



Separation and storage of hydrogen by steam-iron process: Effect of added metals upon hydrogen release and solid stability

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ABSTRACT

During the last decade, the steam-iron process has re-emerged as a possible way to separate and/or storage pure hydrogen through the use of metallic oxides subjected to redox cycles. The most renamed candidate to achieve this goal has traditionally been iron oxide. Nevertheless, the study of its behaviour along repetitive reduction/oxidation stages has shown that the hydrogen storage density diminishes abruptly from the first cycle on.

To cope with this problem, the inclusion of a second metal oxide in the solid structure has been tried. Isothermal experiments of reduction with hydrogen rich flows and oxidation with steam have been carried out with Al, Cr and Ce as second metals, in nominal amounts from 1% to 10 mol% added to the hematite structure, which has been synthesized in laboratory by coprecipitation. Series of up to seven cycles (reductions followed by oxidations in a thermogravimetric system acting as differential reactor for the gas) have shown that to that point, an almost repetitive behaviour can be obtained, recovering the magnetite (Fe₃O₄) structure after each oxidation step.

Since the second metal oxide does not intervene in the reduction/oxidation process, the optimum content of second metal for each species has been determined with the aim to keep the highest hydrogen storage density along cycles.

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1. Introduction

Hydrogen can be stored and regenerated using a method of cyclic reduction and oxidation of metallic oxides, usually iron oxides, known as the steam-iron process [1,2]. This method – which was initially developed in the late 19th/early 20th century to produce hydrogen rich gas from gasified coal [3] – stands on the premise that hydrogen can be provided cheaply from fossil sources, such as natural gas during the transition period towards a full hydrogen economy [4].

The steam-iron process operates in two periodic stages, the net reaction being the redox of the metal oxide:



(1) In the first stage (forward reaction), a gas mixture containing hydrogen (for instance, natural gas with a high enough hydrogen content, or a stream resulting from natural gas reforming, hydrocarbon or biomass pyrolysis or gasification) is used to reduce the metal oxide. The water produced in this stage should

be eliminated in order to shift the equilibrium reaction of Eq. (1) towards the reduced metal.

(2) In the second stage (backward reaction), the previously reduced metal is re-oxidized with steam, producing pure hydrogen, while the oxide is regenerated to a certain extent. Therefore, this process can provide a feasible and convenient way to produce a hydrogen stream suitable to feed a PEM fuel cell avoiding the risk of anode poisoning by carbon monoxide impurities.

Iron oxides (Fe₂O₃, Fe₃O₄) have been typically chosen as metal oxides mediators for the storage and production of hydrogen in the steam-iron system, due to their theoretical high redox capacity per mass unity, availability and economic feasibility [5,6]. The theoretical amount of hydrogen stored and supplied through the redox of iron oxide is calculated to be 4.8 wt% of Fe, which corresponds to the complete oxidation of Fe into Fe₃O₄. However, it has been demonstrated that when pure iron oxide is used, the process is adversely affected by sintering or aggregation of particles, caused by the cyclic operation of reduction and oxidation steps [7–9]. This implies that the practical value of hydrogen storage will be lower along time.

Therefore, the selection or development of materials with a low sintering tendency and constant high conversion rates (both for reduction and oxidation) would increase the feasibility of hydro-

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