Literature review on high temperature proton conducting materials

Electrolyte for fuel cell or mixed conducting membrane for H$_2$ separation

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Acknowledgement
This project is part of the KIMEX project and has been performed in the period September 2008 - December 2008. The ECN project number is 7.0330.

Abstract
Proton conducting materials have become the subject of intensive research due to their potential to reduce the operating temperature of solid oxide fuel cells, thus allowing the use of cheaper construction materials. By using suitable dopants or by making a composite, they can be used for H₂ separation applications as well. Based on the application, fuel cell or H₂ separation, they are denoted as class I and class II conductors in this report. Originally, all research concentrated on perovskites, in particular the Ba and Sr cerates. Today, many other groups are investigated as well.

This report contains the results of a literature survey on these materials. The most important findings are:

1. The main drivers for research of new class I conductors are higher conductivity and stability.
2. The trend in the research of new class I conductors is to sacrifice the conductivity for higher stability.
3. The power density of lab-scale fuel cells with proton conducting electrolyte is half that fuel cells with oxygen ion conducting electrolyte.
4. For operation below 600 ºC, there are many competitors for H₂ separation membranes based on pure Pd. Taking all development uncertainties into account, it is unlikely that class II conductors will play a role in this temperature range.
5. For operation above 600 ºC, the only competitor of class II conductors is the oxygen ion conducting membrane.
6. Systems studies and experiments on the long-term stability are most wanted.

Keywords
Proton conductor, intermediate temperature fuel cell, hydrogen separation, ceramic membrane, perovskite, cermet
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Summary

This report contains then main results of a literature survey on proton-conducting ceramic oxides to be applied at high temperatures, i.e. in the range from 600 to 800 °C. These materials are broadly divided in two classes:

1. materials that require an external circuit for electronic conduction, and
2. materials that show both protonic and electronic conduction.

They are denoted in this report as class I and class II conductors, respectively.

**Class I conductors**

Most research has been performed on the perovskites, notably doped barium and strontium cerates and their mixtures. These show good protonic conductivity (in the order of 10 mS/cm) in the temperature range 500 - 900 °C, though their chemical stability in a H₂O and CO₂ containing atmosphere is not so good. Among the alternatives with comparable protonic conductivity are fluorite-related structures, e.g. the tungstates La₅.₄WO₁₁.₇ and La₅.₃Ca₀.₇WO₁₁.₈₅ of which the chemical stability is not well investigated as yet, and pyrochlores like La₀.₉₅Ca₀.₀₅Zr₂O₆₋₀.₇₅, which have good stability though protonic conductivity only up to 600 °C. Fergusonites are currently investigated by the group of Norby at the University of Oslo. Though their stability has not been well investigated as yet, it is expected to be good. The conductivity is an order of magnitude less than that of the perovskites.

The main drive for research on class I conductors is their application in SOFCs (solid oxide fuel cells) and electrolysis cells, allowing lower operation temperature and thus cheaper stack construction materials than cells with oxygen ion conducting electrolytes. Other applications include steam-methane reforming reactors, water-gas shift reactors, dehydrogenation reactor, ammonia synthesis reactors, H₂ pumps and H₂ sensors. Only perovskites have been tested for these applications. The power densities obtained in lab-scale SOFCs with proton conducting electrolyte is approx. half of that of lab-scale SOFCs with oxygen ion conducting electrolyte. In all of these applications, except for the last three, oxygen ion conducting membranes can also be applied. In contrast with solid oxide fuel cells with oxygen ion conducting electrolyte, all H₂O is produced at the cathode in proton conducting electrolyte fuel cells. This brings new system designs into view, like the temperature swing reformer.

**Class II conductors**

These can be divided in two groups: those derived from a class I conductor by doping it with a metal that enhances the electronic or hole conduction, and the cermets, i.e. composites derived from a class I conductor and an electronic conductor. Their main application is H₂ separation in the temperature range 600 - 1000 °C. The H₂ permeability of the former group is in general much lower than that of the latter group. The most successful application so far is a composite developed by Eltron Research being an equimolar mixture of BaCe₀.₈Eu₀.₂O₂.₉ and Ce₀.₈Y₀.₂O₂.₉, of which the H₂ permeability is comparable with that of Pd.

Many materials classes are currently investigated for H₂ separation membranes as alternative of pure Pd, though all of these operate at temperatures below 600 °C: Pd-alloys, non-Pd crystalline materials, porous ceramics, bulk metallic glasses, ceramic-metal composites (e.g. Pd in Y-stabilized zirconia), and ceramic-salt composites (e.g. RbNO₂ - La₁₋ₓSrₓCoO₃). On the other hand, for applications at operation temperatures above 600 °C, only solid oxides can be used as membrane material. Thus, class II conductors and mixed oxygen ion-electronic conducting membranes are competing in this temperature range. The only system investigated so far using a class II conducting membrane is the HMR (hydrogen membrane reformer) concept, which is developed in CCP (Carbon Capture Project).
Systems studies as well as experimental data concerning the long-term kinetic and mechanical stability of proton conductors, both class I and class II, are most wanted. Other class I materials than the cerates, zirconates and their mixtures should be tested in a fuel cell. Given the great number of promising materials and the uncertainties related to all problems that must be overcome, class II conductors should not be considered as alternative of pure Pd for H₂ separation.
1. Introduction

This report deals with the results of a literature review on proton-conducting ceramic oxides to be applied at high temperatures, i.e. in the range from 600 to 800 °C. These materials are broadly divided in two classes:

1. materials that require an external circuit for electronic conduction, and
2. materials that show both protonic and electronic conduction.

They are denoted in this report as class I and class II conductors, respectively. The first class includes materials which can be applied in fuel cells and electrolyzers, amongst others. The second class contains those mixed protonic - electronic conductors which can be applied, e.g., for H₂ separation from mixed streams. The distinction is not absolute in the sense that all protonic conductors show electronic conduction to some degree. To be useful for H₂ separation, the protonic and electronic fluxes should be of the same order of magnitude because the overall H₂ transport is determined by the smallest of the two fluxes. In the literature, mixed protonic - electronic conductors are also denoted as mixed ionic - electronic conductors, though these also refer to mixed oxygen ion-electronic conductors. Thus, when dealing with MIECs, please carefully read the context to see if the ionic species is protonic or oxygen ion.

The organization of this report is as follows.
Chapter 2 deals with the various details and results of the literature search.
Chapter 3 deals with the class I proton-conducting materials. First the various material groups are described. Then, an overview of applications found in the literature is given. At last, systems studies are presented.
Chapter 4 deals with the class II proton-conducting materials. First, the two main material groups are described, then applications and systems studies are discussed.
Chapter 5 is a discussion of both classes of proton conductors. Also, a comparison with competing materials is made here.
Chapters 6 and 7 give conclusions and recommendations, respectively.
2. Literature search

2.1 Database search

First, a search query was formulated for the two classes of proton-conductors leading to the desired literature. The query of the class I proton-conductors should consist of four terms:

- a term relating to its special property (**proton conduction**),
- a term relating to the nature of the material (**ceramic**),
- a term relating to the way in which it is used (**membrane**), and
- a term relating to its application (**fuel cell**).

For each of the keywords, relevant synonyms were found by trying them on the internet. It is the art of formulating the query such that the search is not too limiting and also not too broad. A total number of a few thousand hits was considered to be acceptable. This led to the following query, in the language of the search machine using the logicals **OR** and **AND**:

```
("proton-conduct*" OR "proton/conduct*" OR "proton conduct*" OR "protonic-conduct* OR "protonic/conduct*" OR "protonic conduct*" OR PCMFC OR PCFC)
AND
(ceramic OR ceramics OR oxide OR oxidic)
AND
(membrane OR electrolyte OR conduct*)
AND
("fuel cell" OR electroly*)
```

Here " signs denote that terms between these signs must be literally present in the object. The * signs may be replaced by any letter combination. For example, the term **electroly*" comprises **electrolyser, electrolyzer, electrolysis**, etc. The abbreviations PCMFC and PCFC stand for "protonic ceramic membrane fuel cell" and "protonic ceramic fuel cell", respectively.

With regard to the class II proton conductors, also a query consisting of four terms was formulated:

- a term relating to its special property (**mixed ionic-electronic conduction**),
- a term relating to the way in which it is used (**membrane**),
- a term relating to the nature of the gas (**hydrogen**), and
- a term relating to its application (**separation**).

A similar procedure as above led to the following query:

```
("mixed ionic-electronic" OR "mixed ionic/electronic" OR "mixed ionic electronic" OR "mixed protonic-electronic" OR "mixed protonic/electronic" OR "mixed protonic electronic"
OR
"ionic-electronic mixed" OR "ionic/electronic mixed" OR "ionic electronic mixed"
OR
```


"protonic-electronic mixed" OR "protonic/electronic mixed" OR "protonic electronic mixed"
OR MIEC)

AND

(membrane OR electrolyte OR conduct*)

AND

(H2 OR hydrogen)

AND

(separation OR permeation OR production OR removal)

Both searches were restricted to publications after 1998, thus less than 10 years old. Only publications in English, German, French or Dutch language were allowed. The literature search were performed on several databases: ENERGY, INSPEC, COMPENDEX, ENCOMPAT2, ENCOMPLIT2, PASCAL, IFIPAT, INPADOCDB, SCISEARCH, WPIINDEX, CAPLUS and SOLIDSTATE.

The first query led to 2017 hits, the second to 109 ones. Based on the titles of the hits, 251 and 60 abstracts, respectively, were requested. Based on these abstracts, 87 and 19 full publications were requested (Table 2.1). These were put in the same Reference Manager database called HT proton conducting membrane. By further reading and gathering papers from other sources (internet and other ECN projects), the total number of publications in HT proton conducting membrane has increased to about 300 in the course of time.

Table 2.1 Results of both queries

<table>
<thead>
<tr>
<th></th>
<th>1st query</th>
<th>2nd query</th>
<th>both queries</th>
</tr>
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<tbody>
<tr>
<td># hits</td>
<td>2017</td>
<td>109</td>
<td>2126</td>
</tr>
<tr>
<td># abstracts</td>
<td>251</td>
<td>60</td>
<td>311</td>
</tr>
<tr>
<td># requests</td>
<td>87</td>
<td>19</td>
<td>106</td>
</tr>
</tbody>
</table>

From the difference in number of hits for both queries (2017 vs. 109 for class I and class II materials, respectively), one can already conclude that the field of high temperature proton-conductors for hydrogen separation is much younger than that of fuel cell application. On the other hand, much more materials compete with class II than class I materials for hydrogen separation and fuel cell application, respectively, as will become clear in this report.

2.2 Other sources

Other sources of information were also used to derive information on proton conducting materials. Although these should also be searched by the above queries, they were screened separately for abstracts on proton-conducting materials. They might have been missed by the search queries, or they might have been too recent to be stored in the investigated databases.

First, several conference proceedings were consulted. The following conference proceedings were available as a book, on CD or downloadable from the internet as indicated:

• 9th International Conference on Inorganic Membranes, June 2006, Lillehammer, Norway,
• 10th International Conference on Inorganic Membranes, August 2008, Tokyo, Japan (abstracts can be found on the internet at http://www.icim10.org/)
• Solid Oxide Fuel Cells 9, May 2005, Québec, Canada,
• Solid Oxide Fuel Cells 10, June 2007, Nara, Japan,
• 5th European Fuel Cell Forum, July 2002, Lucerne, Swiss,
• 6th European Fuel Cell Forum, July 2004, Lucerne, Swiss,
• 7th European Fuel Cell Forum, July 2006, Lucerne, Swiss,
• 8th European Fuel Cell Forum, July 2008, Lucerne, Swiss,
• 12th International Conference on Solid State Proton Conductors, August 2004, Uppsala, Sweden, and

In September 2008, the 14th International Conference on Solid State Proton Conductors was held at Kyoto, Japan. Proceedings will become available as a special issue of Solid State Ionics and could not be used for this review.

Another information source is the Information Bridge of the Department of Energy (DOE) in the US, available at http://www.osti.gov/bridge. This website contains the scientific reports on DOE funded projects. Six recent, useful report were found at this site.

As last sources of information, Chapter 10 of the book entitled Inorganic Membranes: Synthesis, Characterization and Applications, edited by Mallada and Menéndez, Elsevier Amsterdam, 2008 (Fontaine et al. 2008), and the ECN confidential report Inventory of membrane materials for H2 separation in pre-combustion CO2 capture (ECN-X--07-002, January 2007, H.M. van Veen and Y.C. van Delft) have been consulted.
3. Class I proton conductors

3.1 Proton conduction theory

Before dealing with the materials themselves, first the theory on proton conduction will be treated briefly. For an extensive treatment, the reader should consult Fontaine et al. (Fontaine et al. 2008). Transport of hydrogen as H$_2$ or H would require defects, namely atoms or molecules occupying lattice or interstitial sites. Here, transport phenomena will be restricted to the more commonly encountered and important charged species, and only in ceramic oxides to which the proton conducting materials reviewed in this report belong. Defect-structure-wise, there are two main routes to hydrogen transport in such materials. The simplest would be to dissolve protons compensated by electrons originating from the H$_2$ gas, as follows:

$$H_2(g) + 2O_0^\circ \leftrightarrow 2OH_0^\bullet + 2e^\text{'}.$$

(3.1)

Using the electro-neutrality condition, we find:

$$[OH_0^\bullet] = n = K_1^{1/4} p_{H_2}^{1/4} [O_0^\circ]^{1/2},$$

(3.2)

where $n$ and $p_{H_2}$ are the electron density and partial H$_2$ pressure, respectively, and $K_1$ is the equilibrium constant of reaction (3.1). The Kroger-Vink notation has been used to denote the species: the subscript and superscript denote the lattice site and the charge of the species. Charges are expressed with respect to the lattice structure. As to the charge notation, the dot, 'x' and ' in the superscript denote one positive charge, zero charge and one negative charge, respectively, of the species. Thus, $O_0^\circ$, for example, denotes a neutral oxygen atom at an oxygen lattice site, where 'neutral' means that the '2-' charge of O is compensated by a '2+' charge of the surrounding lattice. Protons and electrons move in the same direction. The reaction (3.1) was reported for ZnO, hardly in any other system. Instead, one tends to use acceptor-doped oxides in which the concentration of protons and all other positive defects are enhanced by the dopant. The acceptors are most often substitutionally dissolved lower-valent cations, though, in principle, interstitial anions and or substitutional higher-valent anions (e.g. N$_3^-$ substituting O$_2^-$) could also be used. The acceptors are compensated by oxygen vacancies, denoted by $V$ in the reactions below. When the doped oxide is exposed to water vapour, the following reaction occurs:

$$H_2O(g) + V_0^{\bullet\bullet} + O_0^\circ \rightarrow 2OH_0^\bullet,$$

(3.3)

with:

$$[OH_0^\bullet] = \frac{[O]K_2p_{H_2O}(-1 + \sqrt[4]{1 + 8[\mathcal{A}']/([O]K_2p_{H_2O})})}{4},$$

(3.4)

and

$$n = \frac{K_1^{1/2} p_{H_2}^{1/2} [O]}{[OH_0^\bullet]},$$

(3.5)

where $p_{H_2O}$ is the water vapour pressure, $K_2$ is the equilibrium constant of reaction (3.3), [O] and [A'] are the oxygen site and acceptor concentration, respectively, and $K_i$ is the intrinsic ionization constant of electrons over the band gap. The protons, rather than the hydroxide ions, move
by jumping from the one stationary oxide ion host to the other (Grotthuss mechanism), the oxygen vacancies, $V_{O}^{\bullet\bullet}$, move in the opposite direction. It can be shown that for the general case of an oxide with mixed proton, oxide ion and electron conductivity, the flux of protons can be expressed as

$$j_{H^+} = -\frac{RT}{4F^2L} \int \sigma_{H^+}[2(t_{O^2-} + t_e) d\ln p_{H_2} + t_{O^2-} d\ln p_{O_2}], \quad (3.6)$$

where the minus indicates that the protons move in the direction of decreasing $p_{H_2}$, $F$ is the Faraday’s constant, $L$ is the membrane thickness, $I$ and $II$ denote the upstream and downstream sides of the membrane, respectively, $\sigma_{H^+}$ is the proton conductivity, $t_e$ is the transport number of species $i$, being the fractional contribution to the total conductivity. In general, the partial conductivity $\sigma_i$ of species $i$ with charge $z_i$ is linked to its concentration $c_i$ (mol/m³), mobility $\mu_i$ (m²/V.s) and self-diffusion coefficient $D_i$ (m²/s) through the Nernst-Einstein relation:

$$\sigma_i = z_i F c_i \mu_i = \frac{(z_i F)^2 c_i D_i}{RT}. \quad (3.7)$$

When the oxygen ion transport number is zero, Equation (3.6) reduces to:

$$j_{H^+} = -\frac{RT}{2F^2L} \int \sigma_{H^+} t_e d\ln p_{H_2}, \quad (3.8)$$

Using the relation between $\sigma_{H^+}$ and $p_{H_2}$, and assuming that the material exhibits dominating electronic conduction so that $t_e = 1$, the above Equation can be integrated to yield a relation between $j_{H^+}$ and $p_{H_2}$.

3.2 Material classes

Class I proton conductors have been particularly studied in the perovskite oxides, in particular in the II-IV-type oxides like (Ca,Sr,Ba)(Ce,Zr,Ti)O$_3$, though perovskites of type I-V (e.g. KTaO$_3$), II$_2$-(III/V) (e.g. Sr$_2$ScNbO$_6$), II$_3$-(II/V) (e.g. Ba$_3$CaNb$_2$O$_9$) and III-III (LaYO$_3$) have been investigated as well. The roman numbers denote the column in the Periodic Table from which the element is taken, while subscripts denote the stoichiometry of the chemical formulas. To make these materials proton-conducting, the simple perovskites (I-V, II-IV, III-III) must be doped with an element of lower valency than the B-site atom, e.g. Y in BaCeO$_3$. Proton-conductivity in the complex perovskites (II$_2$-(III/V) and II$_3$-(II/V)) can be realised by making them off-stoichiometric e.g. Ba$_3$Ca$_{1.18}$Nb$_{1.82}$O$_{9-\delta}$ or BCN18. Measured proton conductivities are in the range 0.01 - 10 mS/cm. The mobility of the protons depends on the softness of the lattice and is therefore favoured by large, basic atoms on the A site of the perovskite, e.g. Ba. The perovskite oxides have an exothermic reaction with steam, the enthalpy for this reaction lies between -50 and -250 kJ/mol. This implies that the oxides will be dominated by proton transport at low temperature and start to loose protons around 500 - 900 °C in most cases. At higher temperatures, oxygen vacancies are getting more energetically preferable so that oxygen permeation may become dominating at these temperatures. Rare earth sesquioxides Ln$_2$O$_3$ and phosphates LnPO$_4$ have been studied in the past. They are more easily hydrated but then lose proton mobility, so that the conductivity is lower than for the perovskites. In the complex perovskite BCN18, a high grain boundary density was created at reducing conditions which decreased the mechanical strength considerably (Schober et al. 1999). Figure 3.1 shows the proton conductivities of various doped perovskites and rare earth sequioxides.
Proton conductivities of various oxides with a perovskite or fluorite-type structure, as calculated from data on proton concentrations and mobilities (Kreuer 2003)

The best investigated perovskites are the cerates BaCeO$_3$ and SrCeO$_3$. Due to their basic character, they are unstable under gas atmospheres containing H$_2$O, CO$_2$, H$_2$S, SO$_2$ or SO$_3$, forming Ba(OH)$_2$, BaCO$_3$, BaS or BaSO$_4$, or the Sr equivalents. Doping has been performed with different dopants (Y, Tm, Yb, Lu, In, or Sc, amongst others). It was found that the larger the ionic radius or, similarly, the more basic the dopant, the larger the conductivity for the same dopant level (Matsumoto et al. 2007).

Zirconates have better chemical stability than the corresponding cerates, though their conductivity is an order of magnitude lower and their mechanical stability is not so good if prepared via the solid-state route. Attempts to improve the chemical stability of the cerates include therefore mixing cerates with zirconates (Barison et al. 2008; Haile et al. 2001), while the addition of small amounts of BaCeO$_3$ to Y-doped BaZrO$_3$ improves the mechanical stability of BaZrO$_3$ (Kreuer 2003). Doping with Zn (Lin et al. 2008a) or Sc (Azad and Irvine 2007) instead of Y yields even better chemical stability and conductivity than without. Besides, Zn addition reduces the sintering temperature by 200 °C. Co-doping the cerate-zirconate mixture with Pr yields a higher conductivity than the pure cerate, while maintaining the chemical stability of the cerate-zirconate mixture (Melnik et al. 2008). Another method is to make a protective layer on top of the functional layer consisting of a cerate perovskite (Serra-Alfaro et al. 2007). Recently, BaCe$_{0.9}$Y$_{0.1}$O$_{2.95}$ nanoparticles (5 - 50 nm) were prepared by the Taillades et al. (Taillades et al. 2007) using three wet techniques (flash combustion, hydrolysis of complex metal acrylates, reverse micelles). When deposited on NiO/BCY10 yields as a thin film (60 μm), the water uptake became constant (0.08 - 0.12 wt%) and corresponded with hydration of more than half of the oxygen vacancies. No indications of carbonate formation were found.

Materials with an inherent oxygen deficiency and therefore do not have to be doped, are the Brownmillerite compounds like Ba$_3$In$_2$O$_5$, a vacancy ordered variant of the perovskite (Rolle et al. 2005), and the complex perovskite Ba$_{6-x}$Ca$_x$Nb$_2$O$_{11}$ with 1.6 ≤ x ≤ 2.8 (Ashok et al. 2008). These materials can hydrate to Ba$_3$In$_2$O$_5$.H$_2$O and Ba$_{6-x}$Ca$_x$Nb$_2$O$_{11}$.OH$_2$, respectively. Proton conductivities have remained moderate as it has not been possible to fully hydrate these phases
without ordering the protons. A more recently investigated example is lanthanum oxoborate
La$_{26}$O$_{27}$(BO$_3$)$_8$ in which there is one oxygen vacancy per formula unit (Noirault et al. 2007).
This vacancy appears locally disordered and can be hydrated to obtain La$_{26}$O$_{26}$(OH)$_2$(BO$_3$)$_8$.
The latter has stable proton conductivity of the order of 1 mS/cm in wet atmospheres at 700 °C and
is the first example of an undoped material of low-symmetry crystal structure exhibiting proton
conduction. An example of a material showing disordered, yet structural vacancies is mayenite
Ca$_{12}$Al$_4$O$_{33}$, a compound with a charged framework and one oxide ion compensating this, residing
randomly in one of six structural cages (Hayashi et al. 2005).

In the last couple of years, new classes of oxides with oxide ion tetrahedra rather than the
perovskite's octahedra have gained attention. One of the new classes are acceptor-doped rare
earth ortho-niobates LnNbO$_4$ and ortho-tantalates LnTaO$_4$ (Haugsrud and Norby 2006a; Haugs-
rud and Norby 2006c; Haugsrud and Norby 2007; Mokkelborst et al. 2008; Norby et al. 2006b;
Norby et al. 2006a). These materials have a moderate proton conductivity approaching 1 mS/cm
at 900 °C. The solubility of dopants is very low (of the order of 1 mol%). Ca-doped LaNbO$_4$ has
shown the highest proton conductivity of approx. 1 mS/cm at 700 °C. They belong to the mineral
family of Fergusononites and exhibit a monoclinic (Fergusonite) to tetragonal (Scheelite)
phase transformation at a temperature that increases with decreasing rare earth radius and in-
creases on going from Nb (500 - 830 °C) to Ta (1300 - 1450 ºC). The tetragonal phase shows
higher proton conductivity than the monoclinic one. The material, though, is robust and survives
the phase transformation well (Norby 2007).

Other compounds with oxygen tetrahedra have also emerged as proton conductors in the last years:

- gallates: Ln$_{1-x}$Ba$_{1+x}$GaO$_{4-x/2}$ and Ln$_{1-x}$Sr$_{1+x}$GaO$_{5-x/2}$ where Ln stands for a lanthanoid
  (Kendrick et al. 2006),
- a number of rare earth meta- and oxy-phosphates, borates or silicates (Amezawa et al.
  2005; Kitamura et al. 2005; Kitamura et al. 2006), and
- eulytite-structured phases: Bi$_4$(SiO$_4$)$_3$ and Ba$_3$La(PO$_4$)$_3$ (Norby 2007).

For the latter compound, Ba$_3$La(PO$_4$)$_3$, the original source document, a conference proceeding
could not be obtained. Instead, a patent was found considering it a solid acid (Chisholm and
Haile 2006). The conductivity of doped pyrochlore compounds, La$_2$M$_2$O$_7$ where M is a tetrava-
lent metal, and La$_3$NbO$_7$ compounds have been investigated (Omata and Otsuka-Yao-Matsuo
2001; Shimura et al. 2002), with large protonic contribution. The latter compound is part of a
group, which have been investigated as superconducting materials (epitaxially grown film on
Ni-W substrate).

Tungstates with a fluorite-related structure really exhibit interesting behaviors regarding low
temperature application and mixed conduction. As a proton conducting electrolyte in a solid ox-
ide fuel cell, undoped La$_6$WO$_{12}$ exhibits a volume proton conductivity of 0.5 mS/cm at 400 °C.
If we compare this value to 10% Y-doped BaZrO$_3$ (BZY) under similar conditions, BZY exhib-
its almost two orders of magnitude lower dc conductivity due to the very high grain boundary
resistance (HAILE et al. 2001). It should be said, though, that the pure bulk (grain-interior) con-
ductivity in BZY is twice that of the tungstate. As will be discussed in the next chapter,
La$_6$WO$_{12}$ exhibits both protonic and electronic conduction making it suitable for membrane ap-
plications as well. The chemical stability of the tungstates is doubtful (Haugsrud 2007). Reaction
with C-containing species may trouble the tungstates, since WC$_x$ compounds are very sta-
ble. The volatility of WO$_x$ species is another worry, in particular, during synthesis and fabrica-
tions. These materials should, however, benefit from the low activity of W in both these re-
spects. On the other hand, the high activity of La may be detrimental with respect to stability
against water vapor and CO$_2$. On the other hand, Shimura et al. mention good stability of
La$_{5.8}$WO$_{11.7}$ compounds (Shimura et al. 2001), the conductivity of which is an order of magni-
tude larger than that measured by Haugsrud for undoped La$_6$WO$_{12}$. They also mention phase
separation upon Ca doping, not discussed by Haugsrud.
High proton conductivities have been reported for the pyrophosphates SnP$_2$O$_7$ and TiP$_2$O$_7$ in the temperature range 75 - 300 ºC (Nagao et al. 2006). This is probably caused by hydration of excess P$_2$O$_5$, not hydration of oxygen vacancies or P$_2$O$_7^{4-}$ ions. Modest proton conduction seems to have been found in TiP$_2$O$_7$ at higher temperatures (400 - 1200 ºC) (Norby et al. 2006c). Again, the original source document could not be traced.

Many metal oxides take up large quantities of protons or hydrogen by intercalation, often at moderate temperatures. Examples include NiOOH, MnO$_2$, Nb$_2$O$_5$ and WO$_3$, which may be reduced forming hydroxides, oxyhydroxides and so-called bronzes. However, many of them are not considered stable at high temperatures in hydrogen due to their high oxidation states. The hydrogen bronzes, for example, loose hydrogen as water at temperatures above 200 ºC (Whittingham 2004). Therefore, these materials have not been considered here.

Table 3.1 shows an overview of structures of class I proton conductors which have been investigated in the last 4 years, with the most important properties of a typical example:

- the temperature range $T$ in which the proton conducting material can be applied,
- total conductivity $\sigma_{\text{tot}}$ and, if available, the ionic and protonic transport numbers $t_{\text{ion}}$ and $t_{\text{H}^+}$, respectively, at 700 ºC, unless specified,
- maximum power density $P$ at 700 ºC of a fuel cell using the proton conductor as electrolyte,
- the electrolyte thickness of the fuel cell, $d$, upon which $P$ depends, and
- the chemical stability towards CO$_2$ and H$_2$O.

The indicated temperature range is the range used for the measurements, and thus not the full operation window. For example, the proton conducting properties of brownmillerite compounds have not been investigated below the order-disorder temperature (ca. 400 ºC for Ba$_2$In$_2$O$_5$), while there is water uptake at temperatures below 400 ºC implying proton conduction. The conductivity values have been determined by AC impedance spectroscopy, the transport numbers by combining the total conductivity data with the OCV measurements of a concentration cell over which a concentration gradient of H$_2$, H$_2$O or O$_2$ is applied. Only a few groups (the group of Norby, amongst others) have specified the partial conductivities of the various charges species involved (H$^+$, O$^{2-}$, electrons or holes).

As mentioned before, the chemical stability is a point of concern since hydroxides or carbonates may easily form from the basic constituents of the class I conductor, for example, for BaCeO$_3$:

$$\text{BaCeO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2 + \text{CeO}_2$$

and

$$\text{BaCeO}_3 + \text{CO}_2 \leftrightarrow \text{BaCO}_3 + \text{CeO}_2.$$

Despite that, chemical stability has hardly been investigated experimentally, except for the perovskite-structured cerates and zirconates. Stability of gallates, phosphates and pyrochlore structures against CO$_2$ is good. The fergusononites are presumably stable in H$_2$O and CO$_2$ containing atmospheres. In Table 3.1, the stability is ranked by a ‘+’, ‘0’ or ‘-’ sign for good, modest and poor stability, respectively. Clearly, the required chemical stability depends on the application. For hydrocarbon reforming, for example, stability in a H$_2$O and CO$_2$ containing atmosphere is required. But for electrolysis, only water stability is required.

Only for a few class I conductors, a fuel cell has been prepared. The fuel cell uses atmospheric H$_2$ and air as fuel and oxidant, respectively, unless specified. Other fuels have been investigated as well, like methanol, ethanol, propanol, ammonia (Maffei et al. 2007) and H$_2$S. Again, the mixed oxygen-proton conducting composites are performing best.
### Table 3.1 Overview of state-of-the-art class I proton conductors

<table>
<thead>
<tr>
<th>Structure</th>
<th>Typical example</th>
<th>(T (^\circ \text{C}))</th>
<th>(\sigma_{\text{tot}}) (mS/cm)</th>
<th>(t_{\text{ion}}) (-)</th>
<th>(t_{\text{H}^+}) (-)</th>
<th>(P) (mW/cm(^2))</th>
<th>(d) (μm)</th>
<th>(\text{CO}_2) stab.</th>
<th>(\text{H}_2\text{O}) stab.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite</td>
<td>(\text{BaCe}<em>{0.6}\text{Zr}</em>{0.2}\text{Y}<em>{0.2}\text{O}</em>{3-\delta})</td>
<td>500 - 900</td>
<td>30</td>
<td>1</td>
<td>1</td>
<td>266</td>
<td>10</td>
<td>0/+</td>
<td>0/+</td>
<td>(Kreuer 2003; Lin et al. 2008b)</td>
</tr>
<tr>
<td></td>
<td>(\text{BaCe}<em>{0.3}\text{Zr}</em>{0.46}\text{Y}<em>{0.8}\text{Pr}</em>{0.04}\text{O}_{3-\delta})</td>
<td>500 - 800</td>
<td>40</td>
<td>1</td>
<td>1</td>
<td>300</td>
<td>30</td>
<td>+</td>
<td>+</td>
<td>(Melnik et al. 2008)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{0.9}\text{Ba}</em>{0.1}\text{Ga}<em>{0.8}\text{Mg}</em>{0.2}\text{O}_{3-\alpha})</td>
<td>400 - 800</td>
<td>20</td>
<td>1</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>(Chen and Ma 2008; Liu and Zhang 2008)</td>
</tr>
<tr>
<td></td>
<td>(\text{BaCe}<em>{0.8}\text{Y}</em>{0.2}\text{O}_{3-\delta})</td>
<td>600 - 700</td>
<td>2 - 3)</td>
<td>1</td>
<td>1</td>
<td>400</td>
<td>10 - 15</td>
<td>- 15</td>
<td>+</td>
<td>(Yoo and Lim 2008)</td>
</tr>
<tr>
<td>Brownmillerite</td>
<td>(\text{Ba}_2\text{InSnO}_5)</td>
<td>450 - 700</td>
<td>3</td>
<td>0.5</td>
<td>0.10</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>(Schober 2001)</td>
</tr>
<tr>
<td></td>
<td>(\text{Ba}<em>2\text{In}</em>{1.26}\text{Ce}<em>{0.51}\text{O}</em>{4.91})</td>
<td>400 - 750</td>
<td>20</td>
<td>?</td>
<td>?</td>
<td>140)</td>
<td>350</td>
<td>?</td>
<td>?</td>
<td>(Decés-Petit et al. 2005)</td>
</tr>
<tr>
<td>Gallate</td>
<td>(\text{La}<em>{0.9}\text{Ba}</em>{1.1}\text{GaO}_{3.95})</td>
<td>500 - 900</td>
<td>0.13</td>
<td>?</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>SOFC-IX 1142</td>
<td>(Kendrick et al. 2006)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{0.9}\text{Pr}</em>{0.1}\text{Ba}<em>{1.1}\text{GaO}</em>{3.95})</td>
<td>500 - 900</td>
<td>2.6</td>
<td>?</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(Kendrick et al. 2006)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Pr}<em>{0.8}\text{Sr}</em>{2.2}\text{GaO}_{4.9})</td>
<td>500 - 900</td>
<td>6.5</td>
<td>?</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(Kendrick et al. 2006)</td>
<td></td>
</tr>
<tr>
<td>Monazite</td>
<td>(\text{La}<em>{0.99}\text{Sr}</em>{0.01}\text{PO}_{4})</td>
<td>500 - 925</td>
<td>0.03</td>
<td>1</td>
<td>1)</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>(Kitamura et al. 2006)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{0.99}\text{Sr}</em>{0.01}\text{P}<em>{2}\text{O}</em>{8})</td>
<td>300 - 700</td>
<td>0.25</td>
<td>1</td>
<td>1)</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>(Amezawa et al. 2005)</td>
</tr>
<tr>
<td>Eulytite</td>
<td>(\text{Bi}_3\text{(SiO}_3\text{)}_3)</td>
<td>500 - 850</td>
<td>0.025</td>
<td>1</td>
<td>1)</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>Kitamura 2007</td>
</tr>
<tr>
<td>Fergusonite</td>
<td>(\text{La}<em>{0.99}\text{Ca}</em>{0.01}\text{NbO}_4)</td>
<td>300 - 1100</td>
<td>6</td>
<td>0.9</td>
<td>0.95</td>
<td>1)</td>
<td>1100?</td>
<td>+?</td>
<td>+?</td>
<td>(Mokkelbost et al. 2008; Norby et al. 2006a)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{0.99}\text{Ca}</em>{0.01}\text{TaO}_4)</td>
<td>300 - 1100</td>
<td>0.1</td>
<td>?</td>
<td>+?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>(Haugsrud and Norby 2007)</td>
</tr>
<tr>
<td>Fluorite</td>
<td>(\text{La}_{2.6}\text{Sr}_0.4\text{NbO}_7)</td>
<td>600 - 1000</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>(Shimura et al. 2002)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{8}\text{WO}</em>{11.7})</td>
<td>600 - 1000</td>
<td>35</td>
<td>0.9</td>
<td>0.9</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>(Shimura et al. 2001)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{8}\text{Ca}</em>{0.3}\text{WO}_{11.85})</td>
<td>300 - 1050</td>
<td>0.7</td>
<td>0.9</td>
<td>0.7</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>(Haugsrud 2007)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{1.9}\text{Ca}</em>{0.05}\text{Zr}<em>{0.6}\text{O}</em>{6.975})</td>
<td>377 - 1027</td>
<td>68</td>
<td>1</td>
<td>1)</td>
<td>+?</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>(Omata and Otsuka-Yao-Matsuo 2001)</td>
</tr>
<tr>
<td></td>
<td>(\text{La}<em>{2.6}\text{O}</em>{2.7}\text{(BO}_3\text{)}_8)</td>
<td>300 - 750</td>
<td>1</td>
<td>1</td>
<td>1)</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>(Noirault et al. 2007)</td>
</tr>
</tbody>
</table>

---

1) at 810 ºC, estimated, measured value 280 mW/cm\(^2\) due to leakage
2) at 750 ºC, 50% H\(_2\)/50% N\(_2\), in some samples In\(_2\)O\(_3\) was observed by XRD which has high electronic conductivity
3) based on the \(\sigma(H_2/H_2O)/\sigma(D_2/D_2O)\) ratio being close to the theoretical value \(\sqrt{2}\), implying pure proton conduction
4) only at \(T < 600\) ºC
5) at 900 ºC
6) calculated from measured electrolyte resistance in fuel cell, thus including contact resistances with electrodes
Even without chemical reaction, degradation of the material may occur when it is exposed to various gradients (chemical, mechanical, electrical or thermal gradients). The multicomponent material may become chemically inhomogeneous, it may decompose into new phases or a new morphology may be established. All three phenomena have a purely kinetic origin, that is the fluxes of mobile components will disappear if the applied gradient is removed, but the instability may remain. This type of instability, kinetic demixing, has been investigated even less than chemical instability. An example is the migration of the metal component in cermet-based membranes for H₂ separation, discussed in the next Chapter. Mechanical stability is another type of stability which is of importance for membrane materials. Factors contributing to stress in the material are thermal cycling, and chemical expansion. The stresses, \( \sigma_{th} \) and \( \sigma_{chem} \) respectively, induced by both phenomena can be described by (Fontaine et al. 2008)

\[
\sigma_{th} = \frac{E\alpha\Delta T}{1-\nu}
\]

and

\[
\sigma_{chem} = \frac{E\frac{1}{3}\beta_c\Delta\delta}{1-\nu}
\]

Here, \( E \) is Young's modulus, \( \alpha \) is the coefficient of linear thermal expansion, \( \nu \) is the Poisson's ratio, \( \Delta T \) represents a thermal gradient, \( \frac{1}{3}\beta_c \) is the linear chemical expansion, \( \Delta\delta \) is the change in oxygen non-stoichiometry due to a partial O₂ gradient. The thermal stress due to \( \Delta T = 100 \) K is 220 MPa using \( E = 130 \) GPa, \( \nu = 0.3 \) and \( \alpha = 1.2 \times 10^{-5} \) K⁻¹. For \( \Delta\delta = 0.0135 \) and \( \frac{1}{3}\beta_c = 0.1 \), a chemically induced stress of 250 MPa is found. Reported values of the fracture strength of III-III-type perovskites are typically in the range 100 - 200 MPa, so lower than the above stresses. Finally, creep resistance is preferred to maintain the membrane dimensions, but it may also offer a stress relaxation mechanism. Again, literature data are very limited. High creep rates at the operation temperature of oxygen permeable membranes have been reported, particularly for materials with high Sr content (Bakken et al. 2002).

### 3.3 Applications

#### 3.3.1 Fuel cell

The most important application of class I proton conductors is in the field of fuel cells. The reactions involved are

\textit{anode:} \hspace{0.5cm} H₂ → 2H⁺ + 2e \hspace{0.5cm} (3.11)

\textit{cathode:} \hspace{0.5cm} 2H⁺ + 0.5O₂ + 2e → H₂O \hspace{0.5cm} (3.12)

In contrast with fuel cells using an oxygen conducting membrane, water is produced at the cathode side here. Thus, the fuel is not diluted with water, making higher fuel utilizations possible than in oxygen conducting fuel cells. Another advantage is that the operation temperature window of the class I conducting materials (600 - 800 °C) is generally lower than that of oxygen conducting materials (800 - 1000 °C). Thus, the fuel cell operation temperature can be lowered. This makes the use of cheap steels for cell separator plates and housings possible, with consequent cost reduction. Another way to maintain the performance of the oxygen conducting fuel cells at lower temperatures is to use thinner electrolytes. This is another current research trend. The power densities shown in Table 3.1 are less than 400 mW/cm².
Most experimental work on high-temperature fuel cells with proton-conducting membranes was done using H₂ fed cells. State-of-the-art results are reported in Table 3.1 for such cells. Integrating the electrolyte with compatible electrodes is an important issue. A recent interesting method consists of growing proton conducting ceramic crystals on a Pd-based, thin film serving both as anode and H₂ separation membrane. The crystals display anisotropic proton conductivity, and are grown so that the crystal axis with the highest conductivity is oriented normal to the surface of the hydrogen membrane. As a result, proton conductivity is significantly enhanced. Preliminary fuel cell performance data has been obtained demonstrating the promise of this novel fuel cell in the temperature range of 300-600 °C (Liu et al. 2008).

Direct hydrocarbon reforming in the fuel cell making efficient use of the produced heat, would be more advantageous just as for the oxide ion conducting electrolyte fuel cells. To date, hardly any literature is available using CH₄ as fuel for the proton conducting fuel cell. The patent of Coors shows experimental results obtained using a fuel cell consisting of a BaCe₀.₉Y₀.₁O₂₋₀.₉₅ electrolyte with a thickness between 0.2 and 1 mm (Coors 2003). Figure 3.2 shows the principle of steam permeation reforming. Only the oxygen sublattice is shown. For clarity, no external circuit is required for the process. Oxygen ion vacancies at the electrolyte surface at the air side are annihilated by reaction with water vapour to produce two protons on oxygen sites according to reaction (3.3). The reverse of this reaction occurs at the fuel side, creating a concentration gradient over the membrane in oxygen ion vacancies and protons. Oxygen ion vacancies diffuse through the ceramic electrolyte from the fuel to the air side, protons diffuse from the air to the fuel side by hopping between oxygen ions. The produced water at the fuel side is consumed by reaction with hydrocarbon molecules and CO. Thus, effectively a steam flux, \( J_{H₂O} \), is permeating the membrane from the air to the fuel side by so-called ambipolar diffusion, driven by the concentration gradient., given by

\[
J_{H₂O} = \frac{D_{OH} \cdot D_{\nu}}{L(D_{OH} - 2D_{\nu})} \left( (C_{II} - C_I) + \frac{b}{a + \gamma} \ln \left( \frac{a(C_I + b)}{aC_{II} + b} \right) \right)
\]

(3.14)

where \( D_{OH} \) and \( D_{\nu} \) are the self-diffusivities (cm²/s) of \( OH^- \) and \( \nu^- \), respectively, \( L \) is the membrane thickness (cm), \( C_I \) and \( C_{II} \) are the steam concentrations (mol/cm³) at the moist and dry surfaces, respectively, \( \gamma = 2[P_a] \) where \([P_a]\) is the concentration of the dopant \( P \) in the perovskite \( AB_{1-x}P_xO_{3-δ} \), \( a = (D_{OH} - 2D_{\nu}) \) and \( b = 2D_{\nu} \).

In the hydrocarbon fed fuel cell, the produced hydrogen at the fuel side dissociates according to reaction (3.11). The protons travel from fuel to air side and constitute the Faradaic flux. Other than the normal charged particle interactions, these two fluxes are totally independent. The steam permeation flux can be quite large. For a 25 μm thick BaCe₀.₉Y₀.₁O₂₋₀.₉₅ membrane, the maximum, calculated steam flux occurs at 850 °C, and equals 10.6 μmol/s.cm² or 15 cm³ STP/min.cm². This would require a cell area of 680 cm² for a 5 kW fuel cell stack, yielding 7350 mW/cm² (Coors 2007). This is two order of magnitude larger than the experimentally obtained power density (see below) due to the different electrolyte thickness and neglecting of polarization losses and surface kinetics. The proton conducting membrane allows steam permeation. This is a clear advantage compared with an oxide ion conducting electrolyte. Here, the steam must be supplied at the anode side since no steam can be transported through the electrolyte. Thus, the water due to the cell reaction accumulates at the anode, where it interferes with the steam reforming reaction in such a way that even coking of the anode structure may occur (Kreuer 2003).
Figure 3.2 Principle of steam permeation reforming (Coors 2003): oxygen vacancies (110), 2 protons (111), electrolyte surface (112), water molecule (116), hydrocarbon molecule (120), CO molecule (122) and CO$_2$ molecule (124)

Figure 3.3 shows the principle of steam permeation reforming with external circuit. Only CH$_4$ is supplied to the anode side, while an air/steam mixture is supplied to the cathode side. Figure 3.4 shows the current-voltage characteristics of a 1" diameter cell using the mentioned electrolyte and Pt electrodes. The I-V curves are nearly straight over the entire range from open circuit to short circuit, indicating that it is the ohmic resistance that determines the cell performance. The maximum power density is approx. 60 mW/cm$^2$ at 150 mA/cm$^2$ and 832 °C. This seems small compared with the power densities of H$_2$ fed fuel cells mentioned in Table 3.1. When the same cell is fed with H$_2$ instead of dry CH$_4$, the area specific resistance (ASR) reduces strongly: from 2.7 to 1 Ω.cm$^2$ at 832 °C. The steam permeation flux which occurs when CH$_4$ is used as fuel is absent in the H$_2$ fed cell, and is in fact the rate-determining process for the cell. Thus, if a thinner electrolyte would be used, higher power densities would be found. Using the value of the ASR of the H$_2$-fed cell, we find 160 mW/cm$^2$ at 400 mA/cm$^2$ and 832 °C.

Three modelling studies were found dealing with steam reforming protonic fuel cells. In the one study, a one-dimensional electrochemical model was developed to study the solid oxide fuel cell (SOFC) using proton conducting electrolyte (perovskite) and oxygen ion conducting electrolyte (Y-doped ZrO$_2$), denoted as SOFC-H and SOFC-O, respectively (Ni et al. 2008). The study shows that the power density of the CH$_4$-fed SOFC-H is considerably lower than that of the SOFC-O, 244 and 343 mW/cm$^2$ at 800 °C, respectively. This is partly due to the higher ohmic overpotential of SOFC-H. It was also found that the CH$_4$ fed SOFC-H has a considerably higher cathode concentration overpotential and a lower anode concentration overpotential than the SOFC-O. The anode concentration overpotentials of the CH$_4$ fed SOFC-H and SOFC-O were found to decrease with increasing temperature. Therefore, high temperature is desirable for increasing the potential of the CH$_4$ fed SOFC. It was also found that optimal electrode porosities exist that minimize the electrode total overpotentials.
Figure 3.3  Principle of CH₄-fed proton conducting fuel cell (Coors 2003)

Fuel Side

\[
\text{CH}_4(g) + 2\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{CO}_2(g) + 8\text{H}^+ + 8e^- \\
\text{Air Side}
\]

\[
2\text{O}_2(g) + 8\text{H}^+ + 8e^- \rightarrow 2\text{H}_2\text{O}(g) + 2\text{H}_2\text{O}_{\text{ads}}
\]

Figure 3.4  Current-voltage characteristics at various temperatures for a protonic ceramic fuel cell operated on dry methane (Coors 2003)
The results of another, recent study by Biesheuvel and Geerlings contrast those of the above-mentioned work (Biesheuvel and Geerlings 2008). Biesheuvel and Geerlings have found that the efficiency of an SOFC with proton conducting electrolyte is always a few percent higher than that of an SOFC with oxygen ion conducting electrolyte. Besides, the proton-conducting SOFC is claimed to be more robust with respect to coke formation than the oxygen ion conducting SOFC. The differences between the two studies are probably due to the different starting-points regarding the ohmic loss and electrode overpotentials.

In the oldest study, the performance (CH$_4$ conversion, produced electric power, efficiency) of a microreactor composed of channels with a dimension of 1 to 1000 μm in width and depth was calculated (Goto et al. 2003). Three types of membrane microreactors for power production by fuel cells with methane feed were compared:

- the Pd membrane microreactor (Pd-MMR) followed by a polymer electrolyte fuel cell (PEFC),
- the oxide-ion conducting solid oxide fuel cell (SOFC-O), and
- the proton conducting solid oxide fuel cell (SOFC-H).

The sensitivity was investigated with respect to the pre-reform distance in the Pd-MMR reactor (the initial reactor path where no membrane is present, only catalyst) membrane thickness, H$_2$O/CH$_4$ ratio of the feed gas, and the feed flow rate. At optimized conditions, the Pd-MMR/PEFC and SOFC-O systems performed similarly (54% efficiency), whereas the efficiency of the SOFC-H system was less (44%). However, the performances depended strongly on the permeation properties of the membranes as well as on the catalyst kinetics. Besides, the Pd-MMR/PEFC system was rather complex compared with the other two systems.

### 3.3.2 Electrolysis

A fuel cell is changed into an electrolyzer by simply applying a voltage over the cell instead of drawing electric power from a load. If the voltage is sufficiently large, the following reactions occur:

**anode**: $H_2O \rightarrow 2H^+ + 2e + 0.5O_2 \quad (3.15)$

**cathode**: $2H^+ + 2e \rightarrow H_2 \quad (3.16)$

In general, high temperature electrolysis is much more efficient than low temperature, alkaline electrolysis because the Gibbs energy change for water dissociation decreases with increasing temperature. Compared with fuel cell operation where hydrocarbon-containing fuel is used, CO$_2$ stability is not relevant here. This allows the use of cerates which cannot be used in hydrocarbon fuelled fuel cells due to chemical instability. It has been shown that BaCeO$_3$, for example, is relatively stable as a dense electrolyte at temperatures between 150 and 400 ºC in a gas atmosphere with 0.1 atm steam (Bhide and Virkar 1999). A typical example of a single lab-cell operating in both fuel cell and electrolyzer mode is shown in Figure 3.5. At the maximum current density (1050 mA/cm$^2$), the H$_2$ evolution rate as determined by a mass spectrometer, amounts to 7.1 cm$^3$ STP/min.cm$^2$, which is 97% of the theoretical production rate calculated from Faraday’s law (7.3 cm$^3$ STP/min.cm$^2$). The steam content of the process gases was low (only 3%).

An interesting application combining steam electrolysis with NO reduction has been investigated by Kobayashi et al. (Kobayashi et al. 2002), see Figure 3.6. A steam electrolysis cell was constructed with a tubular, proton conductor SrZr$_{0.9}$Yb$_{0.1}$O$_{3-δ}$ as an electrolyte. Here, a 90% steam/10% air gas mixture was fed to the anode, N$_2$ or He with NO, O$_2$ and H$_2$O to the cathode. The steam electrolysis cell efficiently reduced NO on the cathode, using hydrogen produced by steam electrolysis as a reducing agent at around 460 ºC. When a Pt/Ba/Al$_2$O$_3$ catalyst was placed on the cathode, NO was reduced even under an O$_2$-rich atmosphere. Another electrolysis cell was constructed with a tubular, oxide-ion conducting 8 mol% Y$_2$O$_3$-doped ZrO$_2$ as an electrolyte. The cell could reduce NO on the cathode, not only electrochemically, but also chemi-
cally using hydrogen produced by steam electrolysis. However, the latter cell could not reduce NO in an atmosphere containing O₂.

Figure 3.5 Performance of anode supported BaCe₀.₈Y₀.₂O₃-δ cell (electrolyte 10-15 μm thick) with Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃-δ cathode in both fuel cell and electrolysis mode at 600 ºC under air and 50% H₂/50% Ar (both humidified with 3% H₂O) with a gas flowrate of 120 ml/min (Yoo and Lim 2008)

Figure 3.6 Schematic diagram of a steam electrolysis cell with NO reduction (Kobayashi et al. 2002)
3.3.3 Membrane reactor

Proton conducting materials can be used as a membrane in a chemical reactor for several catalytic processes. The overall reaction that takes place can be written as:

\[ A \leftrightarrow mB + nH_2 \]  

(3.17)

where A and B are the reactant and product, respectively, of the reaction. The membrane is sandwiched between two porous electrodes, which are connected to a voltmeter (case a), a resistive load (case b) or an external power source (case c). Figure 3.7 shows the various cases of operation. In cases b and c, the partial reactions are

\[ A \rightarrow mB + 2nH^+ + 2ne \]  

(3.18)

and

\[ 2nH^+ 2ne \rightarrow nH_2, \]  

(3.19)

occurring at the anode and cathode, respectively, and resulting into the overall reaction (3.17), when added together. The difference between cases b and c is that in case b, the \( H^+ \) ions flow in the direction favoured by the chemical potential difference, whereas in case c, they are forced to flow in the opposite direction. The latter mode is therefore called hydrogen pumping, and can be used, amongst others, to concentrate the hydrogen concentration at the \( H_2 \) rich side of the membrane. Two reactor designs exist: double-chamber or single-chamber, depending on if the two electrodes are gas-tight separated from each other or not. The single-chamber reactor has already been used for SOFC fed with a hydrocarbon-air mixture, using suitably chosen electrodes (Hibino et al. 2000). It is much easier to apply to existing catalytic processes than the two-chamber concept.

![Figure 3.7](image)

Figure 3.7 Schematic of a proton-conducting membrane reactor: open circuit operation (a), fuel cell mode (b) and \( H^+ \) pumping mode (c) (Kokkaftis et al. 2007b)
If the electrode at the reactant side (working electrode) serves also as the catalyst for the reaction, protons can be pumped to or away from the catalyst during reaction. This may alter the catalytic activity and/or the selectivity of the reaction under study. Usually, the rate at which the reactant(s) are converted equals half the rate at which protons are pumped to or from the catalyst. In this case, the reaction enhancement, if occurring, is said to be Faradaic. In some cases, though, it is found that the conversion rate surpasses the proton pumping rate, even by orders of magnitude. This is called the NEMCA (Non-Faradaic Electrochemical Modification of Catalytic Activity) effect and has been observed in proton conducting membrane reactors, see the examples below.

An overview of all catalytic reactions that have been studied in a proton-conducting membrane reactor is provided by Kokkofitis et al. (Kokkofitis et al. 2007b). A short summary is given here, filled up with more recent results. As working electrode, mostly Pt or Pd has been used. Fuel cells fed with H$_2$ or CH$_4$, and electrolysis cells, though also membrane reactors, have been excluded. They have been treated separately, because of the relatively large amount of research that has been performed on them.

**Oxidative methane coupling**

This is an important industrial reaction. In the 1980s, numerous studies were performed to find a suitable catalyst that could favour the oxidative methane coupling in methane-oxygen gas mixtures on the one hand, while suppressing the complete mineralization to H$_2$O and CO$_2$ on the other hand. These studies included membrane reactors of all types. The discovery of proton-conducting membrane reactor gave a new stimulus and directed research groups to a different route based on methane dimerization via dehydrogenation rather than partial oxidation, yielding the reactions

$$2CH_4 \rightarrow C_2H_6 + 2H^+ + 2e \quad \text{(or } C_2H_4 + 4H^+ + 4e)$$

and

$$2H^+ + 2e \rightarrow H_2$$

at the anode and cathode, respectively, using the pumping mode. Alternatively, the reactor can be used operated as a cogenerative fuel cell, producing electric power and ethylene (Iwahara et al. 1989). Although several of the investigated materials are very efficient methane coupling catalysts (SrZr$_{0.9}$Yb$_{0.1}$O$_{3-\delta}$), low C$_2$ yields have been reported so far (< 2%), mainly due to the competitive effect of the methane pyrolysis:

$$2CH_4 \rightarrow C + 2H_2.$$ 

Nevertheless, this process yielding two valuable products and their separation (ethylene at the anode, hydrogen at the cathode) is considered as a promising application.

**Decomposition of ammonia, alcohols, alkanes and alkenes**

Decomposition of these fuels has been investigated in a fuel cell mode proton-conducting membrane reactor. Liquid ammonia has been most widely tested as fuel. Table 3.2 shows some recent results. For comparison, H$_2$ fuel cell performance has also been included, and is approx. 10% higher than that of the NH$_3$ fed cell.

Iwahara et al. investigated the use methanol or ethanol as fuel, using Sr or Ba doped cerates as proton-conducting membranes (Iwahara et al. 1989). Cogeneration of electric power and a valuable chemical was obtained when ethane (Iwahara et al. 1986) or propane (Karagiannakis et al. 2006) was used as fuel, which were converted into ethylene and propene, respectively. In both cases, the performance improved when steam was added to the fuel stream.
Table 3.2  Comparison of fuel cell performance data for pure $H_2$ and $NH_3$ at 1 atm and 700 °C

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>power density (mW/cm²)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$NH_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$BaCe_0.8Gd_{0.15}Pr_{0.05}O_{3-δ}$</td>
<td>70</td>
<td>(Maffei et al. 2007)</td>
</tr>
<tr>
<td>$BaCe_0.8Gd_{0.6}O_{3-δ}$</td>
<td>370</td>
<td>(Meng et al. 2007)</td>
</tr>
<tr>
<td>$BaCe_0.7Zr_{0.1}Y_{0.2}O_{3-δ}$</td>
<td>330</td>
<td>(Kui et al. 2008)</td>
</tr>
</tbody>
</table>

Water-gas shift
Kokkofitis et al. studied the water-gas shift reaction using $SrZr_{0.95}Y_{0.05}O_{3-δ}$ (Kokkofitis et al. 2007a), Karagiannakis et al. the reverse water-gas shift using $SrZr_{0.9}Y_{0.1}O_{3-δ}$ (Karagiannakis et al. 2003), using a Pd and Cu working electrode, respectively. In both cases, a NEMCA effect was observed.

Ammonia synthesis
Ammonia is synthesized from gaseous $H_2$ and $N_2$ by the Haber process which requires high pressures and an Fe-based catalyst. It has been shown that $NH_3$ can be produced at atmospheric pressure and temperatures between 400 and 800 °C using a variety of proton-conducting membranes: $Ba_3Ca_{1.18}Nb_{1.82}O_9-δ$ (Li et al.), $BaCe_{0.8}Gd_{0.1}Sm_{0.1}O_{3-δ}$ (Li et al. 2007), $Ce_{0.8}Sm_{0.2}O_{2-δ}$ (Liu et al.), $La_{1.95}Ca_{0.05}Zr_{2}O_{7-δ}$ (Ya-Hong et al.) and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ}$ (Zhang et al. 2007). The observed production rates are in the range $(2 - 8) \times 10^{-9}$ mol/cm².s.

3.3.4 $H_2$ pump
The principle of a $H_2$ pump was demonstrated by Matsumoto et al. who were able to make $H_2$ permeate from a 0.92% or 5% $H_2$ containing gas flow at the anode side to pure $H_2$ gas at the cathode side at 800 °C using $SrCe_{0.95}Yb_{0.05}O_{3-δ}$ (Matsumoto et al. 2002). $H_2$ evolution rates of more than 2 cm³ STP/min.cm² have been observed at current densities of 0.5 A/cm² (Figure 3.8). Increasing the current density beyond the point where all $H_2$ had been electrochemically removed, caused the following reactions to occur

\[ H_2 + O^{2-} \rightarrow H_2O + 2e \]  \hspace{1cm} (3.23)

and

\[ H_2O + 2e \rightarrow H_2 + O^{2-} \]  \hspace{1cm} (3.24)

at the anode and cathode, respectively. This is possible because the gas flows are humidified and the applied electrolyte shows also oxygen ion conduction. The resulting $H_2$ evolution rate-current density graph shows a deviation from linear behaviour at this current density and higher. $H_2$ pumps could be useful in nuclear fusion reactors for tritium recovery from vacuum exhaust and blanket gases. Compared with Pd-alloy based $H_2$ separation membranes, proton conducting membranes offer the following advantages:

- $H_2$ can also be extracted from hydrogen containing compounds such as water vapour and methane,
- the $H_2$ evolution rate can be controlled by the applied electric current,
- pressurization of the supplied gas is not required for $H_2$ removal, and
- proton-conducting materials are radiation resistant.

For Ar gas containing 0.1% $H_2$, 0.1% $CH_4$ and 1.2% $H_2O$, Tanaka et al. found a $H_2$ evolution rate of approx. 0.007 cm³ STP/min.cm² at 800 °C, 3.5 V and 1.2 mA/cm² using $CaZr_{0.3}In_{0.7}O_{3-δ}$ as electrolyte in the electrolysis cell (Tanaka et al. 2004). They used commercially available one-end closed tubes of 15 and 12 mm outer and inner diameter, respectively, and 200 mm length, provided by TYK Ltd.
Figure 3.8  $H_2$ evolution rate at cathode vs. current density for 0.92% or 5% $H_2$ containing gas mixtures at anode. The dashed line has been calculated from Faraday's law (Matsumoto et al. 2002).

Figure 3.9  Operation principle of the sensor with $H^+$ diffusion passage (Taniguchi et al. 2005).

Figure 3.10  Current-potential characteristics of the cell of Figure 3.9 with $BaZr_{0.4}Ce_{0.6}In_{0.2}O_{3-δ}$ electrolyte at 400 °C and $H_2$ concentrations in the range 0 - 5% (Taniguchi et al. 2005).
For a hydrogen economy, $\text{H}_2$ sensing becomes important. High and low-temperature sensors are developed using a proton-conducting oxide. A typical example of a high-temperature material is $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{In}_{0.2}\text{O}_{3-\delta}$ (Taniguchi et al. 2005). The construction of the sensor is shown in Figure 3.9. The sensor element consists of a 0.45 mm thick electrolyte sandwiched between two Pt electrodes. The cell is mounted on a diffusion resistant ceramic plate with glass seal. A $\text{H}_2$ diffusion path has been created in the seal to allow the gas to enter the anode compartment. A voltage is applied over the cell, resulting in a small current. The current increases with applied voltage up to approx. 0.1 V and then starts to saturate (Figure 3.10). This is called the limiting-current mode. Note that the current is orders of magnitude lower than Faradaic current which would result if all supplied $\text{H}_2$ would be conducted through the electrolyte. The sensor can be used for $\text{H}_2$ concentrations up to 100% and for temperatures between 350 and 700 ºC. The response is pretty linear as shown in Figure 3.11. Hydrocarbons in the gas mixture have a negligible effect. The cell has been shown to be stable for 100 thermal cycles.
Figure 3.13 Reforming and regeneration steps of TSR process (Berlowitz and Hershkowitz 2006)

Figure 3.14 Process design of power system using TSR and fuel cell with proton conducting electrolyte (Berlowitz and Hershkowitz 2006). The indicated streams are as follows: the fuel gas (401), the TSR effluent (402), the cathode effluent (403), air (404 and 408), anode effluent (406) and flue gas (407).
For low-temperature sensors, layered perovskites are used. Two types can be distinguished:

- the Ruddelsten-Popper phase: $A'_2[A_{2n-1}B_nO_{3n+1}]$, e.g. $K_2La_2Ti_3O_{10}$, and
- the Dion-Jacobsen phase: $A'[A_{2n-1}B_nO_{3n+1}]$, e.g. $KCa_2Nb_3O_{10}$,

where $A'$ is a monovalent metal, $A$ a divalent or trivalent metal, and $n$ denotes the number of corner-connected $BO_6$ octahedra in the perovskite layer. The perovskite layers are separated by alkali metal ions (THANGADURI and Weppner 2004). These materials have high proton conductivity at low temperature, e.g. the conductivity of $KCa_2Nb_3O_{10}$ is 0.34 mS/cm at 44 ºC. In a reducing atmosphere, oxygen vacancies are created and the same proton conduction mechanism occurs as in class I conductors. The sensor cell consists again of an electrolyte, sandwiched between Pt electrodes. The cell is operated in short current mode. The current depends on the Pt loading and particle size, the nature and concentration of the gas. An example of a step-response is shown in Figure 3.12 for a disc-shaped electrolyte of 1 mm thickness and 2 cm$^2$ cell area using a Pt|$KCa_2Nb_3O_{10}$|Pt sensor at 45 ºC (Sakthivel and Weppner 2007). The response time for reaching 90% of the saturation current (9.32 μA) is 12 s, and the recovery time is 19 s.

3.3.6 Use as catalyst

The catalytic properties of three proton conductors, $BaCe_{0.9}Y_{0.1}O_{2.95}$, $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$ and $Sr_3CaZr_{0.5}O_{8.75}$ for the reverse water-gas shift reaction were determined (Viana and Irvine 2007). This reaction is of importance for the Fischer-Tropsch process where the CO is used as chemical feedstock in the synthesis of higher hydrocarbons or oxygenates. The CO$_2$ conversion at 900 ºC of the above-mentioned perovskites was found to be 45%, 42% and 36%, respectively (equilibrium conversion 53.23%). It seems that the same oxygen vacancies which are responsible for proton conduction, play a role in the reverse water-gas shift reaction by CO$_2$ uptake as CO$_3^{2-}$.

3.4 Systems

3.4.1 Temperature swing reforming

ExxonMobil have developed a process called Temperature Swing Reforming, described in a patent (Berlowitz and Hershkowitz 2006). The process combines a cyclic reforming process, temperature swing reforming (TSR) with a proton-conducting solid oxide fuel cell. It is claimed that this process provides an improvement compared with conventional fuel cell/fuel processor systems in terms of thermal and material efficiencies. The TSR cycle consists of a reforming and regeneration step (Figure 3.13). The bed is divided in two parts: a reforming and a recuperating zone. At the beginning of the reforming step, the temperature of the reforming zone is high (800 - 1600 ºC), while that of the recuperating zone is low (100 - 800 ºC). When a hydrocarbon fuel is reformed, heat is absorbed from the reforming zone and transferred by the syngas product to the recuperating zone where it is stored as sensible heat. Thus, the heat is gradually displaced from the reforming to the recuperating zone during the reforming step. At a certain point, the feed flow to the reforming zone is stopped and an air-fuel mixture is introduced counterflow to the inlet of the recuperating zone. The sensible heat stored here is used for combustion and the hot combustion product transfers the heat to the reforming zone, thus restoring the temperature distribution at the beginning of the reforming step. Good heat management is obtained by integration with a solid oxide fuel which converts the syngas into electricity and heat. In addition, good material flow management is obtained by using a proton conducting electrolyte (Figure 3.14). The remaining fuel in the effluent from the anode is used as combustion gas during regeneration, while the steam in the effluent from the cathode is used for reforming during the reforming step. By using a proton conducting electrolyte, nearly all steam leaves the fuel cell at the cathode side, and almost dry fuel the anode side. Any steam in the combustion gas would result in an efficiency decrease of the combustion step. By using the steam of the cathode exhaust gas, no external steam supply is needed.
4. Class II proton conductors

4.1 Material classes

In contrast with class I proton conductors, the number of publications on mixed protonic-electronic conducting membranes is fairly modest. As will be discussed in Section 4.2.1, there are more competitive, candidate materials for H₂ permeable membranes.

Two different approaches have been followed to prepare high-temperature mixed proton electron conductors to be used for H₂ separation membranes. The first approach is the 'cermet' approach, where a cermet is a composite of a class I proton conductor and a metal (e.g. Ni and Pd) providing electronic conduction. This idea is the same as for preparing mixed oxygen ion-electronic membranes where an oxygen instead of a proton conducting ceramic oxide is used (Balachandran et al. 2007). Both mixed protonic-electronic and mixed oxygen ion-electronic conducting membranes can be used to produce H₂. The first ones separate H₂ from gas mixtures, e.g. gas streams produced by coal gasification or steam-methane reforming, the last ones separate oxygen formed by water dissociation at high temperatures. In the literature, they are sometimes denoted as HTM (hydrogen conducting membrane) and OTM (oxygen conducting membrane), respectively.

To prepare cermet membranes, whether the class I proton conducting powder is prepared separately and afterwards mixed with the metal powder, or the metal component is added to the mixture of oxidic precursors and the whole mixture is calcined. Disks of the desired size (diameter in the order of cm, height in the order of mm) are made by cold isostatically pressing. Tubular membranes have been prepared as well, using an alumina tube as support (Okada et al. 2007). The class I conductor, BaZr₀.₈₉₂₅₋₀.₇₅₂₅O₃₋₁.₇₅₋₀.₇₅, was impregnated into the microporous structure. The impregnation was repeated 10 times after which a dense membrane had been obtained. Then, a thin layer of Pd (6 μm) was coated on top of the membrane by CVD of which the function was to create an electronic conducting path, not to dissociate hydrogen. The total membrane thickness was 40 μm. A relatively high H₂ permeability was determined (Table 4.1). A 'paste' method where the paste can be brushed on a porous support has been patented by the University of Chicago, IL, USA (Song et al. 2007). The paste is a mixture of a metal (Pd, Ni, Nb, V, Ta, or alloys thereof), an oxide (YSZ, alumina, II-IV-perovskite) and organic solvents, the support is a NiO-YSZ mixture. After sintering the paste-support mixture and reducing the NiO, a film of 10 to 20 μm had formed, the metal loading of which varied between 40 and 60 vol%.

Compared with the H₂-permeable metals or alloys (see Section 4.2.1), cermets are less susceptible to crack formation because the ceramic matrix can allow the metal phase to expand and contract as the temperature and H₂ concentration fluctuate. Particle attrition during ball milling of the precursor powder minimizes defects that may lead to cracks. Even if cracks are formed in the metal phase, they are halted by the irregular path of the metal through the ceramic (Roark et al. 2006). Metal migration to the membrane surface has been observed in Pd-containing cermets (Siriwardane et al. 2003). It is not specified if the Pd accumulates at the feed or permeate side. Migration of the metal component is undesirable since it reduces the electronic conductivity. No other migration phenomena have been reported. Possible surface contamination of Pd in syngas with hydrocarbons should also be taken care of, though H₂ permeation experiments using a composite containing 60 vol% Pd in Y-stabilized Zr₂O₃ did not show any degradation during 270 hours at syngas conditions up to 400 ppm H₂S (Balachandran et al. 2008a). The latter membrane material is an example of the group of ceramic-metal composites in which the metal is the H₂ conducting phase and the ceramic phase provides structural support, and which will be discussed in section 4.2.1.
Figure 4.1 $H_2$ permeability of some selected oxides using 50% humidified $H_2$ on feed side and humidified Ar on permeate side (Fontaine et al. 2008)

Figure 4.2 $H_2$ flux versus partial $H_2$ pressure for SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ films of various thicknesses (Hamakawa et al. 2002), using a $H_2$/He and $N_2/O_2$ mixture at the upstream and downstream sides, respectively.
Table 4.1  Properties of membranes based on cermets or a proton conductors doped with multivalent component, at 700 ºC unless indicated

<table>
<thead>
<tr>
<th>material</th>
<th>$T$ (ºC)</th>
<th>thickness (mm)</th>
<th>meas. $H_2$ flux (cm³/min.cm²)</th>
<th>$H_2$ permeability ($10^8$ mol/s.m.Pa¹⁄₂)</th>
<th>$CO_2$ stability</th>
<th>$H_2O$ stability</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cermet-based</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 vol% Ni-BaZrO₁₋ₓCeₓ₋₀.₂Y₂O₃.₆</td>
<td>600 - 900</td>
<td>0.5</td>
<td>0.07</td>
<td>0.4</td>
<td>+</td>
<td>+</td>
<td>(Zuo et al. 2006)</td>
</tr>
<tr>
<td>40 vol% Ni-BaCe₀.₈Y₀.₂O₁₋ₓ</td>
<td>600 - 900</td>
<td>0.08</td>
<td>0.23</td>
<td>0.3</td>
<td>+</td>
<td>+</td>
<td>(Song et al. 2008)</td>
</tr>
<tr>
<td>35 vol% Pd-BaCe₀.₈ₓGd₀.₁₅O₃.₆</td>
<td>500 - 800</td>
<td>2</td>
<td>0.3</td>
<td>7.0</td>
<td>0?</td>
<td>0?</td>
<td>(Krishnamurthy et al. 2001)</td>
</tr>
<tr>
<td>Pd-BaZr₀.₈ₓY₀.₂O₃.₆</td>
<td>500 - 900</td>
<td>0.006</td>
<td>324 ¹)</td>
<td>4.6 ²)</td>
<td>+?</td>
<td>+?</td>
<td>(Okada et al. 2007)</td>
</tr>
<tr>
<td>multivalent component doped proton conductors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCe₀.₈ₓY₁₋₀.₁Ru₀.₁O₃.₆</td>
<td>800</td>
<td>0.5</td>
<td>0.09</td>
<td>?</td>
<td>-</td>
<td>-</td>
<td>(Matsumoto et al. 2006)</td>
</tr>
<tr>
<td>BaCe₀.₉₅Tm₀.₀₅O₃.₆</td>
<td>600 - 950</td>
<td>0.15</td>
<td>0.2 ³)</td>
<td>0.16 ³)</td>
<td>-</td>
<td>-</td>
<td>(Cheng et al. 2005)</td>
</tr>
<tr>
<td>BaCe₀.₉₅Eu₀.₀₅O₃.₆</td>
<td>650 - 850</td>
<td>0.15</td>
<td>0.0013</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>(Song et al. 2005)</td>
</tr>
<tr>
<td>BaCe₀.₉₅Sm₀.₀₅O₃.₆</td>
<td>650 - 850</td>
<td>0.15</td>
<td>0.0001</td>
<td>0.0005</td>
<td>-</td>
<td>-</td>
<td>(Wachsman et al. 2003)</td>
</tr>
<tr>
<td>La₈WO₁₂</td>
<td>600 - 1000</td>
<td>?</td>
<td>?</td>
<td>0.007</td>
<td>-</td>
<td>-</td>
<td>(Larring et al. 2006)</td>
</tr>
<tr>
<td>SrCe₀.₉₅Yb₀.₀₅O₃.₆</td>
<td>600 - 1000</td>
<td>0.002</td>
<td>80</td>
<td>0.01</td>
<td>/0</td>
<td>/0</td>
<td>(Hamakawa et al. 2002)</td>
</tr>
<tr>
<td>50 vol% BaCe₀.₉₅Eu₀.₀₅O₂.₉</td>
<td>600 - 1000</td>
<td>0.5</td>
<td>1.4 ²)</td>
<td>1.7 ²)</td>
<td>+</td>
<td>+</td>
<td>(Elangovan et al. 2007)</td>
</tr>
<tr>
<td>Pd, Ce₀.₈ₓY₀.₂O₂.₉</td>
<td>600 - 1000</td>
<td>0.5</td>
<td>1.4 ²)</td>
<td>1.7 ²)</td>
<td>+</td>
<td>+</td>
<td>(Elangovan et al. 2007)</td>
</tr>
<tr>
<td>competitors for $H_2$ separation membranes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>300 - 450</td>
<td>0.025</td>
<td>41</td>
<td>2.4 ³)</td>
<td>+</td>
<td>+</td>
<td>(Caro et al. 2006)</td>
</tr>
<tr>
<td>Pd₀.₇₇Ag₀.₂₃</td>
<td>300 - 450</td>
<td>0.025</td>
<td>18</td>
<td>1.0 ³)</td>
<td>+</td>
<td>+</td>
<td>(Caro et al. 2006)</td>
</tr>
<tr>
<td>V₀.₅₄Ti₀.₂₈Ni₀.₁₈</td>
<td>250 - 400 ⁴)</td>
<td>0.89</td>
<td>1.26</td>
<td>+</td>
<td>+</td>
<td>(Adams and Korinko 2008)</td>
<td></td>
</tr>
<tr>
<td>Fe metallic glass</td>
<td>400</td>
<td>0.025</td>
<td>0.194</td>
<td>+</td>
<td>+</td>
<td>(Adams and Korinko 2008)</td>
<td></td>
</tr>
<tr>
<td>modified silica</td>
<td>200 - 350</td>
<td>0.001</td>
<td>10 - 40</td>
<td>0.015 ⁵)</td>
<td>+</td>
<td>0</td>
<td>(De Vos 1998)</td>
</tr>
<tr>
<td>60 vol% Pd/Y-doped ZrO₂</td>
<td>500 - 800</td>
<td>0.058</td>
<td>5</td>
<td>2</td>
<td>+</td>
<td>+</td>
<td>(Balachandran et al. 2008a; Song et al. 2007)</td>
</tr>
<tr>
<td>50 vol% RbNO₃ - 50 vol% LSC</td>
<td>200 - 400</td>
<td>0.85</td>
<td>0.1 - 1.0</td>
<td>0.22 - 2.2</td>
<td>+</td>
<td>+</td>
<td>(Roark et al. 2006)</td>
</tr>
</tbody>
</table>

¹) tubular supported membrane, at 600 ºC
²) at 900 ºC
³) at 450 ºC, assuming a non-reported membrane thickness of 25 μm
⁴) at 900 ºC
⁵) from analogous Nb-Ti-Ni alloys (Ockwig and Nenoff 2007)
⁶) Recalculation to the unit mentioned above is probably not done correctly for several of the mentioned materials as the difference is very large.
In the second approach, one of the metals forming the class I proton conductor is multivalent (e.g. Eu$^{3+}$, Yb$^{3+}$, Ti$^{4+}$, W$^{6+}$), promoting n-type conduction. Figure 4.1 shows the results of H$_2$ permeabilities for a number of oxide materials, investigated by Larring et al. (Larring et al. 2006). The main bottleneck, though, seems to be a low electronic conduction. Attempts to measure H$_2$ flux in perovskites having multivalent transition metals like Co, Mn and Fe on the B site have so far been unsuccessful. The group of BaCe$_{1-x-y}$Zr$_x$Y$_y$Pr$_z$O$_{3-δ}$ compounds where 0.4 ≤ x ≤ 0.5, 0.15 ≤ y ≤ 0.20, and 0.03 ≤ p ≤ 0.05 may be another good candidate (Melnik et al. 2008), because these materials show mixed conduction above 700 ºC and are in addition stable in H$_2$O or CO$_2$ containing gas atmospheres. Ru-doped BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$ is a special case, in that Ru is not a multivalent metal, whereas mixed conduction has been experimentally confirmed by Ru-doped BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$ (Matsumoto et al. 2006).

The absence of a metal that may migrate or is sensitive to certain syngas components, makes membranes of class I proton conductors with a multivalent component more robust than the cermet-based materials. A method to prepare membranes based on this type of class I proton conductors and with high stability in CO$_2$ and H$_2$O containing atmospheres in addition, has been recently suggested by a patent of Ceramic, Inc. (Elangovan et al. 2007). They prepared a composite consisting of a non-stoichiometric perovskite A$_{1-x-y}$P$_x$B$_{1-y}$Q$_y$O$_{3-δ}$, where A and B are the divalent and tetravalent ions of the perovskite structure, and P and Q are their respective dopants, and its reaction products upon exposure to CO$_2$ or H$_2$O containing gas atmosphere BO$_2$ or B$_1$Q$_y$O$_{2-δ}$. This decreases the activity of the divalent metal A towards CO$_2$ and H$_2$O, and shifts in addition the equilibrium reaction towards the reactants. High H$_2$ permeability and stability was observed for equimolar mixtures of BaCe$_{0.8}$Eu$_{0.2}$O$_{2.9}$ and Ce$_{0.8}$Y$_{0.2}$O$_{2.9}$.

Table 4.1 shows an overview of the most important properties of the two groups of class II conductors:

- the temperature range T in which the proton conducting material can be applied,
- the measured H$_2$ flux, H$_2$ permeability and membrane thickness,
- the chemical stability towards CO$_2$ and H$_2$O, and
- the development potential.

The H$_2$ flux and permeability have been measured at 700 ºC and using pure H$_2$ as the feed gas, unless indicated. In general, the cermets have a higher H$_2$ permeability than the multivalent metal doped class I conductors. This may be due to the presence of a catalytic activity of the metal in the cermet for H$_2$ disociation and association (Haugsrud 2007; Phair and Badwal 2006). Therefore, the H$_2$ permeability of doped class I conductors may be improved by adding a catalytic layer on both sides of the membrane material. Only one measured selectivity value was found: a H$_2$ to N$_2$ selectivity of 5.7 for the tubular supported membrane mentioned in Table 4.1 (Okada et al. 2007).

The H$_2$ flux depends on the H$_2$ partial pressure difference as shown by the data of Hamakawa et al. (Hamakawa et al. 2002), see Figure 4.2. The process gases, a H$_2$/He and a N$_2$/O$_2$ mixture at upstream and downstream sides, respectively, flowed across the membrane sides at atmospheric pressure. The same authors found that the measured H$_2$ flux is proportional with the inverse membrane thickness down to 2 μm for a supported SrCe$_{0.5}$Yb$_{0.5}$O$_{3-δ}$ membrane, indicating bulk diffusion control in the investigated thickness range. In the abstract of their paper, a maximum H$_2$ flux of 6x10$^{-4}$ mol/ min.cm$^2$ is mentioned while from Figure 7 of their paper follows that the maximum H$_2$ flux is 6x10$^{-5}$ mol/ min.cm$^2$. Here, the latter value has been used in Table 4.1 since it is more in agreement with the other data of multivalent component conductors.

Zuo et al. measured the H$_2$ flux through membranes of Ni-Ba(Zr$_{0.8}$Ce$_{0.2}$)O$_{3-δ}$ with 0.4 ≤ x ≤ 0.8 (Zuo et al. 2006). They found that when using humidified feed gas (4% H$_2$, 3% H$_2$O, balance He) the H$_2$ flux increased by a factor 3 to 4 in comparison with dry feed gas containing 4% H$_2$ and balance He (Figure 4.3). They also found that the stability of their Ni-BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$ membrane is dramatically increased when between 12.5 and 50% of the B-site Ce is substituted by Zr at the expense of a slight decrease of the H$_2$ flux. They measured the variation of H$_2$ flux with time when the feed gas composition changed from a H$_2$/He mixture to a mixture containing 3% H$_2$O, 20 or 30% CO$_2$, 40% H$_2$, balanced by He (Figure 4.4). The H$_2$ flux showed an imme-
diate decrease by a quarter to half of its initial value during the change in composition, but remained stable during the remaining 80 hours of the experiment. The H$_2$ flux decrease depended on the CO$_2$ concentration and Zr content of the membrane. Increasing the CO$_2$ concentration or lowering the Zr content yielded a larger decrease.

Figure 4.3 H$_2$ flux versus temperature for 0.5 mm thick membranes of Ni-BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$, Ni-BaZr$_{0.8-x}$Ce$_x$Y$_{0.2}$O$_{3-\delta}$ and Ni-BaZr$_{0.6}$Ce$_{0.2}$Y$_{0.2}$O$_{3-\delta}$ denoted as BZY/N, BZCY7/Ni and BZCY6/Ni, respectively, using dry (4% H$_2$, balance He) and wet feed gas containing in addition 3% H$_2$O (Zuo et al. 2006)

Figure 4.4 Time dependence of H$_2$ flux through 0.75 mm thick Ni-Ba(Zr$_{0.8-x}$Ce$_x$Y$_{0.2}$)O$_{3-\delta}$ (0.4 ≤ x ≤ 0.8) membranes at 900 ºC using feed gas containing 3% H$_2$O, 20% CO$_2$, 40% H$_2$, balanced by He (Zuo et al. 2006)
A comparison experiment using a Ni-BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$ membrane, the non-substituted reference, showed a strongly decreasing H$_2$ flux upon changing the gas atmosphere due to the formation of an insulating BaCO$_3$ layer on top of the membrane. This corresponds with the findings of Fang et al. (Fang et al. 2008), who found Ba(OH)$_2$ and CeO$_2$ in samples of BaCe$_{0.9}$Y$_{0.1}$O$_{3-δ}$ membranes exposed to different partial water pressures in the temperature range 600 - 750 ºC.

For mixed ionic-electronic conducting membranes for hydrogen separation, it is important that the electronic conduction is high at both the feed and permeate side. Otherwise flux restriction occurs. Most mixed conducting perovskites have certain n-type contribution in a reducing atmosphere, which diminishes fast at higher oxygen pressure where p-type conductivity dominates. This flux restriction will decrease at expected process conditions due to the presence of a low H$_2$ pressure at the permeate side. Figure 4.5 shows an example of results for Ca-doped and undoped La$_6$WO$_{12}$. The conductivity vs. pO$_2$ curves show n- and p-type conduction at low and high pO$_2$, or left and right side, respectively, and a pO$_2$-independent ionic contribution, shown by other means to be mainly protonic.

To determine the power law dependence of the hydrogen flux on the partial hydrogen pressures at upstream and downstream sides, a model fit must be made (Song et al. 2005). Different power laws are observed depending on the conditions. For example, SrCe$_{0.95}$Yb$_{0.05}$O$_3$ shows a 1/4 dependency for wet feed and permeate gases, while it has a 1/2 dependence for dry gases (Larring et al. 2006). Similarly, Nd$_{5.94}$Ca$_{0.06}$WO$_{12}$ has a 1/2 dependence at temperatures above 900 ºC, while it is independent of the H$_2$ pressure at lower temperatures (Haugsrud and Norby 2006b). For the comparison of the H$_2$ permeabilities, the same, although not necessarily valid power law dependence of the H$_2$ pressure was assumed for all materials of Table 4.1 (a square root dependence). The cermet-based membranes show higher H$_2$ permeabilities at 700 ºC than the multivalent component oxides, comparable with that of Pd membranes at 500 ºC. Research is in full progress (Norby et al. 2006b) and new results are awaited. Pyrochlores of Ti$^{4+}$ and other tetravalent cations, oxides with hexavalent Mo and W are investigated. The rare earth ortho niobates and tantalates, mentioned as class I proton conductors, are not very reducible and exhibit too little n-type conductivity. Moving to compounds with higher stoichiometric ratio of the acidic component (e.g. LaNb$_3$O$_9$) appears in general to increase the n-type conduction, but the level of proton conduction is unknown as yet.
4.2 Applications

4.2.1 Hydrogen separation

As mentioned, the most important application of class II conductors is for separation or purification of hydrogen or hydrogen-containing gas mixtures, respectively. A partial H$_2$ pressure difference over a membrane containing class II material allows for a H$_2$ flux with in principle infinite selectivity. A detailed description of how such a class II-based membrane, consisting of 9 layers including protective layers, catalytic layers for H$_2$ dissociation and association and diffusion barriers, would perform like in practical applications is given by a patent of Eltron Research Inc. (Boulder, Co, USA) (Roark et al. 2006). This patent contains lots of experimental data of H$_2$ permeation measurements of layered membranes, being mostly in the range 5 - 25 cm$^3$/min.cm$^2$ at 1 bar partial H$_2$ pressure difference over the membrane. The non-porous, selectively permeable (NPSP) layer not only consists of cermet-based composites, but also of V-Ti alloy, Pd or Pd based alloy and metal-salt composites.

4.2.2 Steam dissociation

The mixed protonic electronic conducting membranes used for H$_2$ separation, could in principle be used for non-galvanic steam dissociation, the difference in H$_2$ partial pressure being the driving force rather than the applied voltage. This application has not been shown using such membranes, though it has been shown for mixed oxygen ion electronic conducting membranes. For example, H$_2$ production rates between 0.1 and 1 cm$^3$/min.cm$^2$ have been found in the temperature range 700 - 900 ºC for a 1 mm thick ceramic metal composite (cermet) membrane consisting of 40 vol% Ni and Gd doped CeO$_2$, using 4% H$_2$/He and 3% H$_2$O/N$_2$ gas mixtures at the permeate and retentate sides, respectively (Balachandran et al. 2007). H$_2$ production rates between 0.01 and 1 cm$^3$/min.cm$^2$ have been found in the temperature range 600 - 900 ºC for a 1 mm thick membrane of SrFeTi$_x$O$_{3-δ}$ (0.1 ≤ x ≤ 0.4), using the same gas mixtures at the permeate and retentate sides as above (Balachandran et al. 2008b).

4.2.3 Hydrocarbon reforming

Hydrocarbon reforming could in principle be performed using a class II conducting membrane for steam permeation as discussed in Section 3.3.1 without external load. The driving force is the steam concentration gradient over the membrane (Figure 3.2). The only experimental data are for a fuel cell using a class II conductor and dry methane a feed operated at zero current density: a steam methane reforming membrane reactor (Figure 3.3). No gas flow rates are given so that no H$_2$ permeance can be calculated. On the other hand, values of the O$_2$ permance in a mixed oxygen ion electronic conducting membrane reformer for partial oxidation of hydrocarbons have been experimentally obtained. An example of such a reactor is shown in Figure 4.6. Partial oxidation of methane and steam methane reforming, which consumes the heat produced by the partial oxidation, occurs at the permeate side, oxygen adsorption followed by oxygen reduction at the retentate side. Measured O$_2$ fluxes in a POM (partial oxidation of methane) reactor are given in the review paper by Caro (Caro 2006). They vary from 2 to 12 cm$^3$/min.cm$^2$ for temperatures between 850 and 900 ºC, an order of magnitude larger than the H$_2$ fluxes of Table 4.1. The largest difficulty in such reactors is the instability of the MIEC membrane at reducing conditions. By material improvement, Eltron Research has developed a MIEC membrane material that was able to maintain a constant CH$_4$ conversion for 1 year at 900 ºC (SAMMELLS et al. 2000). Experimental data of the partial oxidation of ethanol in a membrane reactor are given by Balachandran et al. (Balachandran et al. 2008b). For a tubular membrane with 0.72 mm wall thickness, they have found an O$_2$ flux of 0.1 cm$^3$/min.cm$^2$ and an ethanol conversion of 50% at 900 ºC.
4.3 Systems

4.3.1 Membrane reformer

Within the Carbon Capture Project, dense hydrogen mixed conducting ceramic membranes (HMCM) have been developed, and a techno-economically viable precombustion de-carbonization (PCDC) power generating process has been designed, based on the hydrogen membrane reformer (HMR) concept (Vigeland and Aasen 2005). The two step HMR concept combines steam methane reforming (SMR) and HMCM (Figure 4.7) and has been patented by Norsk Hydro (Åsen and Andersen 2002). The whole system is shown in Figure 4.8. Natural gas fuel, mixed with steam, is fed to the feed side of the membrane section loaded with SMR catalyst in step 1, and undergoes steam methane reforming. The produced $\text{H}_2$ is transported through the membrane and reacts with air, extracted from the gas turbine compressor, generating a $\text{H}_2$, $\text{N}_2$ and $\text{H}_2\text{O}$ containing sweep gas, and providing heat for the endothermic SMR reaction. This sweep gas is used to recover most of the produced $\text{H}_2$ in a second step membrane reformer, generating a high pressure (15 - 20 bar) $\text{H}_2$ fuel containing about 40% $\text{H}_2$, 40% $\text{N}_2$ and 20% $\text{H}_2\text{O}$. The $\text{H}_2$ fuel mixture is then combusted with air in the gas turbine. The residual synthesis gas containing mainly $\text{CO}_2$, $\text{H}_2\text{O}$ and $\text{CO}$ is converted to $\text{CO}_2$ and $\text{H}_2\text{O}$ in an oxidation section. $\text{CO}_2$ can then be captured by condensation of the water vapour, compressed and liquefied, and pumped to the actual injection pressure. For the design of the ceramic structure, information from another CCP project called AZEP, using oxygen transport ceramic membranes for power production with $\text{CO}_2$ capture, was used. In AZEP, plate and tube configurations were considered but the selection ended up with monolith or honeycomb structures with small channels. Permeability measurements were performed on 35 candidate membrane materials. No specification of the investigated materials is given. A 20 to 100 $\mu$m thick dense layer is prepared on a porous tubular support of the same powder as the membrane but with 40% corn starch admixed to create porosity. The data were transformed to flux values at process conditions (20 $\mu$m thick supported membrane, 1000 °C, 20 bar and a steam/carbon ratio of 2, with 20% $\text{H}_2$ extracted from the feed gas, and 0.1 bar $\text{H}_2$ in the permeate) using a model, which required four fundamental material parameters (enthalpy and entropy of $\text{H}_2$ dissolution, activation energy and pre-exponential factor of the $\text{H}_2$ diffusion coefficient). Several materials were found to exceed the target flux (5 ml STP/min.cm²).
A process evaluation was also performed, see Table 4.2. Efficiency loss is estimated to be only 5%-points compared with a conventional CCGT plant without CO₂ capture. This includes compression of purified CO₂ to 150 bar.

<table>
<thead>
<tr>
<th></th>
<th>H₂ membrane CCGT</th>
<th>conventional CCGT</th>
</tr>
</thead>
<tbody>
<tr>
<td>total fuel consumption (MW)</td>
<td>681.0</td>
<td>681</td>
</tr>
<tr>
<td>net power output (MW)</td>
<td>361.9</td>
<td>395</td>
</tr>
<tr>
<td>thermal efficiency, incl. CO₂</td>
<td>53.1%</td>
<td>58.0%</td>
</tr>
<tr>
<td>CO₂ emission (t/hr)</td>
<td>close to zero</td>
<td>144.1</td>
</tr>
</tbody>
</table>
5. Discussion

5.1 Class I conductors - materials

Table 5.1 summarizes the properties of the class I materials, as discussed in Chapter 3, for convenience divided into high and low temperature groups, covering the ranges 500 - 900 °C and 300 - 750 °C, respectively. Here, stability refers to chemical stability with respect to both CO₂ and H₂O, the main process gas constituents. As discussed before, other types of stability should be known (kinetic and mechanical stability). Since hardly any data is available concerning these types of stability, they have been left out from the table, not because they are considered less important than the chemical stability. The conductivity and chemical stability are ranked by '+' and '-' signs to indicate if they perform positively or negatively, respectively, while '0' indicates a position in between. The '?' sign positioned between two of the previously-mentioned signs is used for further refinement. A '?' sign means that no data is available to make a ranking. A '?' sign next to a a '+' or '-' or '0' sign means that either the ranking has been anticipated on the basis of indirect data, or that conflicting data exist which preclude a definitive ranking. For example, the compound LaNbO₄ is expected to be more stable than the well-known doped BaCeO₃ and SrCeO₃ perovskites because of the absence of Ba or Sr, though it has not been determined experimentally. As to the stability of La₅.₈WO₁₁.₇ compounds, as another example, conflicting data exist (Haugrud 2007; Shimura et al. 2001). Consequently, a '?' sign implies that further research is needed to make definite evaluation.

Table 5.1 Properties of class I conductors

<table>
<thead>
<tr>
<th>material</th>
<th>conductivity</th>
<th>stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>high T group (500 - 900 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCe₀.₆Zr₀.₂Y₀.₂O₃₋₄₆</td>
<td>+</td>
<td>0/+</td>
</tr>
<tr>
<td>La₅.₄WO₁₁.₇</td>
<td>+</td>
<td>+?</td>
</tr>
<tr>
<td>La₀.₉₉Ca₀.₀₁NbO₄</td>
<td>0</td>
<td>+?</td>
</tr>
<tr>
<td>Ln₀.₉₉Sr₀.₀₁PO₄</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>La₀.₉₉Ba₁₋₃GaO₃₋₉₄</td>
<td>-</td>
<td>0?</td>
</tr>
<tr>
<td>low T group (300 - 750 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La₁.₉₅Ca₀.₀₅Zr₂O₆.₉₇₅</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ba₂In₁.₃₆Ce₀.₅₁O₁.₉₁</td>
<td>+</td>
<td>?</td>
</tr>
<tr>
<td>La₅Oₓ(BO₃)₈</td>
<td>0</td>
<td>?</td>
</tr>
</tbody>
</table>

Next to the well-known doped BaCeO₃ and SrCeO₃, good alternative materials exist of similar or lower conductivity, in the latter case probably better in other respects. Stability remains the less well investigated issue for most materials. Operation of several class I conductors down to 300 °C is possible, making them competitive with, for example, solid acids for replacing the polymer membrane in PEMFCs with one that is less susceptible to a delicate water management and able to reduce the precious metal loading.

5.2 Class I conductors - applications

5.2.1 Fuel cells

From Table 3.1 follows that the state-of-the-art power density of a fuel cell with proton conducting electrolyte (SOFC-H) is 400 mW/cm². For comparison, state-of-the-art values of the power density of a polymer electrolyte membrane fuel cell (PEMFC), a phosphoric acid fuel cell (PAFC), a solid acid fuel cell (SAFC), a molten carbonate fuel cell (MCFC), an electrode-supported thin electrolyte solid oxide fuel cell with oxygen ion conducting membrane (SOFC-O), and a fuel cell with solid oxide-carbonate composite as electrolyte (SO/carb) are given in Table 5.2.
The SAFC is not mentioned in the Fuel Cell handbook version of 2004. Solid acids have been investigated as a new electrolyte material for fuel cells since the last 5 years. Compounds within this class are based on tetrahedral oxyanion groups, such as CsHSO$_4$, Rb$_3$H(SeO$_4$)$_2$ and (NH$_4$)$_3$H(SO$_4$)$_2$, and exhibit anhydrous proton transport with conductivities of the order of 1 to 10 mS/cm at moderate temperatures (120 - 300 ºC), which should be above their so-called superprotonic temperature characterized by subtle changes in the hydrogen bond network. Unlike the polymers in PEMFCs, proton conduction in oxyanion solid acids does not rely on the migration of hydronium ions H$_3$O$^+$. The operation temperature window allows reduction of the precious metal loading and higher tolerance to poisons, in particular CO in the fuel stream. Water solubility appears to be the most important challenge to overcome. Measures must be taken to prevent condensed water from contacting the electrolyte which it is. Further, recent work of Haile et al. has shown that a humidified gas atmosphere is required to prevent dehydration above the superprotonic temperature of CsHSO$_4$ (Haile et al. 2007). They built H$_2$ and alcohol fed fuel cells with 25 μm thick solid acid based electrolytes, showing excellent power output (Table 5.2).

Another type of fuel cell, not mentioned in the Fuel Cell Handbook of 2004, though competitive with the class I conductor-based fuel cell has been realized by the development of solid oxide-salt composites. The best-performing cell consists of a mixture of the oxides La$_2$O$_3$, CeO$_2$ and Pr$_6$O$_{11}$ (LCP) and 20 wt% carbonate salts (a mixture of Li$_2$CO$_3$ and Na$_2$CO$_3$ in the molar ratio 2 to 1), forming an oxygen conducting and a proton conducting phase, respectively (Zhu et al. 2008; Zhu and Mat 2006). The conductivity of the LPC-carbonate composite is 170 mS/cm at 650 ºC. If pure LCP would be used as electrolyte in the fuel cell, the performance would soon deteriorate due to the reduction of Ce$^{4+}$ to Ce$^{2+}$ and/or Pr$^{4+}$ to Pr$^{3+}$, causing electronic conduction. Stability is improved by making the before-mentioned LPC-carbonate composite. Fuel cells using this composite have been stable for hundreds of hours. The two phases consist of nanoparticles (< 100 nm). The enhanced conductivity is believed to be due to the two-phase contact regions where oxygen ion and proton transport as HCO$_3^-$ ions occurs, so-called interfacial superionic conduction. Compared with the class I conductors, the chemical stability towards CO$_2$ of the LPC-carbonate electrolytes is better. Some evaporation loss may occur due to reaction of the carbonate with steam, though it will be less than in MCFCs due to the lower carbonate content. Electrolyte tiles in molten carbonate fuel cells contain typically 45 wt% LiAlO$_2$ and 55 wt% carbonate mixture (EG&G Technical Services 2004).

Table 5.2 Power densities of various fuel cell types, ceramic-salt based cells are distinguished by the composite composition

<table>
<thead>
<tr>
<th>fuel cell type</th>
<th>T (ºC)</th>
<th>P (mW/cm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>70</td>
<td>150</td>
<td>(EG&amp;G Technical Services 2004)</td>
</tr>
<tr>
<td>PAFC</td>
<td>200</td>
<td>300</td>
<td>(EG&amp;G Technical Services 2004)</td>
</tr>
<tr>
<td>SAFC</td>
<td>240</td>
<td>400</td>
<td>(Haile et al. 2007)</td>
</tr>
<tr>
<td>MCFC</td>
<td>650</td>
<td>150</td>
<td>(EG&amp;G Technical Services 2004)</td>
</tr>
<tr>
<td>SOFC-O</td>
<td>800</td>
<td>490</td>
<td>(Huijsmans et al. 1998)</td>
</tr>
<tr>
<td>LCP-Li$<em>{1.33}$Na$</em>{0.67}$CO$_3$</td>
<td>650</td>
<td>600</td>
<td>(Zhu et al. 2008)</td>
</tr>
</tbody>
</table>

Competitors of SOFC-Hs are, restricting to fuel cells that enable steam-methane reforming in the anode compartment:
- SOFC-O with supported or thin (5-20 μm), oxygen ion conducting electrolyte,
- MCFC, and
- SO/carb.

Table 5.3 summarizes the properties of these fuel cells, again using the above-mentioned '+' , '-' , '0' , and '?' signs. All cells operate at high temperatures, i.e. between 650 and 800 ºC. The power densities are state-of-the-art lab-scale values, not necessarily relating to large-scale stack values. Next to the chemical stability ('chem. stab.'), which includes losses due to evaporation, the mechanical stability ('mech. stab.') is indicated. They are probably slightly better for the ceramic-salt than the molten carbonate containing fuel cells, because of the higher ceramic/carbonate weight ratio and lower vapour pressure of the applied applied carbonate mix-
ture (Li-Na for SO/carb. vs. Li-K for MCFC). Cell voltage decay rates ('cell volt. decay') refer to stack values (EG&G Technical Services 2004; Haugsrud 2007). The possibility of using the cell for electrolysis is indicated by '+' in the column labeled as 'electrol.'. The fact that the carbonate containing fuel cells do not allow electrolysis is that use of a steam containing stream without CO$_2$ would yield an unacceptable loss of carbonate due to reaction with steam. Electrode compatibility ('electrode compatib.') with the electrolyte and status are shown in the last two columns. The more commercial the status, the higher the ranking. Thus, a '-' sign indicates laboratory, basic research stage.

Table 5.3 Properties of high-temperature fuel cells

<table>
<thead>
<tr>
<th>type</th>
<th>$P$ (mW/cm$^2$)</th>
<th>chem. stab.</th>
<th>mech. stab.</th>
<th>cell volt. decay (mV/1000 hr)</th>
<th>electrol.</th>
<th>electrode compatib.</th>
<th>status</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOFC-H</td>
<td>300 - 400</td>
<td>+</td>
<td>-?</td>
<td>?</td>
<td>+</td>
<td>?</td>
<td>-</td>
</tr>
<tr>
<td>SOFC-O</td>
<td>500 - 1000</td>
<td>+</td>
<td>0</td>
<td>-2</td>
<td>+</td>
<td>+</td>
<td>0/+</td>
</tr>
<tr>
<td>MCFC</td>
<td>150</td>
<td>0/-</td>
<td>0</td>
<td>-5</td>
<td>-</td>
<td>+</td>
<td>0/+</td>
</tr>
<tr>
<td>SO/carb</td>
<td>600</td>
<td>0?</td>
<td>0/+?</td>
<td>?</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

5.2.2 Membrane reactor

Proton-conducting membranes can be used for other applications than fuel cells and electrolysis. For some of these (steam-methane reforming, water-gas shift and oxidative methane coupling), oxygen ion conducting membranes can be used as well. At the moment, there is insufficient data for a good comparison. Further development should make clear which type of membrane is most suitable. For other applications (ammonia synthesis), only proton-conducting membranes can be applied. Compared with conventional catalytic reactors, proton-conducting membrane reactors offer several, potential advantages:

- production of two valuable chemicals and simultaneous separation (e.g. dehydrogenation of C$_3$H$_8$ to C$_3$H$_6$), combined with production of electric power if the reactor is operated in fuel cell mode,
- considerable enhancement of the conversion due to the NEMCA effect (e.g. reverse water-gas shift), and
- operation at milder conditions (e.g. requirement for high pressure in NH$_3$ synthesis is replaced by electrical energy supply).

5.3 Class II conductors - materials

Table 5.4 summarizes the properties of the class II materials, as discussed in Chapter 4, using the notation as before. All materials operate in the same temperature range (500 - 900 ºC). The H$_2$ permeability and stability are used as main characteristics. Again, stability refers to chemical stability with respect to both CO$_2$ and H$_2$O. Here, 'APD' refers to the ambipolar diffusion enhanced materials, i.e. the class II conductors being doped with such a metal that the electronic or hole conduction is increased. In the cermets, a distinction is made between Pd and Ni based cermet, the latter having a slightly lower H$_2$ permeability, though better stability. The best performing class II conductor is the ceramic/ceramic composite where an n-type semiconductor has been added to the class I conductor, developed by Eltron Research. Stability has not been fully investigated but is expected to be better than that of APDs or cermets.

Table 5.4 Properties of class II conductors

<table>
<thead>
<tr>
<th>material</th>
<th>H$_2$ permeability</th>
<th>stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>APD</td>
<td>0/+</td>
<td>0/+</td>
</tr>
<tr>
<td>cer./Pd</td>
<td>+</td>
<td>-/0</td>
</tr>
<tr>
<td>cer./Ni</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>cer./cer.</td>
<td>+</td>
<td>+?</td>
</tr>
</tbody>
</table>
5.4 Class II conductors - applications

5.4.1 H₂ separation

As fuel cells are the most important application for class I conductors, H₂ separation is the most important one for class II conductors. A large number of materials for hydrogen separation membranes have been developed in the last 20 years, see Table 5.4. Part of the materials have been discussed by Van Veen and Van Delft in their report (Van Veen and Van Delft 2007): polymers, Pd and its alloys (Pd-Cu and Pd-Ag), carbon and porous ceramics, next to a brief discussion of both types of class II conductors. Four new material groups have been added: non-Pd crystalline alloys, amorphous alloys, metal-salt composites and ceramic-metal composites. This gives a total of 10 materials groups. Of these, polymers, silica and its modifications (member of the porous ceramics group), and molsieve carbon operate most efficiently below 300 °C. Next to other disadvantages (low flux and selectivity of polymers, stability of silica, brittleness of carbon), this makes their use under water-gas shift or steam-methane reforming conditions doubtful (H₂, CO, CO₂, H₂O, CH₄, S compounds, 400 - 800 °C). Other non-silica containing porous ceramics (alumina, zirconia, titania), or SiN or SiC, or even zeolites may offer better prospects, but their development requires much more research (Ockwig and Nenoff 2007).

Crystalline, non-Pd based alloys are known to exhibit high H₂ permeabilities. By choosing the appropriate metals, the disadvantages of the Pd-based alloys (embrittlement, sensitivity to gaseous impurities) can be suppressed, while maintaining a single-phase bcc structure that is required for high H₂ permeation. Factors influencing the H₂ permeance are the grain size, H₂ interactions with chemical or structural defects, and quasicrystallinity (Ockwig and Nenoff 2007). A recently investigated example of a crystalline alloy is V₀.54T₀.28Ni₀.18 (Table 4.1). Unfortunately, this material showed the formation of vanadium-hydride phase in this sample which resulted in the subsequent failure of the membrane (Ockwig and Nenoff 2007).

Amorphous metals are usually reported to have increased strength, ductility, corrosion resistance and, more importantly, H₂ solubility than their crystalline analogues. Furthermore, they contain a more open lattice which decreases the embrittlement dangers due to H₂ interaction, and can withstand repeated cycling, high temperatures and high pressures. Their most important disadvantage is their tendency to crystallize when heated to temperatures above 500 °C since they are thermodynamically metastable. Metallic glasses constitute an important subgroup of the amorphous alloys. The development of metallic glasses in bulk form has led to a resurgence of interest into the potential utilization of these materials for a variety of applications. Prior to this development, metallic glasses were produced exclusively in very thin sections by rapid solidification processing in most cases. The subsequent consolidation into something “bulk” frequently led to devitrification and a loss in the desirable properties characteristic of the glass. An exciting application for these new bulk metallic glass (BMG) materials is use as hydrogen membranes or hydrogen storage materials when light metals are used. The ability to readily cast metallic glass alloys will allow for easier fabrication of membranes and will also ease mass production challenges in comparison to thin section (melt spun) metallic glass ribbons. Bulk metallic glass alloys are traditionally processed from multi-component system comprised of metallic species of varying atomic size. It is this vast difference in atomic sizes that results in slow diffusion/redistribution kinetics and allows for deep undercoolings to the point of freezing in the “liquid” structure to produce amorphous metallic alloys at relatively slow cooling rates (10-100 K/s). At Savannah River national Laboratory, research in BMG alloys as H₂ permeable membranes has recently started. They have tested three commercial BMG foils (Adams and Korinko 2008). The measured H₂ permeability of one of them, MetGlass 12, an Fe containing metallic glass is an order of magnitude lower than that of Pd. The cost is three orders of magnitude lower, making this BMGs an interesting materials group for further H₂ separation studies.

Ceramic-salt composites have been mainly investigated by the group of Zhu et al., who also developed ceramic-salt composites for fuel cells (see Section 3.3.1). The difference is that in the latter case, the ceramic phase is (mainly) an oxygen ion conductor, while in the former case, it
should be electronic conducting. Proton conducting salts include oxyacid salts like the nitrates, sulphates and phosphates of Li, Na, K, Rb and Cs. Conductivities between 10 and 100 mS/cm have been reported for various compositions (Zhu and Mellander 1995b). For some of these salts, the conductivity and structural stability was substantially improved by addition of a second insulating phase like Al$_2$O$_3$, SiO$_2$, CeO$_2$, ZrO$_2$, MgO, CaO or ZnO (Zhu 1999). Moreover, the composite allowed use of the salts at temperatures well above their melting point where the conductivity is at a maximum (Zhu and Mellander 1995a). For example, conductivities between 10 and 100 mS/cm were measured for RbNO$_3$-Al$_2$O$_3$ at 480 ºC, which is well above the melting point of RbNO$_3$ (310 ºC). For H$_2$ separation, the salt must be combined with an electronic conducting phase, preferably a H$_2$ transport metal to increase the H$_2$ permeability. Phair investigated the stability of Pd/alkali nitrate composites with 30 wt% Pd in a reducing atmosphere (Phair 2007). Without Pd, the nitrate did not decompose at temperatures below 600 ºC. However, in the presence of Pd, the nitrate decomposed at significantly lower temperatures, yielding NH$_3$, NO$_2$, NO and alkali metal. The decomposition was assumed to be catalyzed by Pd metal. Instability was also observed in RbNO$_3$/Ag and RbNO$_3$/Ni composites, both 50 vol%/50 vol% (Roark et al. 2006). (Note that we are dealing with metal-salt composites here.) In the first material, the RbNO$_3$ had migrated to the membrane surface and partially enveloped surface Ag. The second composite became soft and moist. XRD analysis revealed the presence of Ni, and probably its oxide or hydroxide. On the other hand, no signs of chemical or mechanical degradation were observed for RbNO$_3$/La$_{1-x}$Sr$_x$CoO$_3$ (50 vol%/50 vol%) after several days of testing.

Ceramic-metal composites are currently investigated by Argonne National Laboratory, and forms the third class next to the two classes mentioned in section 4.1, which they study (Balachandran et al. 2008a). To prepare the composite, a metal with high hydrogen permeability (called a “hydrogen transport metal”) is dispersed in a ceramic support matrix. In these composites, hydrogen is transported almost exclusively through the hydrogen transport metal, and the matrix serves primarily as a chemically stable structural support. An example is a composite consisting of 60 vol% Pd and Y-doped ZrO$_2$. In an experiment using a Pd/yttria-stabilised zirconia cermet, it was found that the membrane retained its integrity during 100 hours at 900 ºC in a syngas atmosphere (61.3% H$_2$, 8.2% CH$_4$, 11.5% CO, 9.0% CO$_2$, 10% He) to which even 100 ppm H$_2$S had been added, as determined by the He leakage rate through the permeate side. Increasing the H$_2$S content to 400 ppm resulted in a 10% loss of H$_2$ flux, but an increase to 3000 ppm yielded more than 70% loss (Balachandran et al. 2006).

The above-mentioned composites are also mentioned by Bredesen et al. in their review paper on high-temperature membranes for CO$_2$ capture in power generation as a promising new class of membrane materials (Bredesen et al. 2004). Here, they are called "metal membranes dispersed in support pores". Lots of metals have been tried. Noble metal membranes prepared by CVD deposition in porous alumina supports show high H$_2$ permeance, despite lower bulk H$_2$ diffusivity. It is believed that the classical solution-diffusion mechanism does not apply to these CVD membranes. Instead, the H$_2$ molecule which splits on the metal surface, migrates as surface species.
<table>
<thead>
<tr>
<th>membrane type</th>
<th>materials</th>
<th>T range (°C)</th>
<th>H₂ flux at dP = 1 bar (mol/m².s)</th>
<th>H₂ selectivity</th>
<th>commercially available</th>
<th>stability issues</th>
<th>poisoning issues</th>
<th>research issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>dense polymer</td>
<td>polymers</td>
<td>&lt; 250</td>
<td>0.01 - 0.02</td>
<td>2 - 15</td>
<td>freestanding membranes</td>
<td>swelling, compaction, mechanical strength</td>
<td>HCl, SO₃</td>
<td>increase H₂/CO₂ selectivity, ceramic support</td>
</tr>
<tr>
<td>dense metallic</td>
<td>Pd and alloys</td>
<td>300 - 600</td>
<td>0.06 - 0.3</td>
<td>&gt; 1000</td>
<td>freestanding membranes</td>
<td>phase transition, segregation, embrittlement</td>
<td>H₂S, HCl, CO</td>
<td>thickness reduction, diffusion barrier, support, stability, large-scale production, seals</td>
</tr>
<tr>
<td>non-Pd alloy</td>
<td></td>
<td>300 - 600</td>
<td>0.01 - 1</td>
<td>?</td>
<td>not</td>
<td>idem</td>
<td>H₂S, HCl, CO</td>
<td>materials, preparation</td>
</tr>
<tr>
<td>amorphous alloy</td>
<td></td>
<td>&lt; 500</td>
<td>0.01</td>
<td>?</td>
<td>foils</td>
<td>crystallization</td>
<td>H₂S, HCl, CO</td>
<td>materials, preparation</td>
</tr>
<tr>
<td>molsieve carbon</td>
<td>carbon</td>
<td>&lt; 400</td>
<td>0.01 - 0.2</td>
<td>4 - 20</td>
<td>Small modules commercial</td>
<td>brittle, oxidizing atmosphere</td>
<td>Strongly adsorbing vapours</td>
<td>defect-free membrane production</td>
</tr>
<tr>
<td>porous ceramic</td>
<td>modified silica, zeolite, SiN, SiC</td>
<td>200 - 350</td>
<td>0.06 - 0.3</td>
<td>5 - 139</td>
<td>prototype tubular silica membranes</td>
<td>steam in basic or acid environment</td>
<td>decrease hydrophobicity, defect-free membrane production</td>
<td></td>
</tr>
<tr>
<td>dense ceramic</td>
<td>class II, group 1</td>
<td>600 - 900</td>
<td>0.001 - 0.2</td>
<td>?</td>
<td>not</td>
<td>steam, CO₂</td>
<td>H₂S, HCl, CO</td>
<td>materials, preparation</td>
</tr>
<tr>
<td></td>
<td>class II, group 2</td>
<td>600 - 900</td>
<td>0.001 - 1</td>
<td>?</td>
<td>not</td>
<td>steam, CO₂</td>
<td>SO₃</td>
<td>materials, preparation</td>
</tr>
<tr>
<td>metal/ceramic-salt composite</td>
<td>oxy-acid salt &amp; Pd/Ag/LSC</td>
<td>200 - 400</td>
<td>0.001 - 0.01</td>
<td>?</td>
<td>not</td>
<td>migration, reaction</td>
<td>H₂S, HCl, CO</td>
<td>materials, preparation</td>
</tr>
<tr>
<td>ceramic-metal composite</td>
<td>Pd &amp; Y-Zr₂O₃</td>
<td>300 - 600</td>
<td>0.1</td>
<td>?</td>
<td>not</td>
<td>migration, reaction</td>
<td>H₂S, HCl, CO</td>
<td>materials, preparation</td>
</tr>
</tbody>
</table>
Table 5.6 compares the class II conductors with the competitors: the dense metallic membranes including the Pd alloys (Pd-Ag and Pd-Cu), the non-Pd crystalline alloys and the bulk metallic glasses (BMGs), the porous ceramics (modified silicas, SiC, SiN, zeolite) and the composites electron-conducting solid oxide/nitrate (‘eSO/nitrate’) and electron-conducting solid oxide/Pd (‘eSO/Pd’), being the most important members of the ceramic-salt and ceramic-metal composites, respectively. A distinction has been made between high and low temperature materials, operating above 500 °C and below 600 °C, respectively. It is important to realize that the operation temperature range of class II materials differs from that of its competitors. There is hardly overlap in operation temperature range, making class II conductors suitable for certain applications for which the other H₂ separation membrane materials are not. For example, large-scale coal gasification requires temperatures in the range 1000 - 1500 °C for entrained flow systems, or 750 - 1000 °C for fluidized bed systems. This requires ceramic high temperature membranes, since cooling of the feed stream and subsequent use of a low temperature membrane would result in efficiency loss.

The properties include H₂ flux (at 1 bar H₂ pressure difference) rather than H₂ permeance since H₂ fluxes are usually specified without membrane thickness, stability divided in chemical stability ('chem. stab.'), mechanical stability ('mech. stab.') and kinetic stability ('kin. stab.'), the H₂ selectivity over CO₂ (H₂ selec.), the sensitivity to poisons ('poison') discussed in Section 4.2.1 (the higher the sensitivity, the lower the ranking), and the status using the same convention as in Table 5.1. From Table 5.5 follows that mechanical and kinetic stability should be investigated for the class II materials, the Pd-alloys and the porous ceramics. The H₂/CO₂ selectivity is in principle infinite for all materials except for porous ceramics, because adsorbed H₂ is dissolved in the membrane material and travels through it in protonic form. In porous ceramics, the H₂/CO₂ selectivity is in the range 20 - 40. Another item, not mentioned, is the sealing of the membrane to the support structure of the separation chamber by a seal that is both mechanically robust and resistant to high temperatures (Phair and Badwal 2006). Generally, the higher the temperature, the more difficult the sealing. At temperatures above 600 °C, proper sealing has not even been demonstrated so far.

Table 5.6 Properties of H₂ separation membranes

<table>
<thead>
<tr>
<th>Material</th>
<th>H₂ flux (mol/m².s)</th>
<th>chem. stab.</th>
<th>mech. stab.</th>
<th>kin. stab.</th>
<th>H₂ selec.</th>
<th>poison</th>
<th>status</th>
</tr>
</thead>
<tbody>
<tr>
<td>high-T (&gt; 500 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>class II</td>
<td>0.001 - 1</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>+</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>low-T (&lt; 600 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-alloy</td>
<td>0.06 - 0.3</td>
<td>0</td>
<td>?</td>
<td>?</td>
<td>+</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>non-Pd cryst.</td>
<td>0.01 - 1</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BMG</td>
<td>0.01</td>
<td>0/+</td>
<td>+</td>
<td>~/0</td>
<td>+</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>por. cer.</td>
<td>0.06 - 0.3</td>
<td>0</td>
<td>?</td>
<td>?</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>eSO/nitrate</td>
<td>0.001 - 0.01</td>
<td>0/+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>eSO/Pd</td>
<td>0.1</td>
<td>0/+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

5.4.2 Steam dissociation
This is in principle possible, but has not been shown so far for a class II conductor. For a mixed oxygen ion electronic conductor, it has been shown.

5.4.3 Hydrocarbon reforming
This has been shown in fuel cells using dry CH₄ feed, operated at zero current density. Membrane reactor using a mixed oxygen ion electronic conducting membrane have been shown to be able to perform partial oxidation of CH₄, oxidative dehydrogenation of alkanes and alcohols.
6. Conclusions

1. Research on proton-conducting oxides is being performed since the beginning of the nineties. The main part of this research has been for pure proton conductors which can be used in intermediate temperature fuel cells (600 - 800 ºC). In the last 5 years, oxides showing mixed protonic and electronic conduction are being investigated for hydrogen separation. In this report, these two classes have been denoted as class I and class II conductors, respectively.

2. So far, research has concentrated on materials development. In the search for new materials, the driving forces are higher conductivity and lower operation temperature. Hardly attention has been paid to long-term stability of these materials. Only one, though extensive, systems study of a CCGT power plant has been found using a membrane based on a class II conductor, financed by the Carbon Capture Project. The efficiency dropped from 58% to 53% when membranes for CO$_2$ capture were used.

3. The best performing class I conductors in terms of conductivity are mixtures of BaCeO$_3$ and Y-doped BaZrO$_3$ (perovskites), and Ca-doped La$_2$Zr$_2$O$_7$ (pyrochlore). Promising, more recently investigated materials include Ca-doped LaNbO$_4$ and LaTaO$_4$, Sr-doped rare earth phosphates (like LaPO$_4$), and gallates. These have lower conductivities (1 to 2 orders lower) than the best-performing perovskites or pyrochlores (in the order of 10 mS/cm), but their long-term stability is expected to be better. Proton conduction dominates over other conduction types in the temperature window 500 - 800 ºC, except for the pyrochlores (up to 600 ºC).

4. Class I conductors showing proton conduction down to 300 ºC are the brownmillerites (like Ba$_2$In$_2$O$_5$) and certain fluorite-related structures (for example, Ca-doped La$_6$WO$_{12}$ and La$_{26}$O$_{27}$(BO$_3$)$_8$). In this temperature range, they become competitive with solid acids and ceramic-salt composites.

5. Two groups of class II conductors can be distinguished: the cermet-based materials and the class I conductors to which a multivalent metal has been added (e.g. Eu$^{3+}$, Yb$^{3+}$, Ti$^{4+}$, W$^{6+}$), promoting n-type conduction.

6. Competitors of the fuel cell with proton conducting membrane (SOFC-H) are the SOFC with thin oxygen ion conducting membrane (SOFC-O), the MCFC, the solid oxide-carbonate based fuel cell (SO/carb), and if temperatures down to 300 ºC are taken into account, also the SAFC.

7. A general advantage of SOFC-H with respect to the other fuel cell types is that all H$_2$O is produced at the cathode side, the fuel is not diluted with it, leading to higher fuel utilization and opening certain applications that cannot be realized with the oxygen ion conducting SOFC (e.g. application in the temperature swing reformer, Section 3.4.1).

8. Specific advantages of SOFC-H with respect to SOFC-O is a lower operating temperature (thus cheaper stack construction materials), but it is not clear if this advantage out-weighs the possible stability issues related to the class I conductors. Compared with MCFC, SOFC-H shows a much higher power density and no corrosion phenomena related to the use of carbonate mixtures.
9. Apart from intermediate temperature fuel cells, class I conductors can be applied in electrolysis, H₂ pump, H₂ sensors, oxidative methane coupling and dehydrogenation membrane reactor, NH₃ synthesis and as catalyst. For electrolysis and dehydrogenation membrane reactor, also oxygen ion conducting membranes can be applied.

10. Many materials classes are currently investigated for H₂ separation membranes as alternative of pure Pd, though all of these operate at temperatures below 600 ºC: Pd-alloys, non-Pd crystalline materials, porous ceramics, bulk metallic glasses, ceramic-metal composites (e.g. Pd in Y-stabilized zirconia), and ceramic-salt composites (e.g. RbNO₃ - La₆-xSrₓCoO₃). These materials are at a more developed stage than class II conductors. For that reason, class II conductors do not seem to play a significant role in this temperature range. On the other hand, at operation temperatures above 600 ºC, only class II conductors and mixed oxygen ion-electronic conducting membranes can be applied. For each application, it should be investigated which membrane type is more beneficial.
**Recommendations**

1. Perform systems studies for power generation with CO$_2$ capture using a class I or class II conducting membrane. To start with, systems studies using an SOFC with oxygen ion conducting membrane, or a Pd(-alloy)-based membrane could be redone by replacing the oxygen ion or H$_2$ conducting membrane with a class I or class II conducting membrane, respectively. By comparing them with competitive systems, this yields a set of performance criteria of the class I and class II conductors. A follow-up experimental study on class II conductors may be done, if the systems studies results look promising.

2. Perform experimental work of class I conductors on lab-scale to duplicate the results of others and to gain experience.
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