Generation of pure hydrogen in a tubular reactor via the Steam Iron Process

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Introduction

For fuel cell applications hydrogen needs to be very pure to ensure a long term stability of the cells - thus hydrogen purification is necessary. The two-step steam iron process yields pure hydrogen.
First, reductive gas products of hydrocarbon reforming reactions reduce an iron oxide contact mass. Secondly, hydrogen gas is produced by re-oxidation of the contact mass by steam. This double step operation can be used as a way of hydrogen storage.

The reactions are carried out in a tubular reactor filled with fine powdered contact mass. The reactor is heated by an electric furnace. Finding the adequate reaction temperature is essential, as at low temperatures carbon formation on the contact mass occurs by shift in the Boudouard equilibrium. Too high temperatures lead to faster sintering and thus to a loss in active surface, which limits the yield of hydrogen [1].

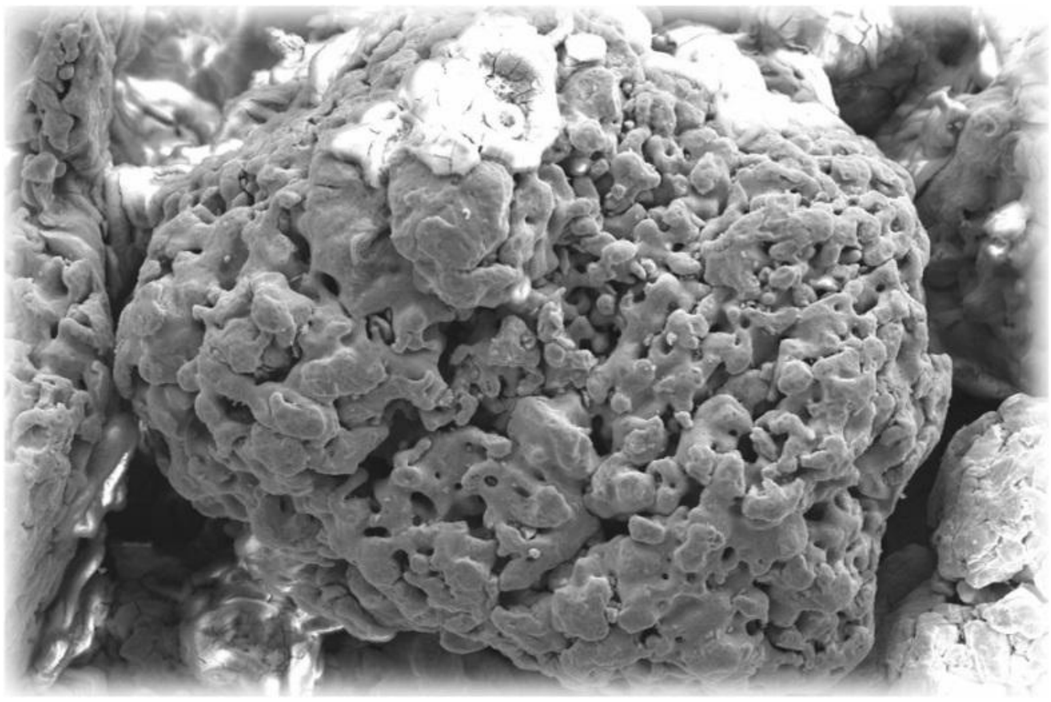

Fig.2: SEM image of sponge iron.

Preparation and Setup

The experiments were performed with hydrogen as reducing species and steam as oxidizing agent. By continuously measuring the amount of product gas, either by gas chromatography or a mass flow controller, a reaction profile is obtained.
The contact masses consist of sponge iron with varied amounts of aluminium oxide for thermal stability. These contact masses are prepared by impregnating sponge iron [2] with aluminium nitrate and then decomposing the nitrate to Al_2O_3 by calcination in an oven at 900 C. The product is then crushed in a mortar and fractionized by sieving.

As reactor and control system a PID Eng&Tech MicroActivity Reference automated catalyst test rig (as seen in Fig.1) was used. This device contains an array of mass flow controllers, resistance heating for the reactor and an evaporator for supplying steam.

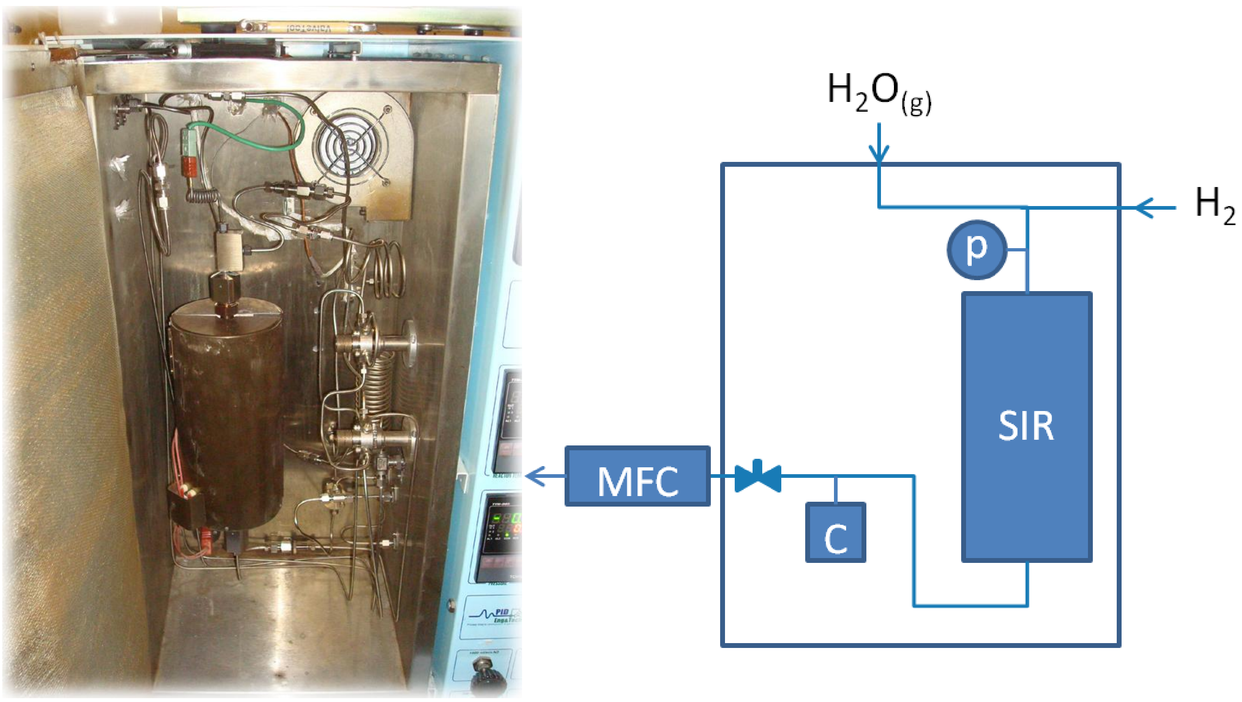

Fig.1: Interior of MicrActivity Reference (left), and schematic view of the test setup (right) – pressure control p, sponge iron reactor SIR, condenser C and detecting mass flow controller MFC.

Characterization of Contact Masses

The contact masses are characterized by different methods.
- Mercury intrusion porosimetry to determine the total surface area.
- XRD analysis and SEM-EDX to investigate the structure and topography of the powdered sample before and after an experimental series, to verify sintering effects on microscopic level and to observe the Al_2O_3 deposition on the iron particles (as seen in Fig.2).
- Elemental analysis for investigating the quantity of aluminium oxide during sample preparation, as milling could alter the composition by grinding away superficial Al_2O_3 deposits.

Experiments and Results

An experimental series consists of multiple oxidation and reduction steps of the iron based contact mass and evaluation of the corresponding gas flows – in and out. Thus gas conversion rates and the amount of generated hydrogen are obtained. The behaviour of different contact masses (different amount of aluminium oxide) is investigated.

Resulting data of a series with 5 wt% of Al_2O_3 and pure sponge iron as contact mass are compared in Tab.1. Conversion rates decrease during the series as a result of contact mass sintering, which was verified during removing the contact mass from the reactor - the non stabilized contact mass shows excessive sinter degradation.

Tab.1: Comparison between two series, showing the hydrogen and steam conversion; reactions marked by * not directly comparable due to partly oxidized sample in furnace.

Reaction	*Mean gas conversion [%]*	
	Contact mass Fe/Al$_2$O$_3$	*Contact mass Fe*
1st reduction*	13,45*	4,00*
1st oxidation	18,39	16,12
2nd reduction	22,06	6,67
2nd oxidation	31,86	6,05
3rd reduction	17,70	7,38
3rd oxidation	13,54	4,03

Conclusion

The results indicate, that stabilization is necessary to keep the system running at a reasonable conversion rate, though optimum concentration of aluminium oxide has yet to be determined.

Acknowledgement

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