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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 2: Hydrogen Production Technologies – Part 1
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-2
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-652-1

Two-step Water Splitting by Cerium Oxide-Based Redox Pairs

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1 Introduction

The utilization of hydrogen as clean energy becomes important for solving global environmental problems and securing future energy supply. A possible method for producing hydrogen is a two-step water splitting reaction in a thermochemical cycle. In the first step metal oxides being in a low oxidation state (oxygen deficit phases) are used for water splitting. By that the water splitting material transforms in a higher oxidation state. In a second step the metal oxide is regenerated by heating using concentrated solar energy. In recent years various redox systems have been studied e.g. Zn/ZnO and Ferrites [1,2]. Especially CeO_2-based solid solutions are considered to be promising redox materials for water-splitting purposes. Ceria in general is beneficial since its fluorite structure allows a wide range of Ce oxidation states (Ce^{4+} - $Ce^{3.x+}$) charged balanced by oxygen vacancies. However, for the reduction of pure cerium oxide, temperatures higher than 1500°C are required. The redox process can be shifted towards lower temperatures by doping ceria with another transition metal oxide. It was found out doping ceria with up to 20% iron oxide allows the regeneration step at 1400°C and the hydrogen production step at 1000°C [3-6]. On the other hand, additional structural vacancies are formed by the Ce^{4+}/Fe^{3+} substitution which typically results in higher atomic mobility, thus leading to increased sinterability and grain growth. This lowers the surface activity of the metal oxide and degrades the efficiency of the water splitting process. A long lifetime of the functional oxide with a constant productivity is the precondition for any industrial application.

For a constant high water splitting activity two main conditions must be fulfilled by the material. On the one hand, transition between metal's oxidation states should take place easily without nucleation barrier. On the other hand the high porosity and surface activity must be retained throughout many cycles. In the present study we report about a novel approach to increase the microstructure stability of $(Ce,Fe)O_x$ solid solutions: The functional compound is applied as a coating on 0.5 mm zirconia spherules. By using a counteracting substrate sintering shrinkage should be reduced in two dimensions. Additionally a higher secondary surface area can be realized and highly effective turbulent fluidized bed technologies can be applied for the water splitting process. Moreover, submicron oxide particles bound on an inert substrate allow toxicological harmless handling which is an important advantage in industrial-scale application.

2 Syntheses

Fe-modificated CeO_2 coatings on ZrO_2-beadlets were produced by a single-step precipitation process using a nitrate route. $Ce(NO_3)_4 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 6H_2O$ were mixed in an atomic ratio of Ce/Fe 80:20 and solved in distilled water and glycerin (10 weight % of water) at 40°C. The whitish ZrO_2 particles were wet by the aqueous nitrate-glycerin solution. The admixture was heated up to 150°C on air to vaporize the water and dried at 500°C for two more hours. The dried material contains coated spherules and surplus $(Ce,Fe)O_x$ oxide, the latter was removed by sieving. Visual inspection after drying suggested that $(Ce,Fe)O_x$ coated ZrO_2 spherules were obtained as evidenced by their orange coloration (Figure 1). At this point the functional oxide exists in its highest oxidation state. To use the functional coating for water splitting purposes the cations must be transferred in reduced oxidation states (Fe^{2+} , potentially $Ce^{(4--x)+}$). For this purpose the coated spherules were mixed with a defined amount of graphite and heated up to 1100°C for one hour. The reaction took place in a tubular furnace in inert gas atmosphere using nitrogen (purity 5.0) with a flow rate of 300ml/hour. Subsequent rapid cool down of the sample is important to freeze the reduced oxidation state. This was performed by removing the sample as fast as possible (< 1sec) from the hot zone of the furnace, still under inert atmosphere.

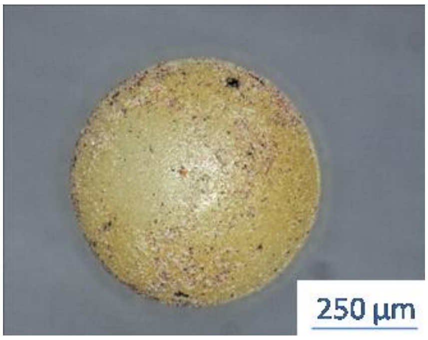

Figure1: $(Ce,Fe)O_x$ coated ZrO_2 beadlets.

As reference material and for easier microstructural analyses of $(Ce,Fe)O_x$ precipitates powder samples without ZrO_2 substrate were synthesized. $Ce(NO_3)_4 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 6H_2O$ in atomic ratio 80:20 were mixed with water and glycerin and heated up to 200°C until water was removed. The powder was milled and heated up to 500°C for two hours.

3 Results and Discussion

The powder is orange and nano-crystalline as evidenced by TEM analyses (Figure 2). To analyze chemical compositions and especially the elemental distribution of the coating transmission electron microscopy (TEM) analysis with corresponding microanalyses were carried out. For this powdered coating material was spread on a holy carbon film supported by a copper grid. This method enables a combination of quantitative chemical analysis with high local resolution. The TEM analysis showed an Fe content of 5-10 at% in the $(Ce,Fe)O_x$ phase. Residual iron could be localized in a second iron oxide phase.

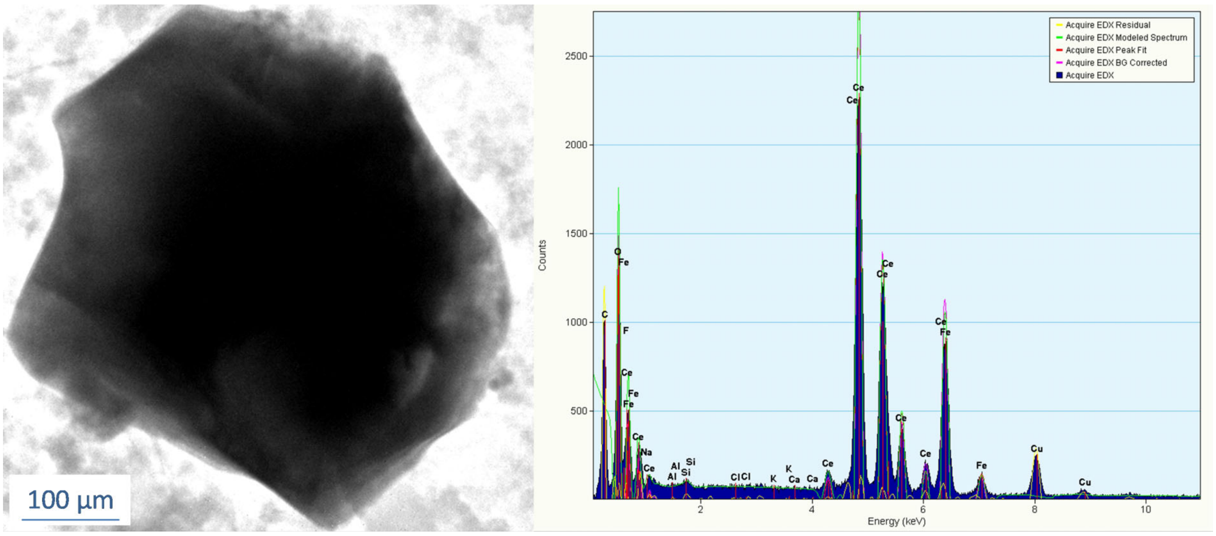

Figure 2: TEM image of (Ce,Fe)O_x coating material with corresponding EDX spectrum.

(Ce,Fe)O_x coatings on ZrO_2-beadlets were characterized by electron microscopy and corresponding microanalysis. After sintering for one hour at 1100°C a disrupted and highly porous coating occurs on the ZrO_2 substrate. The coating has an average thickness of about one micrometer. Figure 3 shows an overview and a detail image of the coating. The degree of coating, i.e. the spherule surface, which is covered by (Ce,Fe)O_x assuming a layer thickness of 1µm is measured by weighing. To do so the average weight of untreated and coated ZrO_2 beadlets was determined thus leading to an average covering degree of ≈12%.

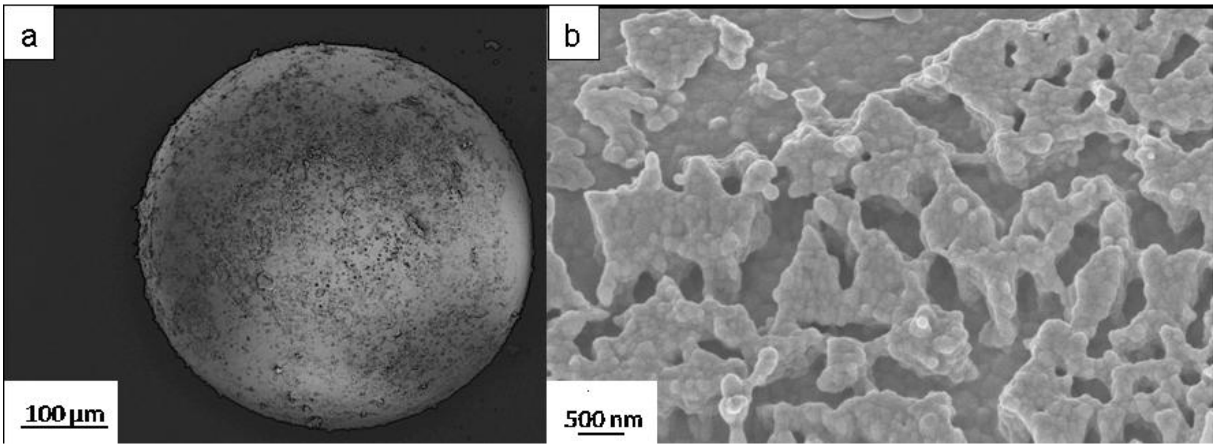

Figure 3: (Ce,Fe)O_x coatings on ZrO_2-beadlets; a) overview image of coating beadlets, b) detail image of disrupted, porous layer.

Thermally induced sintering and coarsening of (Ce,Fe)O_x coatings on ZrO_2-spherules was investigated by heating the material for 100 hours at 1100°C in air atmosphere. After the thermal treatment the disrupted layer was still about 1µm thick and porous. The grain size ranged between 150 and 350 nm and the appearance of the coating on the substrate surface was virtually unchanged. Obviously, the disrupted and porous coating was highly stable against sintering processes and grain coarsening. The interface region of coating and substrate was studied by REM using a cross section specimen. Elemental maps of Zirconium and Cerium show virtually no interdiffusion between coating oxides and ZrO_2 substrate.

To simulate the water splitting reaction in a solar furnace, a test set-up consisting of a water evaporation system, an electrical tubular furnace and a mass spectrometer was employed. For testing a sample is placed in an alumina crucible inside a reaction tube and flushed by nitrogen (purity of 2.8, 500sccm) which is mixed with water vapor during the water splitting step. The amount of water is controlled by a peristaltic pump. The regeneration step is carried out in pure nitrogen at 1200°C for 60 min. The product gas is cooled by a gas cooler (ABB) and analyzed by a calibrated mass spectrometer (Pfeiffer Vacuum). At this point of investigations it is difficult to define the reacting oxide mass and so the produced mass of hydrogen per mass oxide could only be estimated. During the first water splitting step of 10 min ≈2.5mmol H_2 per gram oxide coating were produced. The H_2 formation rate is shown in Figure 4. There is a high peak of hydrogen production at the very beginning of the water splitting step but the production rate rapidly drops down.

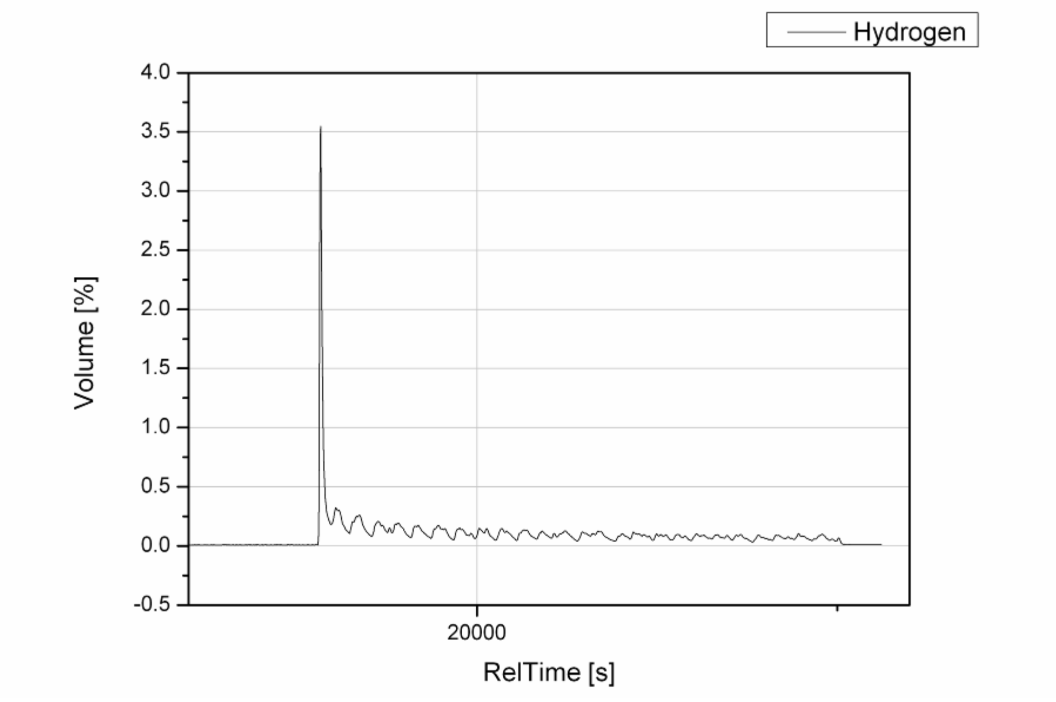

Figure 4: Hydrogen production rate vs. time.

After two cycles, which implicates two water splitting reactions at 830°C and two regeneration steps at 1200°C, $(Ce,Fe)O_x$ coatings exhibit some grain growth with grain size up to 1µm. Microstructural evidence suggests only little reduction in surface area. The general appearance of the insular coating remains virtually unchanged.

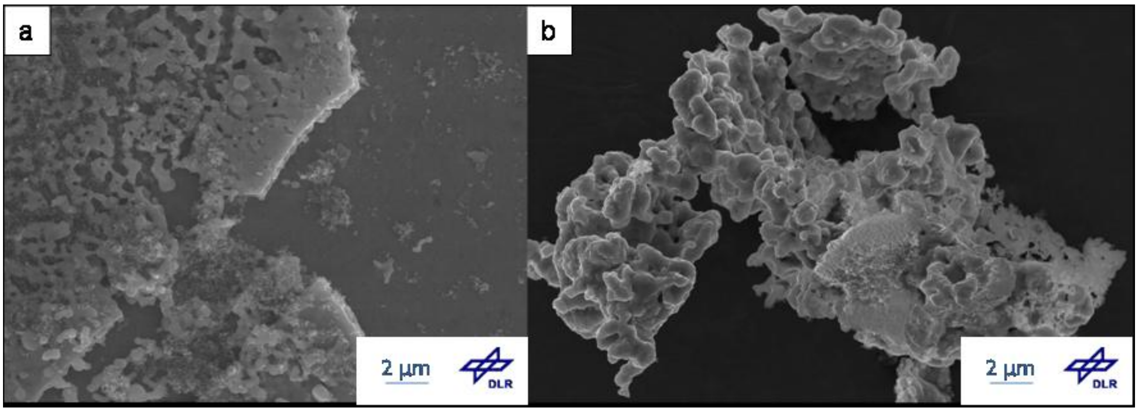

Figure 5: **a) $(Ce,Fe)O_x$ coatings on ZrO_2; b) reference $(Ce,Fe)O_x$ powder without substrate, both after 2 water splitting cycles.**

Obviously, the rigid substrate counteracts volume shrinkage in two dimensions. In contrast, a corresponding substrate-free reference powder which was treated in the same way shows significant densification and hence already after two cycles the surface activity is reduced (Figure 5b). This study shows that coating of inert ceramic spherules with functional oxides is a suitable way to retain relatively high surface areas. This is particularly important because presence of water vapor generally accelerates diffusion-controlled processes (grain coarsening, sintering) in oxide phases. In subsequent investigations the size effect of the substrate beadlets will be studied in more detail.

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