Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Power Sources 145 (2005) 697–701
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

First investigations of structural changes of the contact mass in the RESC process for hydrogen production

H. Kindermann, M. Kornberger, J. Hierzer, J.O. Besenhard, V. Hacker*

Graz University of Technology, Christian Doppler Laboratory for Fuel Cell Systems, Institute for Chemistry and Technology of Inorganic Materials, 8010 Graz, Austria

Accepted 21 December 2004
Available online 31 May 2005

Abstract

The reformer sponge iron cycle (RESC) process was introduced for the stationary, decentralised production of hydrogen from hydrocarbon-containing fuels. The RESC process consists of two steps: the reformation of higher hydrocarbon to synthesis gas and the fine purification of this gas to pure hydrogen with the sponge iron reaction (SIR) process. The SIR process uses iron ore as contact mass. The contact mass (iron oxide) is reduced to iron in the first cycle by a synthesis gas, and is re-oxidised into iron oxide in the second cycle, utilizing steam. Pure hydrogen is produced in the second cycle as reaction product of the process. Iron ore is a very inexpensive base material for the contact mass, but the contact mass still has to be stable over several thousand redox cycles. Test series with varying contact mass compositions have been performed in order to investigate the influence of the composition on the durability of the contact mass. Carbon monoxide and hydrogen were used for the reduction process. Thermogravimetry (TG), X-ray diffractometry (XRD), scanning electron microscope (SEM) and mercury porosimetry were applied for the evaluation of structural changes after cycling the contact mass. The results confirm the importance of the skeletal structure of the pellets.

Keywords: Hydrogen production; RESC; Sponge iron; Hydrocarbon reforming; Mercury porosimetry

1. Introduction

Hydrogen has attracted the attention of policy makers and industrialists as a possible future energy vector, being able to address at the same time environmental concerns and dependence on foreign energy sources (European Commission, High Level Group on Hydrogen, 2004). This long-term perspective might lead the fossil based energy system to a renewable based energy system with hydrogen as energy carrier. A first step for the introduction of hydrogen is a high efficient production of hydrogen out of fossil fuels, since the change of the infrastructure of the energy supply has to be carefully prepared. Hydrogen is therefore produced on-site, and will be offered not as a substitute, but in addition to the current energy carriers.

The reformer sponge iron cycle (RESC) [1–3] offers an uncomplicated and efficient technique for the production of high purity hydrogen from synthesis gas, natural gas and liquid hydrocarbons [4–6].

The RESC process is a process for stationary, decentralised hydrogen production, that is based on a redox reaction of iron in combination with a hydrocarbon reformer. The process is based on the reduction of a contact mass (iron) by a synthesis gas and the oxidation of the contact mass by steam for the production of hydrogen. Several industrial contact masses were investigated [7,8]. This paper investigates the structural change of the contact mass.

2. Experimental investigations

The substantial components of the iron ore pellets, which have an influence on the lifetime, are Fe_2O_3, Al_2O_3, SiO_2 and CaO [9–13]. In nature, the fraction of iron in the pellets

* Corresponding author. Tel.: +43 316 873 8780; fax: +43 316 873 8782.
E-mail address: viktor.hacker@tugraz.at (V. Hacker).

0378-7753/$ – see front matter
doi:10.1016/j.jpowsour.2004.12.074

Table 1
Composition of laboratory iron ore pellets (mass%)

Fe_2O_3	85	85	85	85	85	88	88	88	88	88
Al_2O_3	5	5	5	5	5	2	2	2	2	2
SiO_2	0	2.5	5	7.5	10	0	2.5	5	7.5	10
CaO	10	7.5	5	2.5	0	10	7.5	5	2.5	0
Sum (mass%)	100	100	100	100	100	100	100	100	100	100

is between 62% and 66%, and the content of Al_2O_3 is about 0.17–2%. The fraction of quartz is between 2% and 7%, and lime is about 0–6%. The laboratory pellets which were prepared for this test series cover the average composition of commercial products. The compositions of the pellets are listed in Table 1.

The laboratory pellets were manufactured by the industrial partner voestalpine Stahl GmbH. The components for each contact mass were homogenized in a mixer. The raw material is rolled in a pelletizing plate to iron ore pellets. The bonding agent is bentonite. Subsequently, the iron ore pellets are calcinated at a temperature of 1100 °C. For the investigations, pellet diameters of 4.0 mm up to 6.3 mm were selected.

The iron ore pellets, which consist at the beginning of the test out of haematite and gangue, are heated up in an inert atmosphere to a temperature of 800 °C. Then the contact mass is repeatedly reduced with hydrogen (or carbon monoxide) and re-oxidized with steam. The switch from oxidation to reduction and back is undertaken when the reaction rates become very low (the reaction rate becomes then limited by diffusion). Mass of the pellets, pellet temperature, furnace temperature, gas temperature and the mass flows are continuously measured and recorded. The reactor is loaded with 100 g iron ore pellets. The flow-rate of hydrogen and carbon monoxide are 200 l h^{-1}, respectively, and the mass flow-rate of water is 200 ml h^{-1}. Samples of the pellets are taken after the first and after the fifth redox cycle.

In Fig. 1, the periodic change of temperatures, mass flows and the change in mass are shown. The change in mass follows a characteristic sawtooth profile during the redox cycles. The pellet temperature raises in the oxidation stage due to the exothermic reaction process. In the endothermic reduction, the temperature decreases. Analyses are done with thermogravimetry (TG), scanning electron microscopy (SEM), X-ray diffractometry (XRD) and mercury porosimetry.

2.1. TG

Thermograms show the mass change of a sample online as function of temperature and time. Precision scales are used for the measurement. The working range of the scales is up to 35 kg, and the accuracy is 0.1 g. The data are recorded online with DASYLab software.

2.2. SEM

The SEM is suitable for the illustration of the topography of solids, since the surface can be displayed directly with high depth sharpness. The surface has to be electroconductive in vacuum. Gold is used for coating (sputter coater SC502F). The photos are made with a JEOL 35 electron microscope.

2.3. XRD

The intensity of the reflected X-rays depends on the material composition. This allows a quantification of the

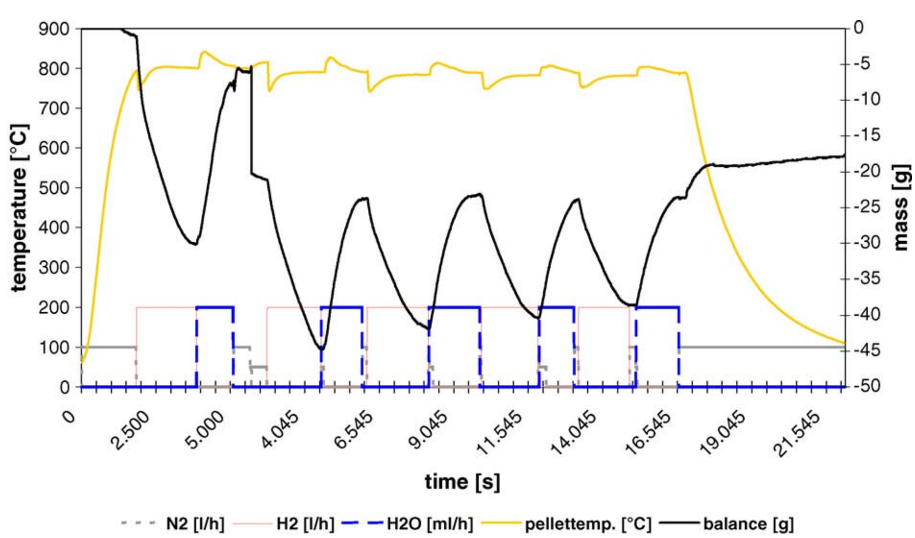

Fig. 1. Measurement of redox cycles with hydrogen: mass and temperature change of pellets, flow of reduction and oxidation gases.