Contents

Preface XI

List of Contributors XIII

1 Dense Ceramic Membranes for Hydrogen Separation 1
Truls Norby and Reidar Haugsrud

1.1 Introduction 1
1.2 Applications and Principles of Operation 2
1.2.1 Simple Cases 2
1.2.2 Examples of More Complex Applications 4
1.3 Defect Chemistry of Dense Hydrogen-permeable Ceramics 5
1.3.1 Materials Classes 5
1.3.2 Neutral and Ionized Hydrogen Species in Oxides 6
1.3.4 Protonic Defects and Their Transport 7
1.3.5 Defect Structures of Proton-conducting Oxides 8
1.3.6 Diffusivity, Mobility and Conductivity: The Nernst–Einstein Relation 10
1.4 Wagner Transport Theory for Dense Ceramic Hydrogen-Separation Membranes 11
1.4.1 General Expressions 11
1.4.2 From Charged to Well-Defined Species: The Electrochemical Equilibrium 12
1.4.3 The Voltage Over a Sample 12
1.4.4 Flux of a Particular Species 13
1.4.5 Fluxes in a Mixed Proton, Oxygen Ion, and Electron Conductor 14
1.4.6 Fluxes in a Mixed Proton and Electron Conductor 15
1.4.7 Fluxes in a Mixed Proton and Oxygen Ion Conductor 18
1.4.8 Fluxes in a Mixed Proton, Oxygen Ion, and Electron Conductor Revisited 19
1.4.9 Permeation of Neutral Hydrogen Species 19
1.4.10 What About Hydride Ions? 21
1.5 Surface Kinetics of Hydrogen Permeation in Mixed Proton-Electron Conductors 21
1.6 Issues Regarding Metal Cation Transport in Hydrogen-permeable Membrane Materials 24
1.7 Modeling Approaches 24
1.8 Experimental Techniques and Challenges 26
1.8.1 Investigation of Fundamental Materials Properties 26
1.8.1.1 Concentration 26
1.8.1.2 Diffusion 27
1.8.1.3 Conductivity 27
1.8.1.4 Transport Numbers 29
1.8.1.5 Other Properties 30
1.8.2 Investigation of Surface Kinetics 31
1.8.3 Measurements and Interpretation of Hydrogen Permeation 34
1.9 Hydrogen Permeation in Selected Systems 35
1.9.1 A Few Words on Flux and Permeability 35
1.9.2 Classes of Membranes 36
1.9.3 Mixed Proton–Electron Conducting Oxides 36
1.9.4 Cermets 42
1.9.5 Permeation in Other Oxide Classes and the Possibility of Neutral Hydrogen Species 43
1.9.6 Comparison with Metals 44
1.10 Summary 45

2 Ceramic Proton Conductors 49

Vineet K. Gupta and Jerry Y. S. Lin

2.1 Introduction 49
2.2 General Properties of Perovskite-structured Proton-conducting Ceramic Membranes 51
2.2.1 Creation of Protonic Carriers 51
2.2.2 Transport Properties 52
2.2.3 Electronic Conductivity and Its Improvement 57
2.3 Synthesis of Proton-conducting Ceramic Membranes 58
2.3.1 Synthesis of Powders 58
2.3.2 Effect of Synthesis Conditions on Membrane Performance 59
2.3.3 Preparation of Thin Films 60
2.4 Hydrogen Permeation 61
2.4.1 The H₂ Permeation Set-up and Sealing System 61
2.4.2 Effects of Process Variables on H₂ Flux 63
2.4.2.1 Effect of Feed and Sweep Side Gas Concentrations 63
2.4.2.2 Effect of Membrane Thickness 64
2.4.2.3 Effect of Temperature 65
2.4.3 Mathematical Models for Hydrogen Permeation 66
2.5 Chemical Stability of Protonic Conductors 68

Contents
# 6 The Evolution of Materials and Architecture for Oxygen Transport Membranes

**John Sirman**

- **6.1 Introduction** 165
- **6.2 Oxygen Separation and Collection** 165
  - **6.2.1 Background for Selection of Materials for Oxygen Separation and Collection** 166
  - **6.2.2 Membrane Materials Concepts** 168
  - **6.2.3 Membrane Architecture Concepts** 174
  - **6.2.4 Summary of Oxygen Separation Materials and Architecture** 180
- **6.3 Syngas Production and Combustion Applications** 180
  - **6.3.1 Background for Selection of Materials for Syngas Production and Combustion Applications** 180
  - **6.3.2 Membrane Materials Concepts** 182
  - **6.3.3 Membrane Architecture Concepts** 183
  - **6.3.4 Summary of Syngas and Combustion Applications Materials and Architecture** 184

# 7 Membranes for Promoting Partial Oxidation Chemistries

**Anthony F. Sammells, James H. White, and Richard Mackay**

- **7.1 Introduction** 185
- **7.2 On the Nature of Perovskite-related Metal Oxides for Achieving Mixed Oxygen Anion and Electron Conduction** 188
  - **7.2.1 Background** 188
  - **7.2.2 Early Work towards the Selection of Mixed Conductors** 189
  - **7.2.3 Requirements for Oxygen Anion and Electronic Conduction within Perovskites** 189
  - **7.2.4 Empirical Factors Relating to Oxygen Anion Transport in Perovskite-related Membranes** 191
  - **7.2.5 Introducing Electronic Conductivity into a Perovskite-related Lattice** 192
- **7.3 The Application of Oxygen Transport Membranes to Partial Oxidation Chemistries** 193
  - **7.3.1 Natural Gas Conversion to Synthesis Gas – General Considerations** 193
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3.2</td>
<td>Methane Partial Oxidation to Synthesis Gas in Membrane Reactors</td>
<td>196</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Liquid Fuel Reforming</td>
<td>198</td>
</tr>
<tr>
<td>7.3.4</td>
<td>Coal/Biomass to Synthesis Gas</td>
<td>200</td>
</tr>
<tr>
<td>7.3.5</td>
<td>Oxygen Reduction Catalysis Requirements in Oxygen Transport Membranes</td>
<td>202</td>
</tr>
<tr>
<td>7.3.6</td>
<td>Methane to Ethylene</td>
<td>203</td>
</tr>
<tr>
<td>7.3.7</td>
<td>Catalysis Considerations for Promoting Methane Coupling Reactions</td>
<td>204</td>
</tr>
<tr>
<td>7.3.8</td>
<td>Catalyst Implementation on Dense Oxygen Transport Media for Oxidative Coupling</td>
<td>206</td>
</tr>
<tr>
<td>7.3.9</td>
<td>Alkane Dehydrogenation</td>
<td>206</td>
</tr>
<tr>
<td>7.3.10</td>
<td>Hydrogen Sulfide Partial Oxidation</td>
<td>207</td>
</tr>
<tr>
<td>7.3.11</td>
<td>Some Thoughts on the Potential Contribution of Membrane Technology towards Realizing a Hydrogen Economy</td>
<td>209</td>
</tr>
</tbody>
</table>

8 Syngas Membrane Engineering Design and Scale-Up Issues. Application of Ceramic Oxygen Conducting Membranes 215
Michael Carolan

8.1 Membrane Design and Engineering 216
8.2 Reactor Design and Engineering 227
8.3 Planar MembraneReactors 232
8.4 Ceramic-to-Ceramic Seals 235
8.5 Ceramic-to-Metal Seals 238
8.6 Summary and Conclusions 241

9 Economics Associated with Implementation of Membrane Reactors 245
Alessandra Criscuoli

9.1 Introduction 245
9.2 Membrane Reactors 246
9.3 Factors Influencing the Economics 249
9.4 Dense Membrane Reactors for the Water-Gas Shift Reaction 251
9.5 Economic Feasibility of Water-Gas Shift Pd-based Membrane Reactors 256
9.6 Future Directions 261

Index 265