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# Selective real-time quantification of hydrogen within mixtures of gases via an electrochemical method

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## ABSTRACT

Herein a highly selective real-time hydrogen quantification method based on electrochemical oxidation of hydrogen in a mixture of dry or humid gases is presented. This approach gives more reliable data for any area of research dealing with hydrogen with impurities or in a mixture of various gases especially for dynamic processes. The method itself is tested and verified by employing defined amounts of hydrogen to the electrochemical test cell with a mass flow controller. The limit of quantification is 0.30 ml H<sub>2</sub> min<sup>-1</sup> and the maximal hydrogen flow investigated in the test cell is 100 ml H<sub>2</sub> min<sup>-1</sup>. The method is applied for two processes with highly dynamic hydrogen evolution reactions: the steam iron process and the catalytic hydrolysis of borohydride as chemical hydrogen storage compound. In comparison to state-of-the-art methods it is possible to detect hydrogen selectively and in real-time.

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## Introduction

Hydrogen is considered to play a major role as energy carrier in a future society based on renewable resources [1–3]. Therefore, research focuses on developments in the fields of production, storage and utilization of hydrogen. For all these areas accurate, selective and reliable methods of hydrogen quantification are necessary to evaluate new technological approaches accordingly.

Most researchers in the field of chemical hydrogen storage determine hydrogen release rates by employing a mass flow meter/controller [2,4–6], by gas chromatography (GC) [7–10] or by water displacement in a graduated cylinder [11–14]. The main issue concerning the utilization of mass flow meters

is the inaccuracy when it comes to impurities and/or humidity in the H<sub>2</sub> stream which disables a quantification in gas mixtures. GC measurements are capable of analyzing complex mixtures of gases but due to poor time resolution fluctuating hydrogen flows cannot be detected. The drawbacks of water displacement techniques are the non-selectivity, the inaccuracy caused by reading the values by hand and the poor time resolution. Therefore it is necessary that the process generates pure hydrogen or potential byproducts are removed. However, the poor time resolution and the error rate can hardly be addressed.

In this study an electrochemical approach is introduced which is capable of quantifying hydrogen selectively in real-time within any gas mixture (except oxygen) at a time

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resolution of one second or less. The presented method is a modified hydrogen crossover measurement which is employed in polymer electrolyte fuel cell (PEFC) science [15,16]. This technique yields more reliable data and therefore fundamental data such as kinetic reaction parameters and activation energies can be obtained more accurately (Fig. 1).

We demonstrate the benefit of this technique by using the cyclic steam iron process and the catalytic hydrolysis of sodium borohydride  $\text{NaBH}_4$  as model systems. The corresponding reactions are given below (equations (1)–(6)) [17–19].



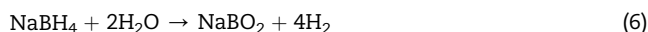
Within this chemical looping process iron acts as an oxygen carrier that is reduced by a syngas that contains hydrogen, carbon monoxide and inert gases and re-oxidized by steam generating pure hydrogen. The combination of the steam iron process with small-scale steam reforming enables the decentralized production of pure hydrogen without additional purification steps. In addition iron can also be used for hydrogen storage. Based on equation (3) a storage density of 4.8 wt% based on the mass of iron is possible [20,21]. Reactions (1)–(3) can be further divided into single steps involving wüstite as intermediate (reduction reactions are given in equations (4) and (5)).



For developing and optimizing this process the gas streams need to be analyzed accordingly. Due to incomplete reactions and the formation of solid carbon during reduction, mixtures of  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  can occur during both reactions. In general this analysis is done by mass flow controllers and/or by gas chromatography. By employing a mass flow controller the data acquisition is continuous but the quantification of hydrogen is limited for moisture and not possible for gas mixtures. Gas chromatography is able to detect complex gas mixtures but samples can only be taken in a timescale of minutes and need

the addition of defined amounts of a reference species for quantification. In contrast the herein presented electrochemical method is capable of detecting the hydrogen flow continuously irrespective of gas mixtures or humidity.

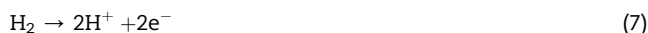
Borohydride based compounds with sodium or any other cation are a potential hydrogen carrier of the group of chemical hydrides [22]. The borohydride hydrolysis reaction (see equation (6)) is an optimal candidate to emphasize the advantage of our quantification method since there are still controversies on the kinetics of this complex reaction. As reviewed by Retnamma et al. there are several proposed models assuming zero-order, first-order, second-order, power law, Langmuir–Hinshelwood, Michaelis–Menten and semi-empirical kinetics. Furthermore they conclude that volume based measurements especially at higher temperatures have to be treated with caution due to water vapor [23].



$$\Delta H = -75 \text{ kJ mol}^{-1} \text{ H}_2$$

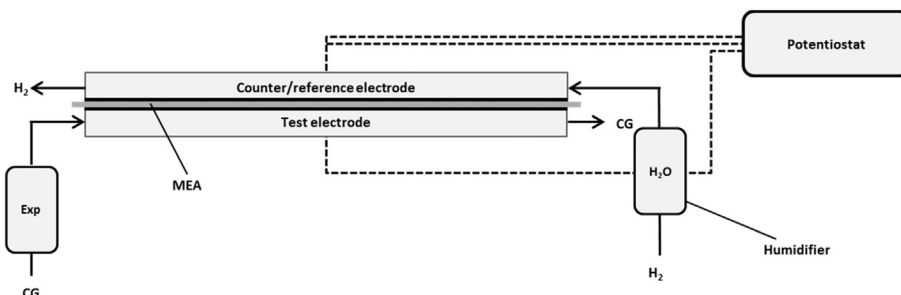
## Method

A potential of 430 mV vs. SHE which equals an overpotential of 430 mV concerning the HOR (hydrogen oxidation reaction) is applied to the test electrode where hydrogen is oxidized immediately. The electrode reaction at the test electrode is the HOR releasing 2 electrons (see equation (7)). Resulting protons are transported through the membrane to the counter electrode where the back reaction takes place and the released electrons are analyzed according to Faraday's Law (conversion factor:  $1 \text{ A} \equiv 7.05 \text{ ml min}^{-1}$ ). The counter electrode of the fuel cell like electrochemical cell is fed with hydrogen in order to be useable as pseudo reference electrode.



$$E^0 = 0.00 \text{ V vs. SHE}$$

The electrochemical cell is an in-house made and previously published fuel cell with an active area of  $25 \text{ cm}^2$  consisting of end plates (steel), current collectors (gold bathed



**Fig. 1** – Schematic illustration of electrochemical test equipment; CG – carrier gas; MEA – membrane electrode assembly; Exp – hydrogen releasing experiment.

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