



## SP5 Public Summary Report

*Based on the Del. 5.5.1.1.: Documented selection with overview stability and durability of perovskite materials*

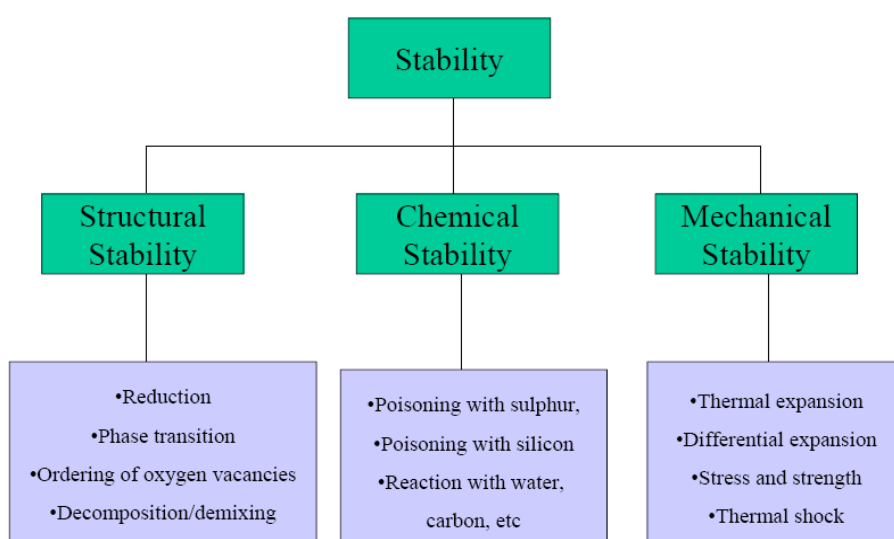
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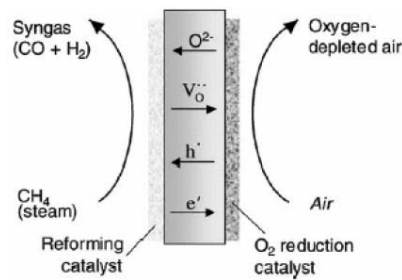
Mixed ionic-electronic conducting perovskite-type oxides have potential for use in different high temperature oxygen generation processes. In these processes, either the oxygen storage properties of the perovskite oxides are exploited or the materials are used as ceramic membranes. This report gives a survey of observations reported in open literature on the structural, chemical and mechanical stability of perovskite- and perovskite-related oxides (Fig. 1). It is provided to support identification of promising materials and possible limits of operation.



**Figure 1:** Structure of the literature report

### ***Oxygen generation materials***

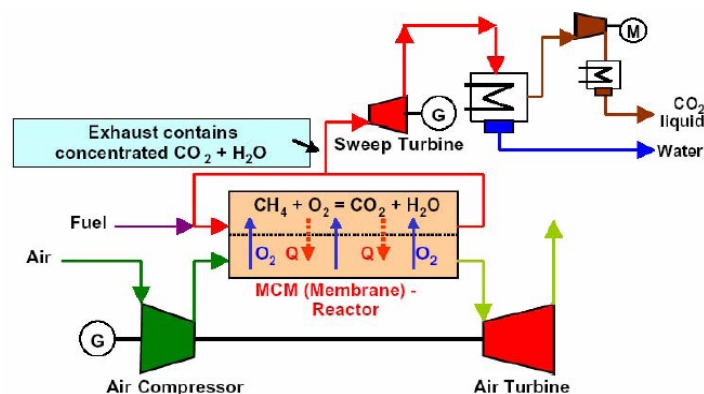
A number of new technologies are in development for oxygen generation at high temperatures (600 °C to 1000 °C). One of the primary technologies under this category is based on transport of oxygen ions through a ceramic membrane made from perovskite or similar materials. At high temperatures, oxygen ions are transported through the ceramic membrane from the high to the low oxygen pressure side via lattice oxygen vacancies. Simultaneously, electrons move in a reverse direction by hopping between the multivalent metal ions. The oxygen flux through the membranes is maximized with decreasing thickness of the membrane material thereby setting the first challenge to the development of a cost effective membrane- based process.



**Figure 2:** The operating principle of a mixed ionic - electronic conducting membrane

It is possible to integrate two options based on ceramic membrane technology into a power cycle aimed at CO<sub>2</sub> capture:

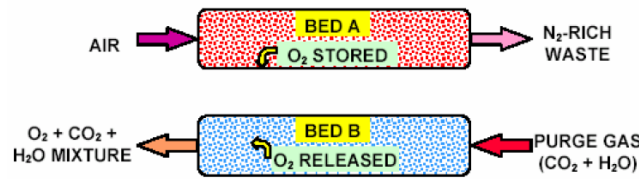
- The first concept (AZEP - Advanced Zero Emissions Power Plant) is based on generating in a separate unit either high purity oxygen or an oxygen rich admixture with steam and/or CO<sub>2</sub> (recirculated from the power cycle to produce a sweep gas). This oxygen rich gas is then routed to an oxy-fuel boiler or to a gas turbine, or is used in a gasifier to produce syngas (CO + H<sub>2</sub>) as a hydrogen rich fuel for further processing. A mixed conducting membrane reactor, which combines oxygen-separation, combustion and heat transfer processes, replaces the conventional burner in a standard gas turbine power plant (Fig. 3), thereby creating the AZEP - substantially reducing technical and commercial risks.
- The second is based on utilising a membrane reactor where the oxygen transported by the ceramic membrane is reacted with hydrocarbon gaseous fuel to produce hydrogen-rich syngas for further processing (e.g. upgrading natural gas to ethylene and ethane or syngas by partial oxidation of methane). This option is limited to gaseous fuels.



**Figure 3:** Conventional gas turbine with a mixed conducting membrane reactor including an integrated membrane for production of oxygen

An alternative to ceramic membrane technology, referred to as Ceramic Autothermal Recovery (CAR), utilises oxygen storage properties on perovskite type materials at high temperature rather than oxygen transport properties. The process consists of cyclic operation in two beds containing the perovskite material in spherical pellets or cylindrical extrudite form similar to well known adsorbent or catalyst material. One bed is fed with a high temperature air stream and the oxygen is stored and retained in

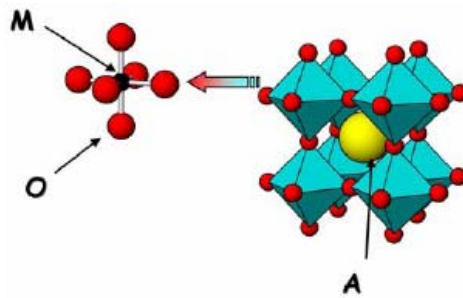
the material while in the other bed the oxygen is released by reduction of partial pressure and is removed (Fig. 4).



**Figure 3:** CAR technology-basic principle

### *Perovskite materials*

The ideal cubic perovskite  $AMO_3$  ( $ABO_3$ ) is commonly visualized as a three-dimensional network of regular corner-linked  $MO_6$  octahedra, the M cations being at the centres of these octahedral and the A cations being centrally located in the spaces between them. The A cation is surrounded by 12 O anions in a dodecahedral environment, the M cation is octahedrally coordinated by six O ions, and the O anions are coordinated by two M cations and four A cations.



**Figure 5:** The ideal perovskite structure

The perovskite materials may suffer from structural, mechanical and chemical integrity.

### *Structural stability*

Perovskite oxides in (slightly and/or highly) reducing environments and/or at high temperatures may undergo several degradation mechanisms due to reduction, phase transition, ordering of oxygen vacancies, or kinetic decomposition/demixing. This implies that there is always the possibility of eventual loss of structural stability of the perovskite phase.

*Reduction:* The use of some perovskite oxides may be limited by the ease of reduction at the conditions as met in the application.

*Phase transitions:* A phase transition may occur at the applied temperature, reducing environment, etc., which may induce a loss of performance. Optimised conditions should be used to prevent such a phase transition. Furthermore, the presence of secondary phases might play an important role in the stability and durability of the perovskite materials, and thus should be minimized.

*Ordering of oxygen vacancies:* There is ample evidence from XRD, electron diffraction and HRTEM that vacancy ordering in the oxygen-deficient perovskites occur to a degree, which depend both on temperature and oxygen partial pressure. In general, the tendency to form ordered structures progressively grows with increasing defect concentrations. Besides volume changes, ordering reduces the number of mobile oxygen vacancies and therefore will have a negative impact on the magnitude of the ionic conductivity.

*Kinetic decomposition/demixing:* This degradation mechanism deals with the chemical unmixing of lattice constituents under the influence of a gradient in the thermodynamic activity of oxygen. The problem relates with the non-negligible and different cation diffusivities in the multi-component oxide.

*Stress-induced cation diffusion:* High temperature creep behavior is strongly related to the diffusivity of cations. A good creep resistance under the conditions where the membrane operates is important for maintaining the membrane dimensions. Constant stress can be generated on the one hand by the oxygen chemical potential gradient across the membrane and on the other hand by the absolute pressure differential across the membrane.

*Lifetime of the MIEC membranes:* The perovskite surface exposed to reducing atmosphere is often partially decomposed up to certain degree. The structural failure affects the long-term performance of the materials. If the decomposed material has poorer ionic conductivity than the starting material, if the decomposition of the surfaces reduces the reaction rates of the electrochemical processes, and if the decomposed layer is not porous, than it is likely that only a thin decomposed layer (self-protecting layer) will form on the reduction side of the membrane.

### ***Chemical stability***

Degradation may occur by possible reduction or any other chemical attack of the oxide at the usually high (800-1000°C) operating temperatures of the ceramic membrane. This may include reaction with contaminants such as water, carbon dioxide, volatile hydrocarbons, nitrogen oxide, sulphuric oxide and hydrogen sulphide, which may be present in both feed and permeate gases.

*Sulphur poisoning:* Since the vast majority of fossil fuels and waste gases contain some sulphur compounds (SO<sub>2</sub>, H<sub>2</sub>S), sensitivity to sulphur poisoning is an important issue. As most of the oxide catalysts, perovskites are expected to be sensitive to sulphur poisoning. In fact, due to the basic properties of lanthanum and to some degree of most of its substituents, thermodynamics would predict even higher sensitivity of perovskites than that of other transition metal oxides. Nevertheless, in reality, poisoning seems primarily controlled by kinetics. Thus, important variations in the rate of poisoning may occur, depending on the composition and reaction conditions. Some perovskite compositions have been shown to be relatively resistant to very low sulphur concentrations (*e.g.* 10 ppm). Other perovskites were found more resistant than the corresponding base-metal oxides.

*Silica poisoning:* After operation of 1000 h in oxygen permeation experiments, a colour change was noted for La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> membranes. Different colours

originate from different phases that silica has formed. The silica reacts with one of the elements of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  forming a new (multi-element) phase, other than a silica phase. This  $\text{SiO}_2$  layer obviously reduced the performance of the membrane. More examples are provided in the report.

*Degradation with carbon and related materials:* Possible coking or formation of carbonates at the membrane surface may induce a loss of performance.

*Reaction with  $\text{H}_2\text{O}$ :* After annealing in the reducing atmosphere ( $\text{H}_2$ ,  $p\text{O}_2 = 2 \times 10^{-22}$  bar) at  $1000^\circ\text{C}$  for 100 h, the surface of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$  is covered by white powders, recognized as  $\text{La}(\text{OH})_3$ , which originates from reaction of  $\text{La}_2\text{O}_3$  with  $\text{H}_2\text{O}$  during cooling from annealing temperature. It is well known that when  $\text{La}_2\text{O}_3$  was hydrated to  $\text{La}(\text{OH})_3$ , the large volume expansion pulverized the sample surfaces.  $\text{LaSrGaO}$  was detected on both sides as second phase and  $\text{La}_2\text{O}_3$  was additionally detected on the front side. Other examples of reaction of perovskite type oxides with  $\text{H}_2\text{O}$  are discussed.

### ***Mechanical stability***

A membrane under operation is subject to mechanical stresses, which mainly result from mechanical constraints imposed by the reactor design (fixation, support, sealing, etc.), internal stresses due to the thermal expansion of the membrane in an inhomogeneous temperature field and internal stresses due to lattice expansion of the membrane resulting from a compositional change of oxygen (chemical expansion). The latter case is probably the most critical and was identified in literature as the cause of tube fracture in POX reactors. The mechanical and chemical stability of oxygen separation membranes materials under operating conditions, i.e. while placed in a strong  $p\text{O}_2$  gradient between air and syngas, and delivering a significant oxygen flux, is thus an important issue.

*Thermal expansion:* Mixed conducting perovskite oxides become oxygen deficient under reducing conditions. Formation of each extra vacancy is associated with the increase in the lattice parameter of the oxide. Thus the lattice expands, as the oxide becomes more non-stoichiometric. The mismatch in thermal expansion coefficient at opposite membrane sides and (a) periodic changes in oxygen partial pressure at either side of the membrane can induce residual stresses.

*Differential expansion:* In all the applications the ceramic membrane is in a gradient of oxygen activity and is therefore subject to differential strain across its thickness caused by the gradient in concentration of oxygen vacancies. This, in turn, induces mechanical stress that could ultimately cause fracture of the membrane. This is a serious limiting factor for many candidate membrane materials. In general the membrane is not free to deform according to any  $p\text{O}_2$ -profile, and therefore the volume expansion will lead to a build-up of mechanical stresses.

*Strength and fracture toughness:* Structural change in the perovskite lattice resulting from elemental segregation has considerable influence on the cohesive strength of the lattice, fracture energy and elastic modulus of the material. Ferroelastic materials exhibit a higher fracture toughness compared to non - ferroelastic compositions. Nonlinearity during fracture toughness measurements can be assigned to the domain switching or the phase transformation during crack propagation.

*Thermal shock:* The combustion catalysts activity and strength survival during the long operation depend on the catalyst resistance to thermal shocks and poisoning (e.g. SO<sub>2</sub> originated from the gas mixture used for combustion). At high temperatures catalyst poisoning becomes less intensive. With this regard catalysts that well resist thermal shocks will regenerate at high temperatures and thus will severe longer.