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Storage and separation of hydrogen with the metal steam process

*Markus Thaler**, *Viktor Hacker*

Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Steyrergasse 21, 8010 Graz, Austria

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ABSTRACT

The chemical reaction of metals and metal oxides with steam at elevated temperatures produces pure hydrogen. Therefore certain metals can be used as gas purification and hydrogen storage material. Storage and transport of metals are basic operations, free from safety issues and hydrogen is produced on demand whenever it is needed by passing steam over the solid reactant.

Metal is commonly generated by the reduction of the corresponding metal oxide. Different routes like thermal reduction, carbothermic reduction or fused salt electrolysis are possible. In this paper metals are evaluated with regard to their applicability in the metal steam process upon thermodynamics and experimental investigations. Light metals with high oxygen bonding capacity were found to be promising materials for hydrogen storage due to their high storage density.

Ge, Mo, W and Fe were found as potential candidates for the separation process with high hydrogen concentration in the product gas and excellent reduction and oxidation capability. However, reduction and oxidation at elevated temperatures cause the solid metals to reduce their surface area due to sintering. As a result the reaction rates decrease significantly after one redox cycle.

1. Introduction

Polymer electrolyte fuel cells are highly efficient electrochemical systems for converting the chemical energy of hydrogen directly to electric energy. During the reaction hydrogen and oxygen are consumed and only water is produced as off-gas. No local emissions of NO_x, hydrocarbons or particulate matter are generated. Due to strict emission directives set by the European policy fuel cells are expected to replace existing energy converters in stationary and mobile applications in near future. The industry is very active in developing the future fuel cell technology with the goal of driving the technology intensely towards commercialization.

However, for the expanded application of hydrogen fuel cells, a well operating infrastructure for hydrogen storage, transport and distribution is required. As hydrogen is an energy carrier - no energy source - it has to be generated from available resources. Preferably renewable sources have to be utilized to avoid CO_2 emissions for a sustainable power generation.

For a widespread use of hydrogen as energy carrier the efficient and economical production, separation and storage of hydrogen are major obstacles. Hydrogen nowadays is produced by steam reforming of fossil methane, thus contributing considerably to the worldwide temperature increase caused by greenhouse emissions. The following

* *Corresponding author.*
E-mail address: thales1@gmx.at (M. Thaler).
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Nomenclature:

x, y	stoichiometric coefficients
Me	metal
SD	storage density
ED	energy density
M	molar mass
ρ	density
p	partial pressure
K	equilibrium constant
H_{H_2}	lower heating value of hydrogen

purification process of hydrogen containing gas mixtures includes several complex and energy consuming steps: the high temperature shift reaction, the low temperature shift reaction, the preferential oxidation and the pressure swing adsorption. Storage of the pure hydrogen is realized either physically by liquefaction and compression or chemically in solid or liquid compounds. The storage technology of hydrogen requires safe handling, short refueling time, nontoxic materials, low costs and high storage densities and lifetime.

Furthermore the hydrogen for polymer electrolyte fuel cells has to be delivered in supreme purity with CO contamination levels below 20ppm to prevent the electrode from poisoning. Additionally the membrane of PEMFCs requires humidified hydrogen feed stream for reliable and sound operation.

Hydrogen separated and stored by the metal steam process can fulfill these demands with excellence [1]. This simple process is based on the reaction of metals with water similar to the Messerschmidt-process which was used for hydrogen production in the early 20th century [2,3]. The decomposition of water by the reaction of steam with reduced metal particles releases pure, humidified hydrogen. Hence the product gas can be directly supplied to PEM fuel cells [4,5].

The hydrogen separation step and the charging of the storage material are implemented by the reduction of metal oxide particles with a CO and H_2 containing gas mixture (Eq. (1)+(2)) or alternative reduction processes. This gas mixture may be provided from steam reforming, partial oxidation or direct cracking of renewable hydrocarbons [6]. Looking at the overall reaction, during this reduction-step also reducing components like CO and CH_4 are converted to hydrogen. Subsequently the produced metal can be stored easily and over a long period of time in airproof vessels until hydrogen is required. Pure hydrogen is generated on demand by reoxidizing the metal with water to the initial form of metal oxide. After complete conversion, the source material can be reduced again. In order to achieve a cyclic process the material for separating and storing hydrogen is reduced and oxidized repeatedly whereby the reduction of the iron oxide represents the charging and the oxidation with steam represents for the discharging of the hydrogen storage material (Fig. 1).

$$Me_xO_y + yH_2 \leftrightarrow xMe + yH_2O \quad (1)$$

$$Me_xO_y + yCO \leftrightarrow xMe + yCO_2 \quad (2)$$

Particular advantages of this process are, the indirect hydrogen storage in form of reduced metal particles and the possibility to use alternative reduction routes like thermal reduction or fused salt electrolysis. The energy for thermal reduction can be provided from any source either solar, nuclear or others.

Although several research groups are working on similar processes [7–9] up to now only one evaluation of the metals suitable for the redox reaction was published. In this paper Otsuka et al. [10] investigated the use of 22 metals in a process with carbon as reducing agent. Only metals with near zero standard Gibbs free energy changes for reduction with carbon and oxidation with steam were found to be suitable for this hydrogen production within a reasonable temperature range.

In the present paper thermodynamic considerations as well as experimental investigations for various metals of the periodic table of the elements are carried out. The intention was to find out which metals are generally suited for the process and which storage densities are theoretically possible among the metals under examination. Besides thermodynamical qualification also physical properties of the metals are taken into account. In particular melting point, theoretical hydrogen storage density, toxicity and handling of the materials are included in the rating. An experimental validation of the theoretical results is performed with reduction and oxidation measurements in a thermogravimetric analysis system.

2. Storage of hydrogen with metals

For the utilization of metals in the metal steam process the introduced substance has to exhibit a preferably high hydrogen yield during each oxidation reaction with water. The amount of hydrogen produced during one cycle is limited by the number of oxygen atoms bond by one metal atom in the oxide state of the metal. Therefore it is beneficial to use metals which are able to attract more than one oxygen atom per metal atom, e.g. WO_3. Additionally the hydrogen yield per kilogram metal can be increased by utilizing light metals.

Depending on their preferred oxidation state the metals under consideration can bond up to three oxygen atoms. In combination with the molecular weight of the 27 elements under investigation significant differences in the achievable

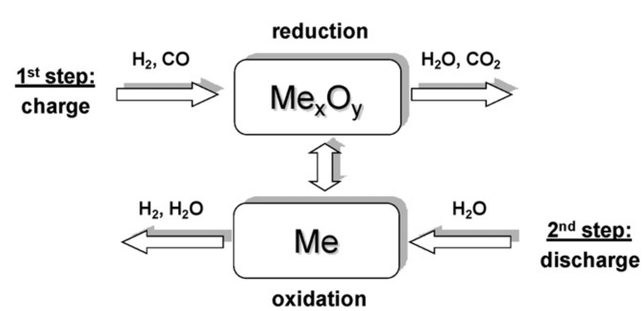

Fig. 1 – The metal steam process for storing and separating hydrogen.