

# CREATIVE SERVICES

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## Ultra High Temperature Ceramics

Producing hydrogen in direct thermal water splitting requires new innovative material solutions. Creative Services has examined existing possibilities and identified new options.

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### Introduction

Hydrogen is generally regarded as a clean alternative to fossil fuels, and making hydrogen using solar energy could provide a renewable and sustainable energy source. Of all solar direct (e.g. biological, physio-chemical, thermal) and indirect (e.g. photovoltaic electricity plus electrolysis) hydrogen production methods the direct thermal water splitting has the highest theoretical efficiency and, as shown by H2 Power Systems Ltd<sup>1</sup>, can be produced very cost effectively.

Direct thermal water splitting is a process in which water is evaporated and the steam is further heated to very high temperatures until the water molecules dissociate (split) into their constituents hydrogen and oxygen. This molecular dissociation is a statistical process. At ambient temperatures only very few molecules dissociate. Their number increases with increasing temperature. At around 2200°C almost five per cent of the water molecules are decomposed into hydrogen, oxygen and a few other composites made up from these two atoms. Therefore, at these ultra-high temperatures considerable amounts of hydrogen and oxygen are present in the hot steam and can be extracted from it.

The extraction of hydrogen directly from the steam does not appear being feasible easily. Only very few materials are available for use above 2200°C and the environment with steam cuts down the options further. Creative Services has studied extracting hydrogen from steam extensively. Physical methods all involve energy consuming processes like quenching or skimming. Chemical methods employ multi step process at various temperatures. Other methods employ selective filters. To obtain rather pure hydrogen, filters from materials with mixed ionic electronic conduction properties may be used. Metals and ceramic oxides have been investigated, in particular in the framework of solid oxide fuel cells. However, the competing onset of oxygen conductivity limits applications to temperatures below 1000°C. Without going into further detail one can say today, that hydrogen can be extracted from the hot steam up to about 1000°C, but there is nothing that would work above 2000°C.

The other option is to take out the oxygen first, leaving behind a mix of hydrogen enriched steam which can be separated further. Similar to hydrogen extraction, the working environment, basically steam at 2200°C or more narrows down the choices enormously.

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<sup>1</sup> H2 Power Systems Ltd is an Irish company that holds, develops and exploits a particular patented technology for hydrogen production from direct thermal water splitting.

However, and that is the important difference, a few material options survive. In the following we compile the arguments for suggesting stabilized cubic zirconia as a base material whose basic filtering properties can be further improved by different measures.

## Options for a High Temperature Oxygen Filter

Processes that can separate oxygen from hot steam.

- i. quenching
- ii. skimming (physical or chemical segregation)
- iii. molecular sieving
- iv. ion electron conduction

The first two processes require that the hot steam in which the molecules are dissociated is treated as a whole. Either it is shock cooled or it is extracted from the heating device for the skimming. In both cases the part of the gas that is not dissociated is going through a heating-cooling cycle which consumes energy but which has no value for the hydrogen or oxygen production. When quenching, a further cold gas separation process has to be employed. The skimming is not a perfect separation, and several stages have to be applied. These processes are in principal valid separation methods but the practical disadvantages make them energy-voracious, technically complicated and comparatively expensive.

The latter two processes are based on filtering. Filters provide rather cost effective and technically simple gas separation.

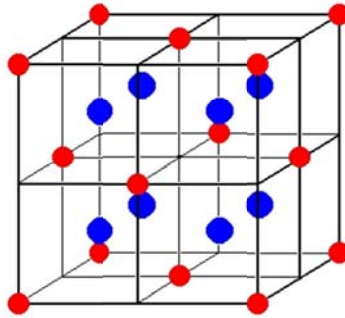
In molecular sieving the filter material has holes or channels through which the gas can propagate. Separation on the molecular level requires very fine holes or channels approximating the size of the molecules to be filtered. If the channels in the filter are narrow enough so that the gas propagation process is in the Knudsen diffusion domain, the lighter gases will be filtered preferably. The process' selectivity depends on the size of the holes or channels. This changes again when the sieving with very small holes or pores becomes sensitive to the size of the molecules. For simple molecules like  $H_2$ ,  $O_2$  or  $H_2O$  the van der Waals radii (or interaction radii) are in a narrow range between 0.120 nm ( $H_2$ ) and 0.167 nm ( $H_2O$ ). To produce filters with such small holes or narrow channels, the relevant precision is difficult to achieve. Examples are filters made from carbon nanotubes or pillared clays. Carbon is not acceptable in a hot steam environment; it is consumed very quickly. Pillaring is a commonly used procedure to transform a layered crystalline inorganic compound into a material with mesoporosity and microporosity down to 0.3 nm. Although such filtering is applied in e.g. petro-chemical processes, its capability to selectively filter hydrogen or oxygen from steam is very limited. Furthermore, the use at very high temperature results in pore growth or densification as the pore size required for filtering is different from the pore size that would be thermally stable.

Filtering based on mixed ionic electronic conduction appears to be the only viable solution at the very high temperatures. This type of gas separation is highly selective as it involves a series of molecular processes: adhesion-dissociation-ionisation, separate transport mechanisms of ions and charges, recombination. Primary selection criteria are thermal

stability in steam and conduction properties; possible candidate materials are crystalline metal-oxides, in particular perovskite (structure is similar to calcium titanium oxide  $\text{CaTiO}_3$ ) and fluorite (structure is similar to calcium fluoride  $\text{CaF}_2$ ) materials.

#### Materials with mixed ionic-electronic conductivity.

The basic process in the filtering with mixed ionic-electron conducting materials (MIEC) is the selective transport of ions through a crystalline lattice. In such a crystal atoms are arranged regularly in a three dimensional lattice.



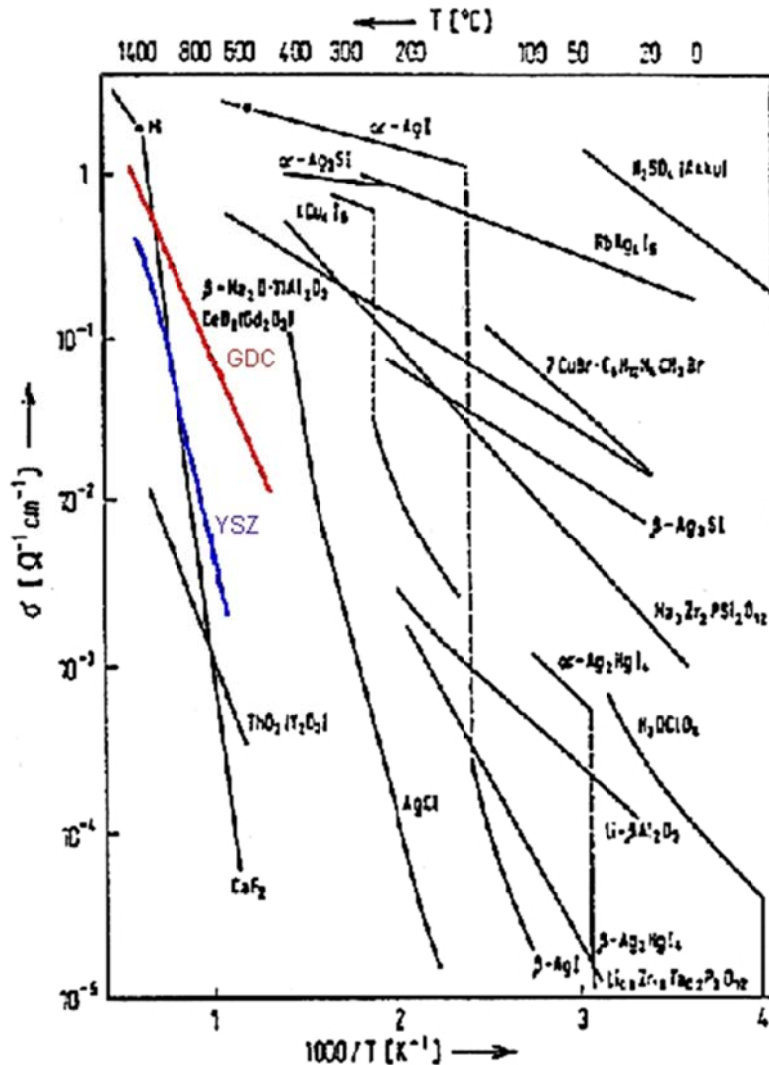
For example in the fluorite structure the metal atoms (red) are sitting on the corners of a larger cube as well as in the centres of the faces of a larger cube. This larger cube can be cut in to eight smaller cubes, each with half the side length of the larger cube. The oxygen atoms (blue) sit in the centres of these eight smaller cubes. The perovskite structure is somewhat more complex as there are three types of atoms present: four metal atoms at the corners, one atom of a different metal in the centre of the larger cube, and six oxygen atoms in the centres of the faces of a larger cube. Many of such elementary cells then form the physical crystal.

Ionic conduction takes place when a particular atom travels through the lattice from one side of the crystal to the other side. The driving force is the difference of concentration of the atoms on the two sides of the crystal. In other words, when there are more atoms on the one side, they exert a “pressure” that will “push” some of them through the crystal. There is of course the basic process that an atom leaves a crystal thus creating a vacancy which in turn is filled by an atom from a neighbouring cell and this way atoms “travel” through the lattice. However, this process does not occur often because each time an atom has to be taken away from its natural (preferred) position. Travelling is the easier the more vacancies are available. Not too many, mind you, as the lattice can become unstable if you take too many of its constituents away. Vacancies for specific types of atoms can also be created by construction of the crystal. The perovskite structure is such a crystal with many vacancies. Fluorite structures can be distorted with small amounts of a dopant material. For example in the cubic zirconium oxide ( $\text{ZrO}_2$ ) additional vacancies for oxygen atoms are created by substituting some of the zirconia by  $\text{YO}_{1.5}$  (actually  $\text{Y}_2\text{O}_3$ ) which binds lesser oxygen and thus leaves some places in the fluorite lattice unpopulated.

Since in a crystalline lattice electrons are shared between the atoms, it is actually an ion (atom with extra charge) that moves around; in particular the oxygen atom tends to pick up an extra electron and moves around as an  $\text{O}^-$  ion. As a consequence such an oxygen ion will have to unload the electron at the end of its trip through the crystal, and this electron has to move back from where it came from.

Depending on pressure and temperature, all crystals exhibit ion and electron conduction to some extent. The details depend on the choice of the atoms and the crystalline structure. To filter oxygen, crystals containing oxygen are the best conductors.

Electronic and ionic conductivities combine according to  $(\sigma_{\text{ion}} \cdot \sigma_{\text{electron}}) / (\sigma_{\text{ion}} + \sigma_{\text{electron}})$  to make up the mixed conductivity that is relevant for the gas filtering.



Ionic conductivities  $\sigma$  for various materials (image source lost) as a function of temperature. Ionic conductivity generally increases with temperature (like electronic conduction) exponentially. A change in slope can be observed for many materials at the high temperature end of the data. This is usually related to a change of the crystalline structure: materials might undergo phase transitions, exhibit segregation or develop a liquid component.

Electronic conductivity increases strongly with temperature. For filtering at ultra high temperatures it may be assumed, therefore, that ionic conductivity is limiting the permeability for oxygen of the material. Perovskite and fluorite materials exhibit both ionic and electronic conductivity. Typically, oxygen permeability of perovskites sets on at around 500°C. At SOFC operating temperatures around 900°C electronic conductivity is already of the order of

100 S/cm (while ionic conductivity is orders of magnitude smaller, usually below 0.1 S/m). The electronic conductivity rises exponentially  $\sim \exp\{-\text{const.}/T\}$ . Presuming a monotonous behaviour of the material, the theoretical gain going from 900 to 2200°C is about 11'000 i.e. four orders of magnitude.

A viable filter should have a mixed conductivity much larger than 1 S/cm.

#### MIECs for 2200°C.

Of the materials only few survive when the operating temperature exceeds 2000°C. It is telling that there are essentially no data for ionic conductivities published in the temperature region above 1800°C.

Basically two fluorite materials which might work at very high temperatures have been examined in literature: yttria (and calcia) stabilized cubic zirconia (YSZ) and gadolinium doped ceria (GDC), which is also cubic. We have not been able to find any high temperature (>1000°C) conductivity data for perovskites although for example  $\text{LaCrO}_3$  has a melting point of 2470°C.

Selection criteria, beyond the oxygen filtering capacity measured by mixed ionic-electronic conductivity, are as follows:

- The material must be stable at the desired operating conditions, in particular at temperatures above 2200°C. This requires a high melting point. The thermally most stable oxides have a cubic (fluorite) structure at high temperature which requires that the material does not undergo crystal phase transitions.
- The material must be inert in steam. This requirement excludes essentially all materials other than metal oxide ceramics.
- The material must have some mechanical strength at operating conditions. For example tubular filters must not bend or collapse under a pressure difference. Due to heating and cooling and the related expansion and contraction, thermal and mechanical stress situations occur that the material has to stand.
- The material must have a decent lifetime. Grain and pore evolution at high temperature can modify the material's stability and other characteristics. Evaporation from the bulk must be considered as well as effects of segregation. If such filters should be used for example in solar hydrogen production, thermal cycling is an additional constraint which, in some cases can actually lead to healing of aging phenomena.
- For practical reasons the material should not be poisonous or radioactive or present any other health hazard.

The table below compiles some high melting point<sup>2</sup> oxides:

Material	Melting Point	comment
ErCrO <sub>3</sub>	2300°C	high evaporation
Nd <sub>2</sub> O <sub>3</sub>	2300°C	
SrZrO <sub>3</sub>	2300°C	
La <sub>2</sub> O <sub>3</sub>	2285°C	
Tb <sub>4</sub> O <sub>7</sub>	2330°C	
Sm <sub>2</sub> O <sub>3</sub>	2335°C	
Dy <sub>2</sub> O <sub>3</sub>	2340°C	
Eu <sub>2</sub> O <sub>3</sub>	2350°C	
MgCr <sub>2</sub> O <sub>4</sub>	2350°C	high evaporation
Tm <sub>2</sub> O <sub>3</sub>	2410°C	
Er <sub>2</sub> O <sub>3</sub>	2364°C	soluble in steam
Ho <sub>2</sub> O <sub>3</sub>	2395°C	
Cd <sub>2</sub> O <sub>3</sub>	2395°C	
Gd <sub>2</sub> O <sub>3</sub>	2385°C	
Yb <sub>2</sub> O <sub>3</sub>	2420°C	
Y <sub>2</sub> O <sub>3</sub>	2410°C	
Sc <sub>2</sub> O <sub>3</sub>	2450°C	
SrO	2430°C	soluble in steam
Lu <sub>2</sub> O <sub>3</sub>	2470°C	
LaCrO <sub>3</sub>	2470°C	high evaporation
CeO <sub>2</sub>	2500°C	
BeO	2507°C	soluble in steam
CaZrO <sub>3</sub>	2350°C	
SiZrO <sub>4</sub>	2550°C	eutectic
CaO	2580°C	soluble in steam
BaZrO <sub>3</sub>	2620°C	high evaporation
Sc <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	2700°C	
ZrO <sub>2</sub>	2715°C	
HfO <sub>2</sub>	2790°C	
MgO	2852°C	soluble in steam
UO <sub>2</sub>	2870°C	radioactive
ThO <sub>2</sub>	3235°C	radioactive

**Magnesia** (MgO) is hygroscopic and care must be taken to protect it from moisture. Although its hydroxide decomposes into MgO and H<sub>2</sub>O at rather low temperature (350°C), magnesia is not suitable in an environment where water is present.

**Hafnia** (HfO<sub>2</sub>) is very similar to zirconia with a somewhat higher melting point and lower oxygen permeability. However, because of its natural abundance of only 2% compared to zirconia (98%) it is a rather expensive.

**Zirconia** (ZrO<sub>2</sub>), because it undergoes volume changing phase transitions in its pure composition, is usually stabilized with 8<sub>mol</sub>% to 10<sub>mol</sub>% yttria (Y<sub>2</sub>O<sub>3</sub>) in the cubic phase

<sup>2</sup> The melting points are from various sources and have sometimes considerable errors.

("YSZ"). Zirconia can be stabilized also with other oxides like MgO, CaO or Sc<sub>2</sub>O<sub>3</sub>. Furthermore zirconia can be doped with other oxides to modify its properties. Two examples are:

- Scandia increases ionic conductivity<sup>3</sup>
- Erbium increases mechanical strength<sup>4</sup>

**Ceria** has a somewhat lower melting point than YSZ. It crystallizes in cubic structure. The growth microstructure is strongly columnar, and therefore CeO<sub>2</sub> films are soft and porous. Doped ceria is used in SOFC as electrolyte because of its high electronic and ionic (oxygen) conductivity already at comparatively low temperature (900°C). There are indications that the cerium reacts with hydrogen<sup>5</sup>.

**M<sub>2</sub>O<sub>3</sub>-type oxides** have lower permeabilities (ionic conductivity) than fluorite (MO<sub>2</sub>) and perovskite (ABO<sub>3</sub>) structures.

**Compounds:** There are several compounds (like Sc<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> = Sc<sub>2</sub>O<sub>3</sub> + 2 ZrO<sub>2</sub>), in the table that have a melting point above 2300°C. Their structure is neither fluorite nor perovskite. In general, compounds need to be studied with care because they can segregate. Furthermore, small changes in the composition may have important consequences e.g. lowering of the melting point.

#### Manufacturing and cost constraints.

The flux through a filter is then given as

$$J = \frac{A}{d} \cdot P \cdot fct(p_1, p_2)$$

where

J	oxygen flux
A	filter surface area
d	filter thickness
P	oxygen permeability of the filter material
P <sub>1</sub> , P <sub>2</sub>	oxygen partial pressures on the two sides of the filter
fct(...)	function of

While permeability and pressure dependence are inherent to the choice of the material i.e. the physical-chemical processes that govern the filtering, filter surface and thickness can be modified through the manufacturing process.

For most applications, oxygen filters will be tubular. Long ceramic tubes that reach into the space with the high temperature steam, but also connect to a gas extraction system in regions where it is cooler and where more conventional techniques can be employed. Oxygen can be

<sup>3</sup> *Conductivity and Microstructural Characterisation of Doped Zirconia-Ceria and Lanthanum Gallate Electrolytes for the Intermediate-Temperature, Solid Oxide Fuel Cell*; J. A. Kimpton; doctoral thesis Swinburne University, Melbourne 2002

<sup>4</sup> J. Martinez-Fernandez, A. Sayir, and S. C. Farmer; Creep Resistance of ZrO<sub>2</sub> Ceramic Improved by the Addition of a Small Amount of Er<sub>2</sub>O<sub>3</sub>; NASA Glenn Research Center, 2002

<sup>5</sup> K. Eguchi et al.; "Process of solid state reaction between doped ceria and zirconia"; Solid State Ionics 135 (2000) 589–594

extracted by pumping or flushing, where the flushing is energetically and technically less favourable.

The filters should have a very thin wall. It is a challenge to ceramic production methods to produce long tubes, practically of the dimension of one meter length, with diameter of the order of one centimetre and wall thickness of the order of millimetre. For commercially available tubes the ratio of about 1 to 5 for wall thickness vs. diameter seems to be a limit. Such a limit is also imposed if there is a pressure difference between the inside and the outside of the filter tube.

To produce such tubes, ceramics companies offer various processes: most common are casting or extrusion. An interesting new technology is additive layer manufacturing with laser sintering of the ceramic powder. Each process requires a careful tuning of the ceramic mass (slip, dough, powder) that is used to achieve the macroscopic dimensions i.e. to make the tube. Parameters are for example the size of the grains and the binder that are necessary to obtain a stable green body and sintered part.

Unfortunately, the microscopic properties required for stable use of the filter tube at high temperatures are not necessarily the same as those needed for the manufacturing. Residual pore fraction, size and distribution play an important role as well as the grain size. In principle for each filter material selected, the best manufacturing process has to be found after its high temperature characteristics have been figured out.

The manufacturing process is a considerable cost factor. Raw zirconia powder for example costs of the order of 15 euros per kilogram. When bought as ready-made tube<sup>6</sup> off-the-shelf, the price can reach and exceed thousand euros per kilogram. Produced in large quantities, perhaps at a dedicated production site, the production cost for oxygen filters can be much reduced and cost of less than one thousand euros per square meter of filter surface is certainly achievable.

## Conclusion

Zirconia is the most prominent candidate because it is widely used for high temperature applications, and it is essentially the only economic material available. An extrapolation<sup>7</sup> indicates that it might have sufficient oxygen permeability to be used in a commercially viable solar hydrogen generator. However, this extrapolation needs to be verified.<sup>8</sup>

Beyond the simple tubular filter with dense walls made of cubic zirconia there are various ways of increasing its filter capacity:

- Reduce wall thickness going towards use of capillary filters or asymmetric filters. The latter are filters composed of the very thin (micrometre) filtering membrane mechanically supported by porous structure. A gain between 5 and 25 seems possible, but such filters have to be developed and their thermal stability needs to be examined.

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<sup>6</sup> based on quotes for zirconia tubes from Coorstek, Dynamic Ceramics or McDaniel, 2011

<sup>7</sup> *Recherches sur la production d'hydrogène par la dissociation thermique directe de la vapeur d'eau*; F. Lapique et al.; Entropie 110 (1983) 42-53

<sup>8</sup> See our report Solar Thermal Hydrogen Production at <http://www.creative-services.fr/innovation/>



- The composition of the cubic zirconia can be modified by doping with additional and different materials that enhance a particular characteristic. Replacing yttria by scandia increases the materials ionic conductivity. Or adding a good electron conductor can increase this aspect of the transport mechanism. However, neither has been studied and theoretically derived anticipations need to be checked in the experiment.

## **Outlook**

H2 Power Systems Ltd (“H2PS”)<sup>1</sup>, a company in Dublin, Ireland, had taken on the task of developing the equipment necessary for testing materials in steam above 2200°C. H2PS has tested a number of materials for thermal stability and filtering properties at temperatures exceeding 2200°C. We hope that H2PS can continue its activities and that it will eventually publish the interesting results it has obtained.