Oxygen and hydrogen innovative separation techniques for pre- and oxy-combustion capture

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ABSTRACT

Carbon dioxide capture in an energy conversion process eventually falls in one of the following three categories:

1) CO_2 separation from synthesis gas subsequent to CO conversion (water gas shift). This solution implies the re-allocation of the heating value contained in the original feedstock in a "decarbonized" fuel (hydrogen) that runs the power cycle. Hydrogen can then be used as a substitute of the original fossil fuel with minor modifications of commercial power cycles or exported from the plant (e.g. as "premium fuel" in the transportation sector)
2) Carbon dioxide concentration in the exhaust gas. In this case the energy conversion process is modified (typically by using oxygen combustion) and suitable techniques are applied so that CO_2 can be removed at a convenient stage of the process at high purity degree.
3) CO_2 separation from flue gases (post-combustion capture). It is put into practice through an end-of-pipe separation process placed ahead of the stack, with no or minimal modifications of conventional plants.

A variety of different techniques, including membranes, can be adopted to arrange processes for CO_2 capture according to one of the above listed options. More in detail high-temperature membranes for oxygen or hydrogen separation can be conveniently adopted in plants of categories 1 and 2 in a number of different processes:

- delivery of pure O_2 streams by means of separation membranes for oxyfuel combustion, coal gasification for electricity and H_2 production, autothermal reforming of natural gas for H_2 production;
- H_2 separation membrane reactors used for methane steam reforming (MSR), Water Gas Shift (WGS) of syngas produced by MSR or coal gasification.

Both oxygen and hydrogen separation membranes, however, are still in the development phase. In this paper a review of the state of the art of these membranes and of the potential applications is provided. Technological barriers to overcome in order to obtain full scale development are also identified.

As far as concerns O_2 membranes focus is put on mixed electronic-ionic conducting perovskites and related structures (dense ceramic membranes). These materials show a sufficient stability at the operating temperatures involved in the separation process integrated in power plants (750-950ºC), whilst acceptable oxygen fluxes can be obtained (~5 ml/min·cm^2). Consequently, intensive research has been devoted in the last decade to the preparation and characterization of ferrite, cobaltite and nickelate-based membranes.
The most important efforts to develop such structures up to the prototype level have been undertaken in USA where two consortia led, respectively, by Praxair and Air Products & Chemicals have been funded by DOE in 8 years projects. The development phase at lab level has been concluded and research is now focusing on membrane scale-up and module design

in order to bring technology to the prototype level. As far as concerns Europe, Mixed Conducting Membranes is one of the technologies for O_2 separation under development in the DECARBit project, financed by EC in the frame of the 7th FP.
A preliminary estimation of the economic advantage achievable by applying the mixed conducting transport membranes has been performed by NETL in case of substitution of conventional, cryogenic air separation unit for oxygen production in a IGCC plant.. Focusing on a IGGC plant of a typical size of about 410 MW_{EL} calculations indicate that, if compared to standard cryogenic ASU, the use of membranes reduces the oxygen plant cost of more than the 35%, and the electricity cost of the 4%, approximately. Even higher advantages can be expected in connection with oxyfuel coal combustion. According to data presented in public literature, a plant incorporating oxygen transport membranes can provide about 5% decrease in the cost of the electricity compared to a cryogenic ASU based configuration, simply as a consequence of the efficiency increase. An additional 10% cut is expected because of the reduction in capital investment if the mentioned targets will be achieved, which results in a 37% drop of the CO_2 mitigation costs.
As far as concerns hydrogen separation, focus is put on palladium alloy membranes.
Due to the considerable cost of palladium, research efforts have been addressed to obtain low thickness deposits on cheaper materials, such as ceramics and macroporous metals, by various techniques, including electroplating, sputtering, chemical vapour deposition, and electroless plating. Modelling studies, performed by Haldor Topsoe in the frame of the CCP project, indicate that the cost of CO_2 capture in coal gasification plants can be significantly reduced (more than 30%) by using thin Pd membranes (less than 10 micron thick} for the Water Gas Shift of the syngas in a membrane reactor.
Pd alloy membranes obtained by electroless plating for the syngas treatment are currently developed in USA by a consortia led by Pall. A prototype palladium membrane has been tested by Shell for over 6000 at 500°C in a gas mixture simulating natural gas reforming.
As far as concerns Europe Pd-23%Ag membranes obtained by magneton sputtering have been successfully tested by Sintef at the lab stage in the CACHET project, financed by EC in the frame of the 6th FP. Composite membranes made by a thin Pd layer deposited by electroless plating on a modified macroporous stainless steel support are also currently developed at ERSE in the frame of a project financed by the Italian Authority for the Energy. These membranes have been successfully tested at the lab level. for the WGS of a syngas mixture at 400°C.
It can be concluded that membranes for oxygen and hydrogen separation can be considered as a key component for power generation plants with CO_2 capture (pre-combustion and oxyfuel). These membranes have been till now developed at the laboratory stage; research is now focusing on technological aspect such as module design and scale/up of the production process; demonstration in the field is foreseen in the near future.

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