquid Storage	15
1.4.1	Liquefaction	15
1.4.2	Thermodynamic Analysis	17
1.4.2.1	Pressure Build-Up	21
1.4.2.2	Boil-Off	23
1.4.2.3	Cooling and Filling	24
1.4.2.4	Back-Gas	27
1.4.3	Tank Systems	28
1.4.4	Distribution Facilities	30
1.5	Hybrid Storage	30
1.5.1	Supercritical Storage	31
1.5.2	Hydrogen Slush	32
1.6	Comparison of Energy Densities	32
1.7	Conclusion	35
	References	36

<b>2</b>	<b>Physisorption in Porous Materials</b>	39
	<i>Barbara Panella and Michael Hirscher</i>	
2.1	Introduction	39
2.2	Carbon Materials	44
2.3	Organic Polymers	48
2.4	Zeolites	50
2.5	Coordination Polymers	51
2.6	Conclusions	58
	References	59
<b>3</b>	<b>Clathrate Hydrates</b>	63
	<i>Alireza Shariati, Sona Raeissi, and Cor J. Peters</i>	
3.1	Introduction	63
3.2	Clathrate Hydrate Structures	64
3.3	Hydrogen Clathrate Hydrate	66
3.4	Kinetic Aspects of Hydrogen Clathrate Hydrate	73
3.5	Modeling of Hydrogen Clathrate Hydrates	74
3.6	Future of Hydrogen Storage	76
	References	77
<b>4</b>	<b>Metal Hydrides</b>	81
	<i>Jacques Huot</i>	
4.1	Introduction	81
4.2	Elemental Hydrides	82
4.2.1	Ionic or Saline Hydrides	82
4.2.2	Covalent Hydrides	82
4.2.3	Metallic Hydrides	83
4.3	Thermodynamics of Metal Hydrides	83
4.3.1	Introduction	83
4.3.2	Low Concentration	85
4.3.3	High Concentration	86
4.4	Intermetallic Compounds	88
4.4.1	Thermodynamics	88
4.4.1.1	Miedema's Model	89
4.4.1.2	Semi-Empirical Band Structure Model	91
4.4.2	Crystal Structure	92
4.4.3	Electronic Structure	94
4.5	Practical Considerations	94
4.5.1	Synthesis	95
4.5.2	Activation	95
4.5.3	Hysteresis	96
4.5.4	Plateau Slope	97
4.5.5	Reversible Capacity	98
4.5.6	Hydrogenation Kinetics	98
4.5.7	Cycle Life	99

4.5.8	Decrepitation	99
4.6	Metal Hydrides Systems	100
4.6.1	AB <sub>5</sub>	100
4.6.2	TiFe	101
4.6.3	AB <sub>2</sub> Laves Phases	102
4.6.4	BCC Solid Solution	103
4.7	Nanocrystalline Mg and Mg-Based Alloys	104
4.7.1	Hydrogen Sorption Kinetics	105
4.7.2	Reduction of the Heat of Formation	107
4.7.3	Severe Plastic Deformation Techniques	108
4.8	Conclusion	109
4.8.1	Alloys Development	109
4.8.2	Synthesis	110
4.8.3	System Engineering	110
	References	110
<b>5</b>	<b>Complex Hydrides</b>	<b>117</b>
	<i>Claudia Weidenthaler and Michael Felderhoff</i>	
5.1	Introduction	117
5.2	Complex Borohydrides	118
5.2.1	Introduction	118
5.2.2	Stability of Metal Borohydrides	118
5.2.3	Decomposition of Complex Borohydrides	119
5.2.4	Lithium Borohydride, LiBH <sub>4</sub>	120
5.2.4.1	Synthesis and Crystal Structure	120
5.2.4.2	Decomposition of LiBH <sub>4</sub>	120
5.2.5	Sodium Borohydride, NaBH <sub>4</sub>	122
5.2.5.1	Synthesis and Crystal Structure	122
5.2.5.2	Decomposition of NaBH <sub>4</sub>	122
5.2.6	Potassium Borohydride KBH <sub>4</sub>	122
5.2.7	Beryllium Borohydride Be(BH <sub>4</sub> ) <sub>2</sub>	123
5.2.8	Magnesium Borohydride Mg(BH <sub>4</sub> ) <sub>2</sub>	123
5.2.8.1	Synthesis and Crystal Structure	123
5.2.8.2	Decomposition	123
5.2.9	Calcium Borohydride Ca(BH <sub>4</sub> ) <sub>2</sub>	124
5.2.9.1	Synthesis and Crystal Structure	124
5.2.9.2	Decomposition	125
5.2.10	Aluminum Borohydride Al(BH <sub>4</sub> ) <sub>3</sub>	126
5.2.10.1	Synthesis and Crystal Structure	126
5.2.10.2	Decomposition	126
5.2.11	Zinc Borohydride Zn(BH <sub>4</sub> ) <sub>2</sub>	126
5.2.12	NaBH <sub>4</sub> as a Hydrogen Storage Material in Solution	126
5.2.12.1	Regeneration of Decomposed NaBH <sub>4</sub> in Solution	128
5.3	Complex Aluminum Hydrides	128
5.3.1	Introduction	128

5.3.2	LiAlH <sub>4</sub> 130
5.3.2.1	Synthesis and Crystal Structure 130
5.3.2.2	Decomposition of LiAlH <sub>4</sub> 130
5.3.2.3	Role of Catalysts 131
5.3.3	Li <sub>3</sub> AlH <sub>6</sub> 132
5.3.3.1	Synthesis and Crystal Structure 132
5.3.4	NaAlH <sub>4</sub> 133
5.3.4.1	Synthesis and Crystal Structure 133
5.3.4.2	Decomposition and Thermodynamics of NaAlH <sub>4</sub> 133
5.3.4.3	Role of Catalysts 135
5.3.5	Na <sub>3</sub> AlH <sub>6</sub> 138
5.3.5.1	Synthesis and Crystal Structure 138
5.3.6	KAlH <sub>4</sub> 139
5.3.6.1	Synthesis and Crystal Structure 139
5.3.6.2	Decomposition of KAlH <sub>4</sub> 140
5.3.7	Mg(AlH <sub>4</sub> ) <sub>2</sub> 140
5.3.7.1	Synthesis and Crystal Structure 140
5.3.7.2	Decompositon 141
5.3.8	Ca(AlH <sub>4</sub> ) <sub>2</sub> 142
5.3.8.1	Synthesis and Crystal Structure 142
5.3.8.2	Decomposition of Ca(AlH <sub>4</sub> ) <sub>2</sub> 143
5.3.9	Na <sub>2</sub> LiAlH <sub>6</sub> 144
5.3.10	K <sub>2</sub> LiAlH <sub>6</sub> 145
5.3.11	K <sub>2</sub> NaAlH <sub>6</sub> 145
5.3.12	LiMg(AlH <sub>4</sub> ) <sub>3</sub> , LiMgAlH <sub>6</sub> 146
5.3.12.1	Synthesis and Crystal Structure 146
5.3.12.2	Decomposition 146
5.3.13	Sr <sub>2</sub> AlH <sub>7</sub> 146
5.3.14	BaAlH <sub>5</sub> 147
5.3.14.1	Synthesis and Crystal Structure 147
5.4	Complex Transition Metal Hydrides 148
5.4.1	Introduction 148
5.4.2	Properties 148
5.4.3	Synthesis 149
5.4.4	Examples of Complex Transition Metal Hydrides 150
5.5	Summary 150
	References 151
<b>6</b>	<b>Amides, Imides and Mixtures 159</b>
	<i>Takayuki Ichikawa</i>
6.1	Introduction 159
6.2	Hydrogen Storage Properties of Amide and Imide Systems 160
6.2.1	Li–N–H System 160
6.2.2	Li–Mg–N–H Systems 161
6.2.3	Other Metal–N–H Systems 165

6.3	Structural Properties of Amide and Imide	167
6.3.1	Lithium Amide and Imide	168
6.3.2	Sodium Amide	171
6.3.3	Magnesium Amide and Imide	171
6.3.4	Other Amides and Imides	172
6.4	Prospects of Amide and Imide Systems	173
6.4.1	Kinetic Analysis and Improvement	173
6.4.2	NH <sub>3</sub> Amount Desorbed from Metal–N–H Systems	176
6.4.3	Practical Properties	177
6.5	Proposed Mechanism of the Hydrogen Storage Reaction in the Metal–N–H Systems	178
6.5.1	Ammonia-Mediated Model for Hydrogen Desorption	178
6.5.2	Direct Solid–Solid Reaction Model for Hydrogen Desorption	180
6.5.3	Hydrogenating Mechanism of the Li–Mg–N–H System	181
6.6	Summary	182
	References	182
<b>7</b>	<b>Tailoring Reaction Enthalpies of Hydrides</b>	<b>187</b>
	<i>Martin Dornheim</i>	
7.1	Introduction	187
7.2	Thermodynamic Limitations of Lightweight Hydrides	189
7.3	Strategies to Alter the Reaction Enthalpies of Hydrides	191
7.3.1	Thermodynamic Tuning of Single Phase Hydrides by Substitution on the Metal Site	191
7.3.1.1	Lightweight Hydrides Forming Stable Compounds in the Dehydrogenated State	193
7.3.1.2	Lightweight Hydrides with Positive Heat of Mixing in the Dehydrogenated State	196
7.3.2	Thermodynamic Tuning of Single Phase Hydrides by Substitution on the Hydrogen Sites: Functional Anion Concept	199
7.3.3	Multicomponent Hydride Systems	203
7.3.3.1	Mixtures of Hydrides and Reactive Additives	203
7.3.3.2	Mixed Hydrides/Reactive Hydride Composites	207
7.4	Summary and Conclusion	210
	References	211
<b>8</b>	<b>Ammonia Borane and Related Compounds as Hydrogen Source Materials</b>	<b>215</b>
	<i>Florian Mertens, Gert Wolf, and Felix Baitalow</i>	
8.1	Introduction	215
8.2	Materials Description and Characterization	216
8.3	Production	219
8.4	Thermally Induced Decomposition of Pure Ammonia Borane	221
8.4.1	Pyrolysis	221
8.4.2	Decomposition in Organic Solvents	227

8.4.3	Decomposition of Ammonia Borane in Heterogeneous Systems	232
8.5	Hydrolysis of AB	233
8.6	Substituted Ammonia Boranes	235
8.7	Recycling Strategies	238
8.7.1	Recycling from B-O-Containing Materials	239
8.7.2	Recycling of BNH <sub>x</sub> -Waste Products	240
8.8	Summary	243
	References	244
<b>9</b>	<b>Aluminum Hydride (Alane)</b>	249
	<i>Ragaiy Zidan</i>	249
9.1	Introduction	249
9.2	Hydrogen Solubility and Diffusivity in Aluminum	250
9.3	Formation and Thermodynamics of Different Phases of Alane	252
9.4	Stability and Formation of Adduct Organo-Aluminum Hydride Compounds	260
9.5	Phases and Structures of Aluminum Hydride	266
9.6	Novel Attempts and Methods for Forming Alane Reversibly	269
9.7	Conclusion	275
	References	275
<b>10</b>	<b>Nanoparticles and 3D Supported Nanomaterials</b>	279
	<i>Petra E. de Jongh and Philipp Adelhelm</i>	
10.1	Introduction	279
10.2	Particle Size Effects	281
10.2.1	Thermodynamics	281
10.2.2	Kinetics	287
10.3	Non-Supported Clusters, Particles and Nanostructures	290
10.3.1	Transition Metal Clusters	291
10.3.2	Interstitial Hydrides, Focussing on Palladium Hydride	293
10.3.3	Ionic Hydrides, Focussing on Magnesium Hydride	296
10.4	Support Effects	301
10.4.1	Stabilization of Small Particle Sizes	302
10.4.2	Limiting Phase Segregation in Complex Systems	303
10.4.3	Metal–Substrate Interaction	305
10.4.4	Physical Confinement and Clamping	307
10.4.5	Thermal Properties of the System	309
10.4.6	Mechanical Stability and Pressure Drop	309
10.5	Preparation of Three-Dimensional Supported Nanomaterials	311
10.5.1	Support Materials	311
10.5.1.1	Silica	312
10.5.1.2	Carbon	314
10.5.1.3	Other Support Materials	316
10.5.2	Preparation Strategies	317
10.5.2.1	Solution Impregnation	318

10.5.2.2	Melt Infiltration	320
10.6	Experimental Results on 3D-Supported Nanomaterials	322
10.6.1	Ammonia Borane, (NH <sub>3</sub> BH <sub>3</sub> )	323
10.6.2	Sodium Alanate, (NaAlH <sub>4</sub> )	325
10.6.3	Magnesium Hydride (MgH <sub>2</sub> )	329
10.6.4	Lithium Borohydride (LiBH <sub>4</sub> )	331
10.6.5	Palladium	333
10.7	Conclusions and Outlook	334
	References	336

**Index** 341

