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Ceramic membranes for the separation of hydrogen produced from biomass gasification

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Abstract

European Union aims to reach net-zero greenhouse gas emissions by 2050, but the present energy system is still strongly dependent on fossil fuels. It is therefore essential to push the production of carbon-free energy vectors, possibly with clean technologies and with a circular approach, i.e. exploiting waste materials. In such context, hydrogen is attracting a booming attention from the scientific community, as it can be employed as green energy carrier producing with only water as by-product. Currently, most hydrogen is produced through standard process, (e.g. steam methane reforming), based on fossil fuels. Therefore, it is necessary to identify renewable sources for hydrogen production, in order to develop large-scale, affordable and sustainable production strategies.

An interesting possibility is to obtain hydrogen from biological scrap, also referred to as biomass. Biomass are a renewable resource that can be gasified to obtain syngas, a mixture of several gaseous species (like CO, H_2, CO_2, CH_4, …), where H_2 can reach up to 50 vol% [1]. Pure hydrogen can be obtained from syngas by means of separation processes.

Besides Pressure Swing Adsorption (PSA) techniques, hydrogen separation can be performed using membranes. The scientific community attention on the topic has increased over the last 20 years, reaching today a very wide number of publications per year. Within the landscape of inorganic membranes, two main classes can be defined: porous membranes (e.g. Zeolites) and dense membranes (i.e. metallic and ceramic). Porous inorganic membranes ensure high permeation and chemical stability, but show poor selectivity, which hampers their use when high H_2 purity is required. Selectivity, instead, is greatly enhanced in dense membranes, that can be either metallic or ceramic. Metallic membranes have superior performances, unfortunately are quickly poisoned even by small amount of sulfur-based contaminants, which are usually present in biomass-derived syngas. On the other hand, ceramic membranes, also referred to as Hydrogen Transport Membranes (HTMs), have higher tolerance to pollutants [2], but lower hydrogen fluxes.

RSE has recently started a project aimed at developing innovative ceramic membranes for H_2 separation from syngas obtained by biomass gasification. Our purpose is to demonstrate HTMs that combine both good permeation performances and strong chemical resistance in the typical operating conditions of this process. To meet such targets, both materials and microstructure of HTMs must be carefully engineered.

We will present the results of our preliminary studies: we started by focusing our work on lanthanide tungstates $Ln_{6-x}WO_{12-\delta}$, (LWO), a class of compounds well known in literature and considered promising thanks to their significant mixed protonic-electronic conductivity and remarkable stability [3]. We applied a cost-effective and scalable solid-state route to synthesize pure phase $La_{6-x}WO_{12-\delta}$ powders. Preliminary membranes, manufactured by powder pressing and sintering, showed the desired phase composition and microstructure.

In order to obtain HTMs with high separation performances, we moved then our attention to the engineering of ceramic material, following two main approaches well known in literature not only in the field of HTMs, but in general within the ceramic membranes area of expertise. To improve transport properties and reach high ambipolar conductivities we studied: (i) the partial replacement of rare earth and W cations with different elements [4,5]; (ii) the fabrication of dual-phase membranes by combining LWO with a good electronic conductor, that can be metallic or preferably ceramic, due to thermo-mechanical compatibility reasons [6].

In parallel to the ceramic material development, the membrane microstructure optimization has been investigated by realizing asymmetric structures where the thickness of the separation layer is reduced to 15 µm, to increase the H_2 flux, and a porous support is coupled to the dense one to ensure a sufficient mechanical strength.

The final step of the new materials development process includes the manufacturing of the membranes through a sequential tape casting process, suitable to be scaled to commercial production of large-area components.

As previously said, we will present our preliminary results, including crystallographic and microstructural analysis of the new developed materials.

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