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Cyclic water gas shift reactor (CWGS) for carbon monoxide removal from hydrogen feed gas for PEM fuel cells

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Abstract

Reduction of the carbon monoxide content in a hydrogen-rich reformate feed gas for fuel cell applications down to a level of 10–50 ppm normally involves high and low temperature water gas shift reactors followed by selective oxidation of residual carbon monoxide. In this contribution it is shown that the carbon monoxide content can be reduced in one single reactor, namely by a cyclic water gas shift reaction process (CWGS) which is based on an iron redox cycle. During the reduction phase of the cycle, the raw gas mixture of H_2 and CO reduces a Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2 sample, while during the oxidation phase steam re-oxidizes the iron and simultaneously hydrogen is being produced. The activity of Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2 was investigated during the reduction by H_2 and CO, and the re-oxidation by H_2O and CO_2. The Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2 showed high activity and stability during 100 repeated reduction/oxidation cycles. Some carbon monoxide in the hydrogen product stream was observed during the re-oxidation phase which was formed by steam gasification of carbon deposited on the iron surface. The carbon formation can be suppressed by controlled oxygen conversion in the Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2. The investigated cyclic process generated hydrogen with a CO content less than 10 ppm.

Keywords: Water gas shift reaction; Iron oxide; Hydrogen production; Carbon monoxide reduction; PEM fuel cell

1. Introduction

Fuel cell technology allows the highly efficient conversion of chemical energy into electrical energy without emissions of environmental pollutants, thereby making fuel cells one of the most promising sources for future power generation.

High-purity hydrogen is required for the operation of the low temperature polymer electrolyte membrane fuel cell (PEMFC). Hydrogen can be produced from hydrocarbon fuels or alcohols by reforming processes. The product streams of reforming processes typically contain mixtures of hydrogen, carbon monoxide, carbon dioxide and steam. The carbon monoxide level in the gas has to be reduced to a level below 20 ppm in order to avoid poisoning of the catalyst at the fuel cell electrodes [1–3]. Conventionally, this is accomplished by a multi-step purification train including high and low temperature water gas shift (WGS) reactors and a preferential oxidation reactor (PROX) or a methanation unit for CO removal [1,2].

The homogeneous WGS reaction, i.e. $CO + H_2O = CO_2 + H_2$, has been employed for 40 years in industrial processes for H_2 production [4,5]. The role of the WGS reaction is to increase the H_2 yield and to decrease the CO concentration [5–7]. The WGS reaction is traditionally carried out in two fixed bed adiabatic reactors, connected in series with a cooler between them [5]. The first reactor operates at temperatures ranging from 300 to 500 °C and employs a Fe/Cr catalyst. The second reactor with a Cu/Zn/Al catalyst operates at lower temperatures (180–300 °C) in order to increase the possible equilibrium conversion of CO, since the WGS reaction is exothermic.

A final reactor for CO preferential oxidation (CO-PROX: $CO + 0.5O_2 \rightarrow CO_2$) is capable to completely remove the CO down to a limit of 20 ppm [2]. During the PROX process the desired CO oxidation reaction is accompanied by undesired H_2 oxidation which – by consuming hydrogen – leads to a loss of fuel efficiency.

As an alternative to the described conventional technology, hydrogen purification from CO can be achieved by a novel cyclic water gas shift reactor which is based on the iron redox cycle [8–12]. This process can be carried out in one single reactor without any additional post-processing steps for the gas. The process is based on repeated reduction/re-oxidation cycles of iron oxides.

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During the reduction phase of each cycle, CO reduces the iron oxide Fe_3O_4 to iron in lower oxidation state, FeO_x, according to Eq. (1). During the re-oxidation phase, steam oxidizes FeO_x and simultaneously hydrogen is being produced according to Eq. (2). The product gas contains also steam and can be supplied directly to a PEMFC. The overall reaction of the process is the water gas shift reaction according to Eq. (3):

$$\text{Phase I}: (4-3x)\text{CO} + \text{Fe}_3\text{O}_4 \Leftrightarrow (4-3x)\text{CO}_2 + 3\text{FeO}_x \quad (\textit{exothermic reaction}) \tag{1}$$

$$\text{Phase II}: (4-3x)\text{H}_2\text{O} + 3\text{FeO}_x \Leftrightarrow (4-3x)\text{H}_2 + \text{Fe}_3\text{O}_4 \quad (\textit{endothermic reaction}) \tag{2}$$

$$\text{Overall}: \text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{CO}_2 + \text{H}_2 \quad (\textit{exothermic reaction}) \tag{3}$$

Overall, this scheme can be seen as a mediated WGS reaction where the CO reducing phase and H_2 production phase are decoupled in time, using iron oxide material as a mediator which can store oxygen. This enables the simple and complete removal of carbon monoxide from any syngas feed.

Fig. 1 illustrates the described novel process concept for CO- and CO_2-free hydrogen production by the WGS reaction. The concept is based on a multi-tubular reactor system which consists of a bundle of simultaneously operated fixed bed reactors (here only two tubes shown for illustration), some of them being in the reduction phase of iron oxide ($Fe_3O_4 \rightarrow FeO_x$) and some of them being in the oxidation phase ($FeO_x \rightarrow Fe_3O_4$). The operating temperature ranges between 650 and 750 °C. While the first tubes are fed with CO/H_2 gas which reduces the iron oxide, the latter are fed with steam for hydrogen production whereby the iron metal is taking up oxygen into its lattice. When the reduction phase of the iron oxides is completed, the first reactor tubes are switched to the re-oxidation mode, i.e. they are fed with water vapour for hydrogen production. Simultaneously, the other reactor tubes are switched from steam feed to CO/H_2 feed. In this manner, a redox cycle is established by switching the feed valves at discrete times. In principle, the proposed one step hydrogen purification process has three major advantages:

(i) Saving of investment costs by cyclic operation of one single process instead of a sequential train of purification units.
(ii) Saving of investment and operational costs by using iron oxides as inexpensive material having oxygen-storage properties.
(iii) In situ separation of the two WGS reaction products CO_2 and H_2 whereby high-purity hydrogen gas is produced which will give a high Nernstian voltage of the PEM fuel cell.

The objective of the present work is to report and discuss experimental performance data for this cyclic hydrogen production process being based on the iron redox cycle. In particular, it will be shown that this process is able to decrease the CO content of syngas down to a level of 10–20 ppm which is an acceptable level for PEM fuel cell operation. In order to identify suitable operating conditions for the process cycle, first the reduction phase and the oxidation phase were investigated separately, and then the behaviour of several subsequent cycles was elucidated.

2. Materials and set-up

2.1. Preparation of oxide materials

The principle of carbon oxide elimination by an iron redox cycle is analogous to the traditional steam iron technology [15,16] for the production of hydrogen-rich gases by reduction of iron ores. Reduction of iron oxides was studied by a great number of research groups, see e.g. [17]. The reduction of hematite (Fe_2O_3) to metallic iron at temperatures higher than 570 °C can be expressed by the following consecutive reaction scheme:

$$\text{Fe}_2\text{O}_3(\text{hematite}) \rightarrow \text{Fe}_3\text{O}_4(\text{magnetite}) \rightarrow \text{FeO}_x(\text{wuestite}) \rightarrow \text{Fe(iron)}$$

During the re-oxidation of metallic iron by steam at high temperatures, iron can be oxidized to magnetite (Fe_3O_4) [8,12]:

$$\text{Fe} \rightarrow \text{FeO}_x \rightarrow \text{Fe}_3\text{O}_4$$

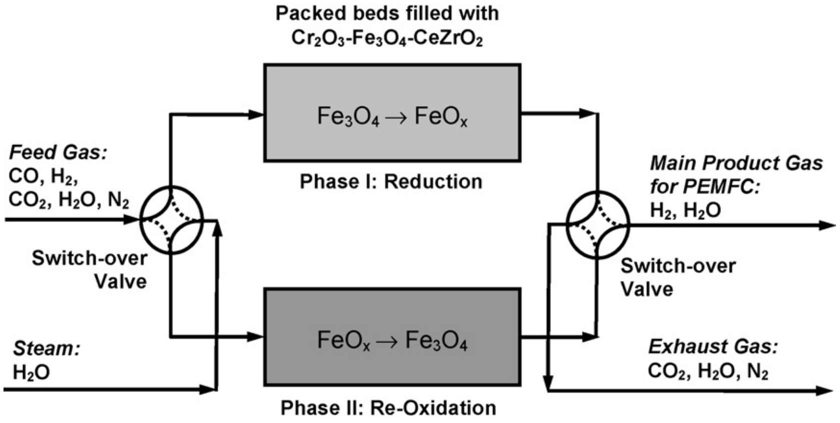

Fig. 1. Flow scheme of the periodically operated water gas shift reactor based on iron oxide, illustrated with two parallel packed beds.

The further oxidation of Fe_3O_4 to Fe_2O_3 can be only achieved by application of gaseous oxygen. Therefore, once the freshly prepared material underwent a reduction–re-oxidation cycle, the iron oxide with highest attainable oxygen content is Fe_3O_4. Already used Fe_3O_4 can be recycled many times. But the reduction/re-oxidation kinetics and the activity of iron oxide over several cycles are significantly affected by fast sintering. We found that the addition of Ce–ZrO_2 and Cr cations to iron oxides essentially decreases the sintering rate of metallic iron and/or iron oxides during the redox cycles [20].

Therefore, in the present study, 5 wt.% Cr_2O_3–40 wt.% Fe_2O_3–CeO_2–ZrO_2 was applied as material for the proposed cyclic redox process. The samples were prepared via urea hydrolysis according to recipes given in [13,14]. Fe–Ce–Zr mixed oxides were synthesized from $Fe(NO_3)_3\cdot 9H_2O$ (99.0%, Fluka), $Ce(NO_3)_3\cdot 6H_2O$ (99.0%, Fluka) and $ZrO(NO_3)_3\cdot 6H_2O$ (99.0%, Fluka). The starting metal salts were dissolved in distilled water in the desired concentration (0.1 M). The ratio between the metal salts can be altered depending on the desired concentration. Here, 40 wt.% Fe_2O_3 in Fe_2O_3–CeO_2–ZrO_2 was chosen. The mixed metal salt solution was added to a 0.4 M solution of urea (99.0%, Fluka) with a salt to urea solution ratio of 2:1 (v/v). This mixture was kept at 100 °C for 24 h. Subsequently, the sample was allowed to cool to room temperature prior to being centrifuged in order to separate a gel product from the solution. The gel product was then washed with ethanol and dried overnight in an oven at 110 °C. Finally, the materials were calcined at 850 °C for 4 h. The amount of Cr_2O_3 added by impregnation to the Fe_2O_3–CeO_2–ZrO_2 was adjusted to 5 wt.%.

2.2. Experimental set-up

The activity tests for the reduction and re-oxidation of the prepared Cr_2O_3–Fe_2O_3–CeO_2–ZrO_2 were carried out in a packed bed quartz tube reactor (inner diameter 10 mm). Typically, 0.05–5 g of oxygen-storage materials were packed between layers of quartz wool. The reactor was placed in an electrical furnace equipped with K-type thermocouples. The temperature of the sample bed was measured by thermocouples fixed to the inside and outside of the reactor tube at the position of the sample bed.

The reduction phase of the cycle was performed by gas mixtures containing carbon monoxide in helium, hydrogen in helium or CO/H_2 in helium. All experiments presented in this work were performed at 740 °C because at temperatures below 720 °C carbon was predicted as stable component from thermodynamic calculations [9].

Before the re-oxidation phase was started, the mixture of rest-hydrogen and carbon monoxide in the lines was removed by helium purging for 10 min. Subsequently, the re-oxidation of the reduced sample by steam (phase II of the process cycle) was performed at a flow rate of 120 ml/min. The concentration of the reagents and products was monitored using an MS Agilent 5973 Network Mass Selective Detector.

The oxygen conversion by sample reduction, X_{O_2}, was calculated as the ratio of the moles of oxygen being released as gaseous products H_2O and CO_2, to the molar amount of oxygen which theoretically can be stored in the Fe_3O_4 and CeO_2. The latter compound also participates in the redoc cycle via Eqs. (4) and (5):

$$\text{Phase I}: \ CO + CeO_2 \Leftrightarrow CO_2 + Ce_2O_3 \tag{4}$$

$$\text{Phase II}: \ H_2O + Ce_2O_3 \Leftrightarrow H_2 + CeO_2 \tag{5}$$

The freshly prepared sample contains Fe_2O_3 which is not stable under the here applied process conditions, but in fact Fe_3O_4 is the iron oxide of highest iron oxidation state being present in this process. Moreover, it is reasonable to assume that the oxygen molecules bound in Cr_2O_3 and ZrO_2 do not participate in the redox cycle. Therefore, X_{O_2} is defined as

$$X_{O_2} = \frac{N_{H_2O} + 2N_{CO_2}}{4N_{Fe_3O_4} + 0.5N_{CeO_2}} \times 100\% \tag{6}$$

where N_i stands for the number of moles of component i.

3. Results and discussion

3.1. Reduction and re-oxidation experiments

First, experiments were carried out using hydrogen or carbon monoxide as reducing gas. The formation rates of H_2O and CO_2 during the reduction step were measured on-line as a function of time by use of mass spectrometry. Fig. 2 presents the formation

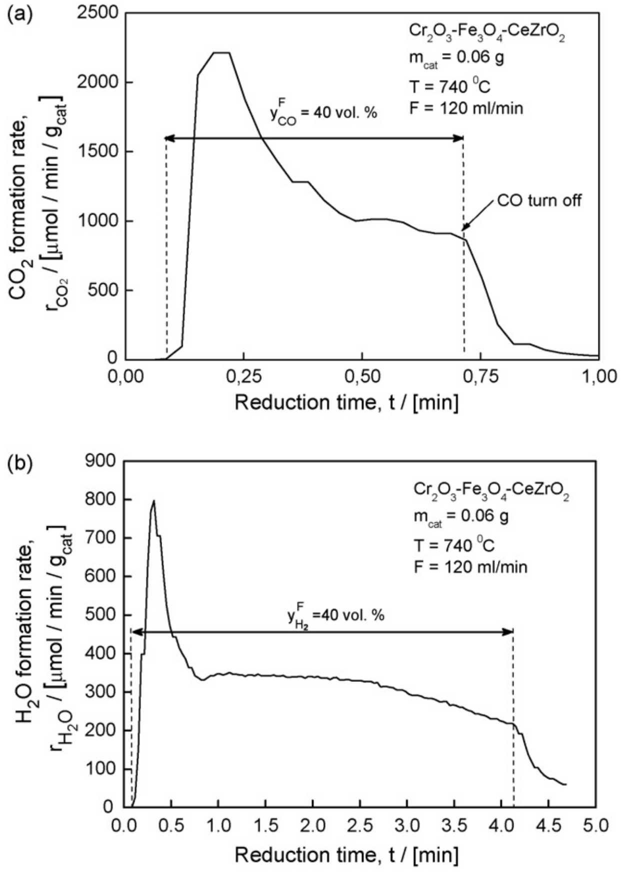

Fig. 2. (a) Formation rate of CO_2 during the reduction phase with CO/He feed; (b) formation rate of H_2O during the reduction phase with H_2/He feed (reaction conditions are given in the legends).

rates obtained with the fixed bed reactor filled with 6 mg of Cr_2O_3–Fe_2O_3–CeO_2–ZrO_2 being fed with a mixture of 40 vol.% CO in helium (Fig. 2a) or 40 vol.% H_2 in helium (Fig. 2b). It can be seen that the formation rates pass over sharp maxima in the initial phase of the reaction and then decrease because of the decreasing amount of movable rest-oxygen being stored in the iron oxide sample. The formation rate of H_2O is considerably lower than that for CO_2. This means that, at the same reduction time, with CO one is able to reduce the sample substantially more deeply than with H_2. In both cases, the rate peak is followed by a long tailing which is due to diffusion resistances of iron ion transport within the material [21].

By averaging of the CO_2 or H_2O formation rates over a certain period of time (here: 20 s), effective formation rates were determined. The results at different feed mole fractions of carbon monoxide and hydrogen in helium, $y^F_{CO_2}$ and $y^F_{H_2}$, respectively, are depicted in a logarithmic diagram in Fig. 3. Obviously, increasing the feed concentrations of both species leads to a significant increase of average formation rates and thereby also of the oxygen conversion degree. The effective reaction orders w.r.t. carbon monoxide and hydrogen were $m = 0.54$ and $n = 0.60$, respectively. This indicates a significant influence of internal diffusion resistances [21].

By contacting the reduced sample with steam, hydrogen was produced and thereby Fe_3O_4 and CeO_2 were formed for the reduction phase period of the next cycle. The observed rate of hydrogen production as a function of time of re-oxidation is shown in Fig. 4 for two samples of same mass. The difference between these two samples was their oxygen uptake capacity, i.e. the oxygen conversion degree during the preceding reduction phase. Due to the fact that the hydrogen-reduced sample lead had a lower initial oxygen content, more hydrogen was produced than in case of the CO-reduced sample.

Thus, the obtained results from single-phase experiments indicate that H_2/CO gas mixtures can be purified from CO by use of an iron redox cycle over the prepared Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2 sample. During the reduction phase, carbon monoxide is consumed and during the subsequent oxidation phase, CO-free hydrogen is produced from water vapour.

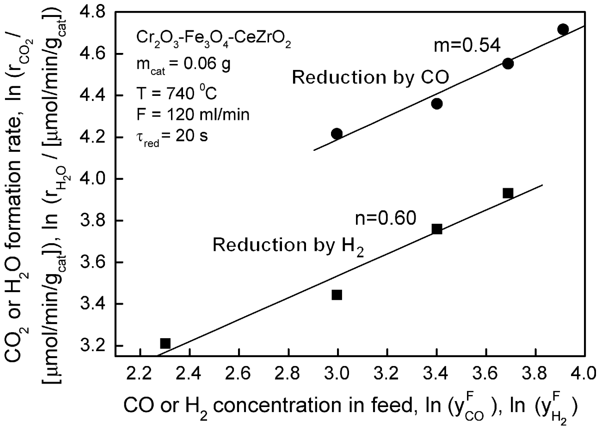

Fig. 3. Average formation rates of CO_2 and H_2O during the reduction phase with CO/He or H_2/He, respectively, vs. the mole fraction of the reducing species in the feed (reaction conditions are given in the legend).

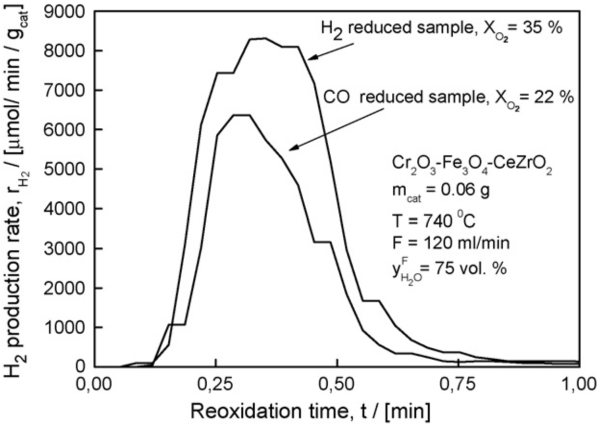

Fig. 4. Formation rates of H_2 during the re-oxidation phase with H_2O/He for two samples after initial sample reduction using H_2 or CO (reaction conditions are given in the legend).

3.2. Redox cycle experiments

Fig. 5 shows the amount of produced hydrogen over 15 subsequent redox cycles with a reducing feed gas mixture of 20 vol.% H_2 and 10 vol.% of CO with helium as carrier gas. (In the real process N_2 will act as carrier gas. But for analytical reasons, N_2 was replaced by He.) Obviously, a stable operation of the cyclic water gas shift reactor was feasible. Because a typical reformate gas mixture usually contains CH_4, CO_2, and H_2O besides H_2 and CO, during the cycles 6–10, 4 vol.% of CO_2 and 8 vol.% of H_2O were mixed into the reducing feed gas. As can be seen, the presence of water and carbon dioxide lead to a substantial decrease of the hydrogen production. This is a result of the lower “reducing power” of the CO_2/H_2O-containing feed gas. Thereby, a lower degree of oxygen conversion of the sample is attained and less hydrogen is formed in the re-oxidation phase of the process cycle.

More detailed single-phase experiments were performed in order to elucidate the influence of the oxidizing components CO_2 and H_2O in the reducing gas on the amount of hydrogen being generated in the re-oxidation phase. Fig. 6a shows the dependency of the hydrogen amount on the molar CO_2/CO ratio, and

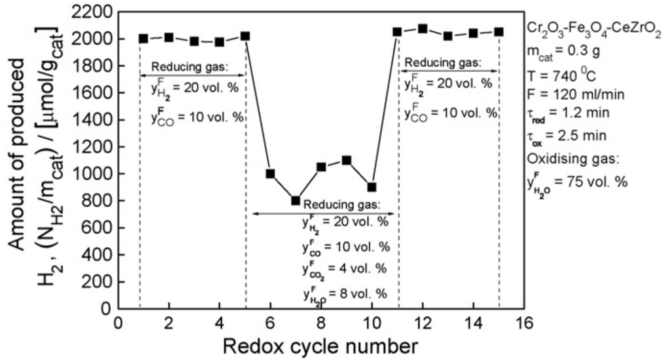

Fig. 5. Amount of hydrogen being produced during 15 subsequent redox cycles using a H_2/CO feed gas mixture in the absence (cycles 1–5 and 11–15) and in presence of H_2O and CO_2 (cycles 6–10) in the feed (reaction conditions are given in the legend).

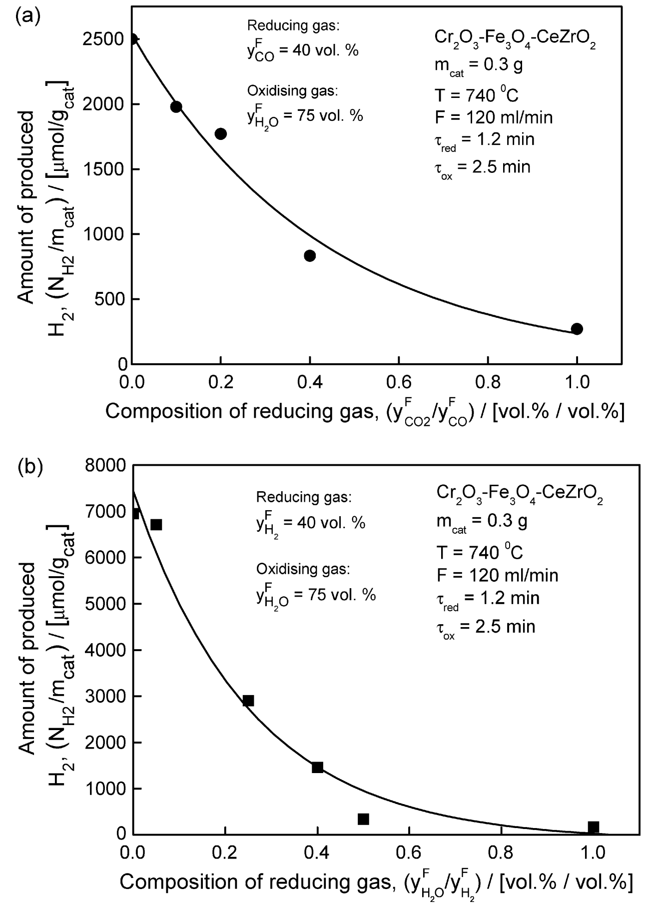

Fig. 6. Amount of hydrogen being produced during the re-oxidation phase in dependence on the composition of the gas being applied in the reduction phase: (a) reduction by CO_2/CO mixtures; (b) reduction by H_2O/H_2 mixtures (reaction conditions are given in the legend).

Fig. 6b presents the analogous dependency for the molar H_2O/H_2 ratio. In these experiments, the sample was reduced always by 40 vol.% CO in helium, while in the re-oxidation phase the water content in the H_2O/He gas was always 75 vol.%. The reduction time span was the same for all experiments. Obviously, the hydrogen production rate decreases strongly with increasing H_2O or CO_2 content in the feed. This is due to fact that the driving force for the desired conversion direction is lowered by the following reverse reactions which take place during the reduction phase if some H_2O and/or CO_2 are present in the reducing gas:

$$(4-3x)CO_2 + 3FeO_x \rightarrow (4-3x)CO + Fe_3O_4 \tag{8}$$

$$(4-3x)H_2O + 3FeO_x \rightarrow (4-3x)H_2 + Fe_3O_4 \tag{9}$$

$$CO_2 + Ce_2O_3 \rightarrow CO + CeO_2 \tag{10}$$

$$H_2O + Ce_2O_3 \rightarrow H_2 + CeO_2 \tag{11}$$

As a confirmation for Eqs. (8) and (10), Fig. 7 shows that CO can be formed from CO_2 at the reduced Cr_2O_3–Fe_2O_3–CeO_2–ZrO_2 sample. In other words: the cyclic water gas shift process can also be used to generate CO-rich gas mixtures from carbon dioxide sources.

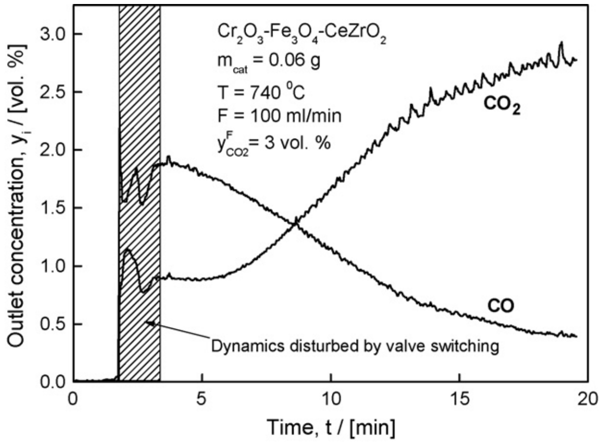

Fig. 7. CO formation during re-oxidation with CO_2/He mixture of a sample being previously reduced by H_2/He feed gas (reaction conditions are given in the legend).

3.3. Carbon deposition

As mentioned above, for PEM fuel cell applications, the CO content in the hydrogen feed gas has to be below 20 ppm. The re-oxidation reactions, Eqs. (2) and (5), do not produce any carbon monoxide. But carbon oxides can be released from the process due to steam gasification of carbon deposits which were formed during the preceding Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2 reduction phase by CO. Carbon can be produced on the sample surface by the Boudouard reaction, Eq. (12):

$$2CO \Leftrightarrow C + CO_2 \tag{12}$$

or via the formation of iron carbide according to Eq. (13):

$$Fe_3O_4 + 6CO \rightarrow Fe_3C + 5CO_2 \tag{13}$$

Both reactions are thermodynamically feasibly at temperatures lower than 750 °C if the oxygen conversion of the iron oxide material is higher than 80% [9,18]. We detected the formation of carbon oxides during the re-oxidation phase in all our experiments in which CO was used in the preceding reduction phase. Table 1 compares the amount of carbon on the sample surface with the oxygen conversion degree in iron oxide materials. It can be seen that the formation of carbon oxides could be minimized by keeping the oxygen conversion below a certain degree.

Table 1
Amount of carbon formed in dependence on the oxygen conversion degree during the reduction of the Cr_2O_3–Fe_3O_4–$CeZrO_2$ sample by carbon monoxide and hydrogen

Oxygen conversion degree (%)	Amount of carbon (μmol)
30	0.026
60	0.028
80	0.052
100	0.143

Reaction conditions: $T = 740\,°C$; $y^F_{CO} = 40$ vol.%; $y^F_{H_2} = 40$ vol.%.

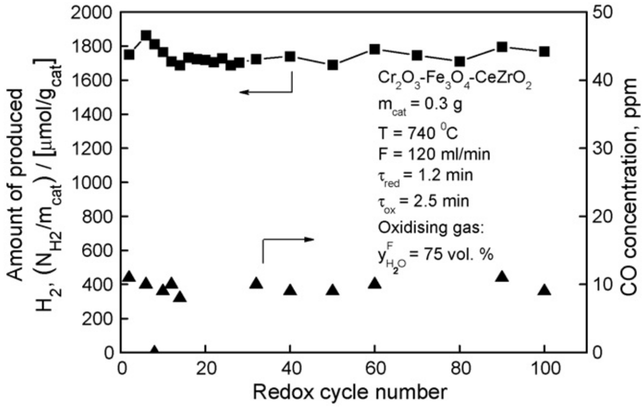

Fig. 8. Amount of hydrogen being produced and CO outlet concentration during 100 subsequent redox cycles using a H_2/CO/He feed gas mixture $y^F_{H_2} = 20$ vol.%; $y^F_{CO} = 10$ vol.%.

3.4. Long-term stability of process cycle

Fig. 8 illustrates the amount of produced hydrogen during 100 redox cycles with 0.3 g of the Cr_2O_3–Fe_3O_4–CeO_2–ZrO_2 sample. The reduction time for each cycle was 1.2 min, while the re-oxidation time was 2.5 min. The formation rate of hydrogen remained nearly constant over time which confirmed clearly the stability of the material activity. The concentration of carbon monoxide arising from carbon deposits, being formed via Eqs. (12) and (13), was around 10 ppm as long as the oxygen conversion degree of the material was kept below 20%.

Fig. 9a provides is more detailed view on the sample reduction phase of the sixth redox cycle. The stability of the re-oxidation phase is confirmed by Fig. 9b where hydrogen production rate data of three selected cycles are plotted together. The shape of the rate curves of both phases reveal qualitative differences to the single-phase experiments given in Figs. 2 and 4. These differences are due to the fact that a higher amount of sample was applied in the long-term cycle experiments, i.e. the sample-mass-to-feed-flow-ratio and also the sample distribution along the space coordinate will change the curve shapes.

However, the obtained data support the feasibility of the proposed iron redox process and the appropriateness of the prepared mixed-oxide sample. The cyclic water gas shift process is a suitable downstream process for CO removal from syngas down to an acceptable level of 10–20 ppm directly after the conversion of the hydrocarbon fuel to syngas, e.g. by partial oxidation.

In order to ensure reliable operation of the iron oxide sample, we define a characteristic ratio R which indicates the gas composition being required for the reduction of the sample:

$$R = \frac{y^F_{CO} + y^F_{H_2}}{y_{CO_2} + y_{H_2O}} \tag{14}$$

A reactor with $R > 4$ operates with a high rate of iron oxide reduction. A reactor with $1 < R < 2$ also reduces the sample but the reduction rate is low. At values $R < 1$ the application of this type of reactor is not reasonable. These rough criteria were derived using thermodynamic data for the chemical equilibria of the main redox reactions, Eqs. (1) and (2), given in [19].

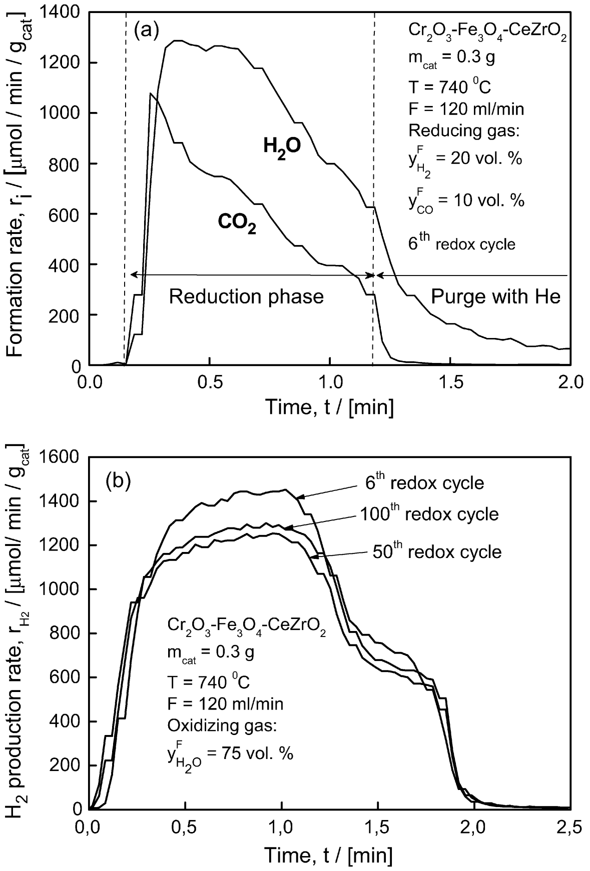

Fig. 9. (a) Formation rates of CO_2 and H_2O during reduction phase of one selected redox cycle vs. time; (b) formation rates of H_2 during the re-oxidation phase of three selected cycles vs. time (reaction conditions are given in the legends).

4. Conclusions

It was possible to demonstrate via systematic experiments that the carbon monoxide content in hydrogen stream for low temperature fuel cells can be effectively decreased with a cyclic water gas shift (CWGS) process. The process is based on a periodic reduction/re-oxidation cycle of iron oxides. The applied, self-prepared iron oxide material, 5 wt.% Cr_2O_3–40 wt.% Fe_2O_3–CeO_2–ZrO_2, showed high activity and stability during 100 repeated reduction/re-oxidation cycles. In the product hydrogen stream of the process, some carbon monoxide was observed which was formed during the re-oxidation phase of the sample by steam gasification of deposited carbon on the sample surface. The carbon formation rate on the sample surface can be controlled by restricted oxygen conversion of the material.

Under technical conditions the proposed process will be performed in a bundle of parallel fixed bed reactor tubes which are fed alternately with syngas and steam. For optimization of a technical scale CWGS process, it is reasonable to describe the obtained rate data be means of an appropriate gas–solid reaction model. As demonstrated in [21], the shrinking core model (SCM) with combined reaction and diffusion control is a suitable basis for description of the reaction of Fe_3O_4 with CO to FeO and subsequently to Fe, and also for the re-oxidation reaction of Fe with steam to FeO and Fe_3O_4.

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