

Achieving Hydrogen Production through Solid Oxide Electrolyzer Stack by High Temperature Electrolysis

Le Jin, Wan Bing Guan, Xiao Ma, Cheng Xu and Wei Guo Wang

ECS Trans. 2012, Volume 41, Issue 33, Pages 103-111.
doi: 10.1149/1.3702417

**Email alerting
service**

Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or [click here](#)

To subscribe to *ECS Transactions* go to:
<http://ecst.ecsdl.org/subscriptions>

© 2012 ECS - The Electrochemical Society

Achieving Hydrogen Production through Solid Oxide Electrolyzer Stack by High Temperature Electrolysis

L. Jin, W. B. Guan, X. Ma, C. Xu and W. G. Wang

Division of Fuel Cell and Energy Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, P.R. China

Based on the reversal reaction of solid oxide fuel cells (SOFC), high temperature electrolysis (HTE) is an effective way for large-scale and low cost hydrogen production. The problem restricted the development for HTE is the stability of steam supplying, conversion rate of steam to H₂, hydrogen production rate and the durability of solid oxide electrolysis cells (SOECs) and stacks. To solve the problems mentioned above, a steam and gas fogged mixer (SGFM) was designed which can be used for not only experimental HTE but also large-scale hydrogen production. A 30-cell SOEC stack was tested combined with the mixer for 1000 hours at 800°C with an electrolysis current of 4 A. The steam-to-hydrogen conversion (SC) rate was calculated to be 70% by determining the water amount at the inlet and outlet of the hydrogen electrode. The hydrogen production rate was 99.3 NL/h.

Introduction

To find new energy carrier instead of oil and gas becomes an important task for energy development in many countries. Hydrogen is a kind of non-pollution and renewable energy carrier. It attracts wide attention because of storable and transportable (1). The key point for hydrogen development is find low cost hydrogen sources. Presently, over 90% of hydrogen is produced from natural gas, but the process is quite costly. High temperature electrolysis (HTE) uses the reversal reaction of solid oxide fuel cells (SOFCs) to produce hydrogen at a rather high efficiency – the thermo-electric efficiency of HTE can reach more than 50% if HTE is combined with renewable or nuclear energy. Therefore, the HTE is an effective way for large-scale economic hydrogen production (2-3).

Steam electrolysis using solid oxide electrolyzer cells (SOECs) for hydrogen production was under development in the early 1980s and has again become of increasingly interest during recent years as a green energy technology. Mainly single cells

have been tested for electrolysis performance and durability, and only a limited number of studies focus on the performance and durability of high temperature electrolysis stacks. To ensure a sufficient H_2 production rate, an SOEC system must consist of several repeating cells assembled in stacks. And high and stable performance of stacks is also required to reduce the cost of H_2 production (4). A large electrolysis stack with tubular SOECs in a serial connection has been tested and demonstrated to be feasible (5). But more works are needed for the stacks with planar SOECs (6). In this paper, durable performance of a 30-cell SOEC stack was tested under electrolysis and the degradation behavior was discussed.

Durable Performance of SOEC Stack

Stable Steam Supply in High Temperature Steam Electrolysis

The most important problem in HTE is stable steam supplying and accurate and stable steam-to- H_2 ratio monitoring. Presently there are mainly three methods for steam supplying. In the first method, N_2 was used as a carrier gas to control the steam-to- H_2 ratio. Deionized water was supplied using a pump. Water were evaporated in heated sand bath, and mixed with the N_2 line. The steam/ N_2 stream was combined with the H_2 steam and directed to the furnace using a heating pipe (7). By this method, the steam-to- H_2 ratio can be controlled effectively. But the steam and H_2 can not mix completely in the heating pipe and the steam-to- H_2 ratio will vary with the mixing condition.

The second method is using dewpoint to control the steam-to- H_2 ratio. N_2 was also used as an inert carrier gas for independent variation of the flow rates of the steam and hydrogen gases. In this method, N_2 was mixed with hydrogen firstly. Then the N_2/H_2 gas mixture was mixed with steam by means of a heated humidifier. The dewpoint temperature of the steam/hydrogen/nitrogen gas mixture exiting the humidifier was monitored continuously using a dewpoint sensor (8-9). This method has been used widely in humidity control. But in practical applications, it is difficult to keep the dewpoint temperature constant. The dewpoint temperature always fluctuates and the fluctuating value may reach up to 10°C . This means that the absolute humidity characterizing the steam-to- H_2 ratio will fluctuate more than 10%. And the fluctuating value increases with the increasing dewpoint temperature. Unstable steam-to- H_2 ratio will cause the fluctuation of electrolysis voltage. This will influence the stability of steam electrolysis for hydrogen production.

The third method for steam supplying was reported by Risoe National Laboratory. Steam was produced by reacting oxygen with hydrogen in a pre-heater, and then transported to the stack. Unlike the other two methods for steam supply, this method was proved to be suitable for long-term steam electrolysis for hydrogen production. But how to controlling the steam flow and the steam-to- H_2 ratio were not mentioned (10).

Against the advantages and disadvantages for steam electrolysis testing system referred above, a new testing system was designed with a steam gas fogged mixer (SGFM), shown in Figure 1. The system includes gas cylinders, mass flow controllers, water supply, HPLC pump, steam gas fogged mixer (SGFM), high temperature furnace, solid oxide electrolyzer cells (SOEC), electrochemical testing equipment, condenser and water collector. The SGFM includes water suction device and heat exchanger. This system can be used not only in experimental steam electrolysis for hydrogen production, but also in large-scale hydrogen production. Nitrogen and hydrogen both can be used as carrier gases. In this paper, we chose hydrogen as the carrier gas and also as the protective gas. Hydrogen was fed into the water suction device and formed a negative pressure in the device. Deionized water was also transported to the water suction device by HPLC pump. Because of the negative pressure, the water was sucked and mixed with the hydrogen. The water and hydrogen were transported to the heat exchanger which kept the temperature constant at 400°C. In the heat exchanger, water evaporated and mixed with hydrogen completely. Then the mixture gas of steam and hydrogen was brought to the hydrogen electrode of stack. In this system, the flow rate of water was controlled accurately by HPLC pump, and the steam and hydrogen mixed completely in SGFM, so that the steam-to-H₂ ratio was stable all the time. The testing result of our water supply system is shown in Figure 2. It can be seen that the flow rate of steam keeps stable with a fluctuation error of only 0.15%.

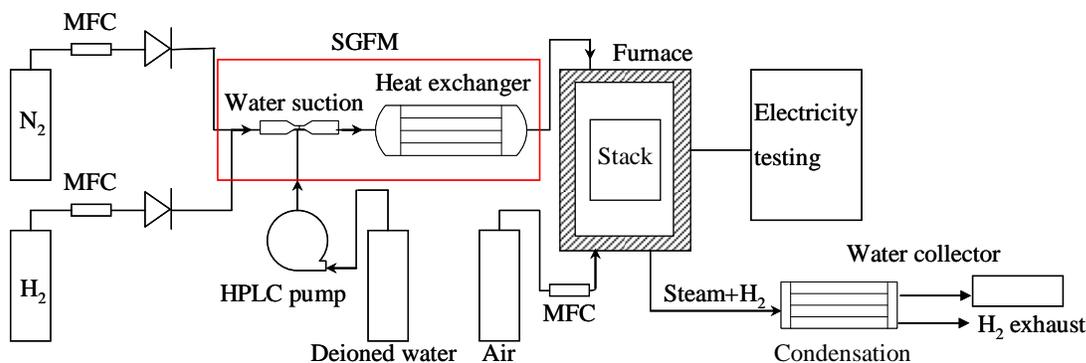


Figure 1. Schematic of experimental setup for high temperature steam electrolysis stack measurements.

Durability of High Temperature Steam Electrolysis for Hydrogen Production

High temperature electrolysis for hydrogen production carries out the inverse reaction of the SOFC. So the reasons causing the degradation of SOEC are the same as SOFC. The SOEC stack degradation factors include sealing, thermal expansion matching of stack component parts, Cr vapor from interconnect, etc. Figure 3 shows a 30-cell stack module and schematic illustration of stack structure. Cells used in SOEC stack are planar NiO-YSZ/YSZ/LSM anode-supported cells. The single cell active area is 70cm². The detailed parameters of cells can be seen elsewhere (11-13). The Fe-16Cr alloy was used

as interconnect for stack.

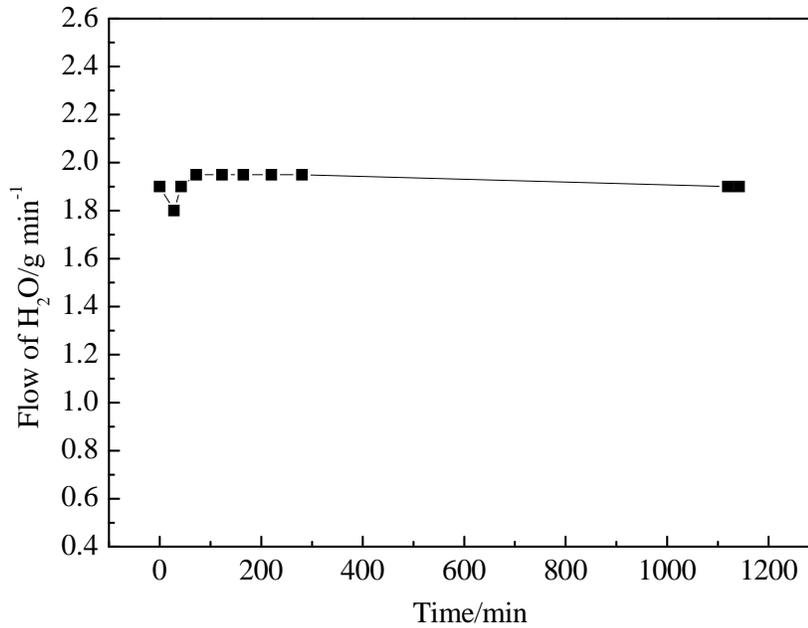


Figure 2. Testing result of water supply by high temperature steam electrolysis system.

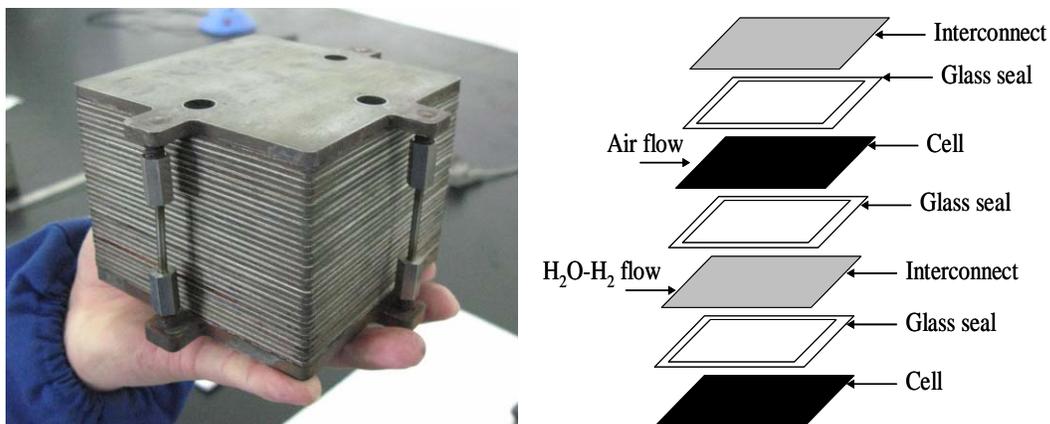


Figure 3. SOEC stack structure and a 30-cell standard stack module produced by NIIMTE.

Figure 4 shows the result of a 2-cell stack working under SOEC and SOFC mode alternately. The total working hour is 2100 hours. At the beginning, the stack was operated under SOFC mode for 980 hours with the degradation rate 4.10%/kh. The stack was then switched to SOEC mode from 1000th to 1200th hour and from 1600th to 2100th hour. In SOEC mode, the electrolysis voltage fluctuated greatly. So a durable performance stack was one of reasons to ensure long-term high temperature electrolysis.

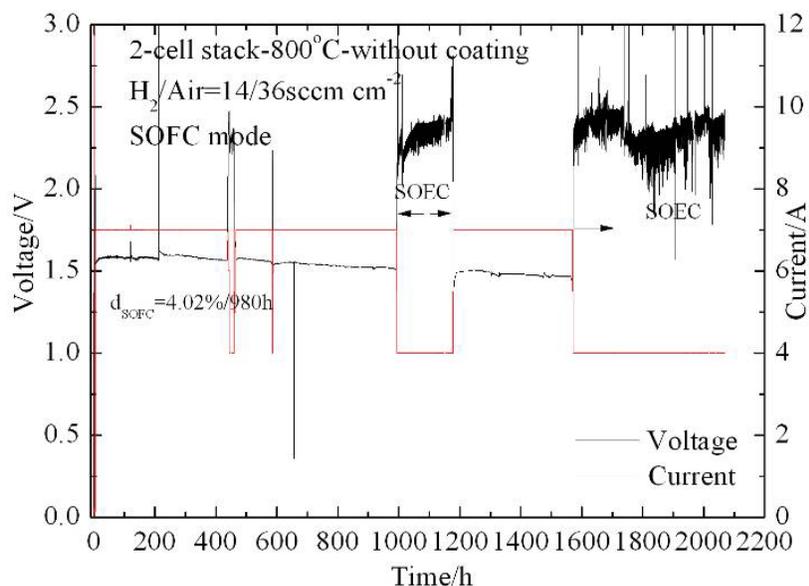


Figure 4. 2-cell anode-supported stack ran under SOFC and SOEC mode alternately.

Figure 5 shows the result of 30-cell stack high temperature electrolysis. The hydrogen electrode of stack was fed by a mixture gas with 0.5L/min H_2 and 2.24L/min steam at 800°C. The steam-to- H_2 ratio is 82%. The oxide electrode was fed by 3L/min air. The electrolysis ran for 1000 hours with an electrolysis current of 4A and an electrolysis voltage of 33V (with per-cell electrolysis voltage of 1V). It can be seen from Figure 5 that the voltage increased slowly during 238th to 429th hour in electrolysis and reached a peak voltage of 38V. In 500th to 618th hour, the voltage also increased and reached up to 35 V. But the stack performance did not decline overall. In summary, besides the durable stack, stable steam flow is also a reason to ensure stable high temperature electrolysis.

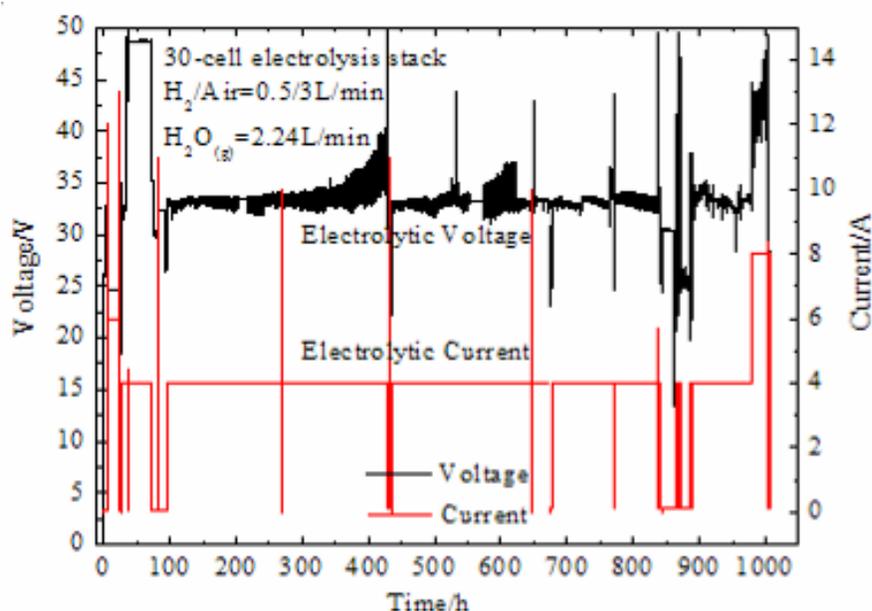


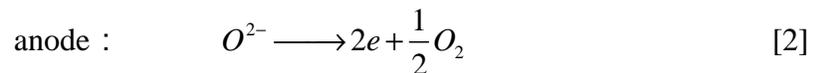
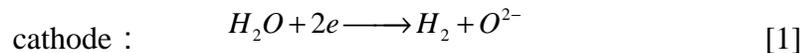
Figure 5. Stability test of a 30-cell stack during high temperature electrolysis.

Efficiency of High Temperature Electrolysis

Steam-to-H₂ Conversion Ratio

The steam-to-H₂ conversion (SC) ratio is one of crucial parameters to characterize the performance of HTE. Yang et al calculated the SC ratio as mole fraction of outlet hydrogen and inlet steam (14). The inlet steam flow was tested by humidifier sensor. But the outlet hydrogen flow included the hydrogen from inlet as protective gas. So the calculated value of SC ratio was higher than actual value.

The mechanism of HTE of steam in the unit cell can be described as follows. A mixture of steam and hydrogen is introduced into the high temperature cathode chamber (hydrogen electrode), and then the gas mixture penetrates through the porous cathode via the interface between the cathode and the solid oxide electrolyte. A water molecule is electrically split into hydrogen and an oxygen anion by two electrons transported from the anode through external cable. The produced hydrogen is back-diffused to the cathode chamber. The reduced oxygen anion is drawn to the anode through the solid oxide electrolyte by the electrochemical potential driven by an AC/DC potentiostat, thus liberating the two electrons and then oxidized to oxygen. The oxidized oxygen continuously penetrates the porous anode and is collected and evacuated at the anode chamber. The liberated electrons are transported to the cathode through the electric cable, too. According to the above mechanism, the following electrochemical reactions can be delivered:



Because the electrons were drawn to the cathode (hydrogen electrode), so the hydrogen fed to the cathode as protective gas will not convert into H₂O. And the SC ratio can be expressed as follow:

$$\eta_{ele} = (m_{H_2O,in} - m_{H_2O,out}) / m_{H_2O,in} \quad [4]$$

where $m_{H_2O,in}$ is the mass of steam fed to the stack, $m_{H_2O,out}$ is the mass of water collected at the outlet of the stack, and $(m_{H_2O,in} - m_{H_2O,out})$ is the mass of water reacting to produce hydrogen during HTE. As shown in Figure1, steam condensation equipment and

water collecting equipment were designed at the outlet of hydrogen electrode. The exhausting gas from hydrogen electrode was the mixture gas of steam and hydrogen. When the mixture gas flowing to the steam condensation equipment, steam was condensed into water and separated from hydrogen. Water was collected and the hydrogen exhausted. So the SC ratio of 30-cell stack was calculated by formula (4) and the result was shown in Figure 6. The average SC ratio was 73.9% with the steam-to-H₂ ratio 82% (water flow 1.8g/min and hydrogen flow 0.5L/min). When the water flow increased to 2.09g/min and 2.24g/min (means the steam-to-H₂ ratio 84% and 85% separately), the SC ratio were decreased to 53.4% and 53.8%. That means stable steam-to-H₂ ratio is important to durable long-term HTE.

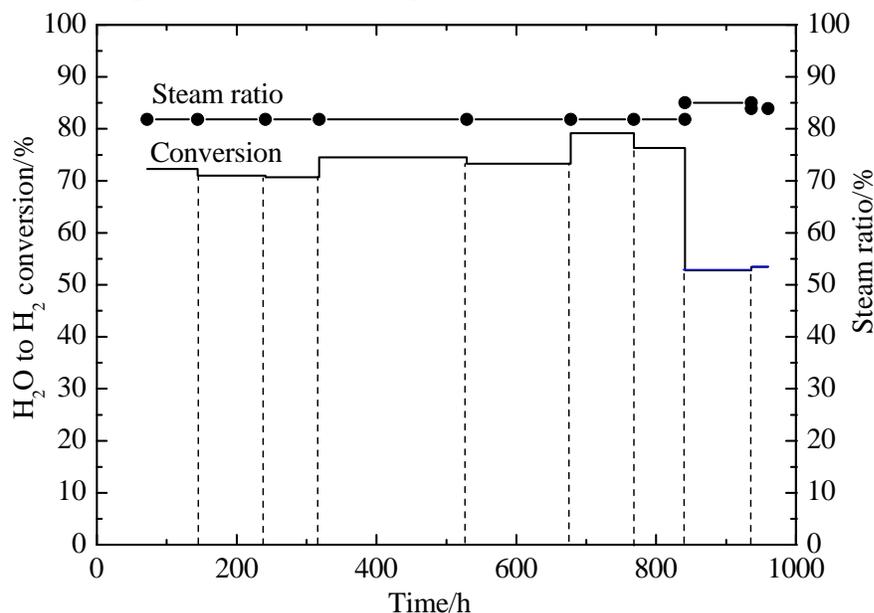


Figure 6. SC ratio of 30-cell stack HTE for hydrogen production.

Hydrogen Production Rate

Herring et al. proposed two methods to calculate hydrogen production rate as follows (15). 1) Measured inlet and outlet dewpoint temperatures permit direct determination of inlet and outlet steam mole fractions and the corresponding hydrogen production rate. 2) The molar rates of hydrogen production during electrolysis can also be predicted independently from the measured stack electrical current by Faraday Law. Agreement between the two hydrogen production rate values is generally very good. In this article the hydrogen production rate was calculated by the first method that is determining the mass of inlet and outlet water. From eq(3), the mole mass of hydrogen produced by electrolysis is equal to the mole mass of steam consumed in reaction. So the calculating formula of hydrogen production rate was as follow:

$$V_{H_2} = V_{H_2O} = f_{H_2O,in} \times \eta_{ele} \quad [5]$$

where V_{H_2} and V_{H_2O} are hydrogen production rate(NL/h) and steam consumption

rate(NL/h) respectively, and $f_{H_2O,in}$ is the inlet steam flow(L/min). With water flow 1.8g/min (0.1mol/min) and average steam-to-H₂ ratio 73.9%, hydrogen production rate as high as 99.3NL/h was achieved with this 30-cell stack.

Conclusion

In this paper, reasons for degradation of HTE were discussed. Steam-to-H₂ conversion (SC) ratio and hydrogen production rate were calculated. A steam gas fogged mixer (SGFM) was designed and combined with a HPLC pump to supply steam stably and maintain the steam-to-H₂ ratio constant. By the electrolysis testing system, a 30-cell SOEC stack was tested. It electrolyzed for 1000 hours with electrolysis current 4A and steam-to-H₂ ratio 82% under 800°C. The average SC ratio of 30-cell stack was 73.9% with the hydrogen production as high as 99.3NL/h.

Acknowledgments

This work was supported by high temperature electrolysis for hydrogen production program, Chinese Academy of Science.

Reference

1. L. Barreto, A. Makihira, and K. Riahi, *Int. J. Hydrogen Energ.*, **28**, 267 (2003).
2. S. H. Jensen, X. F. Sun, S. D. Ebbesen, R. Knibbe, and M. Mogensen, *Int. J. Hydrog. Energy*, **35**, 9544(2010).
3. B. Yu, W. Q. Zhang, J. M. Xu, and J. Chen, *Int. J. Hydrog. Energy* **35**, 2829 (2010).
4. J. Udagawa, P. Aguiar, and N. P Brandon, *J. Power Sources*, **180**, 46(2008).
5. D. W. Schmidberger R, *Int. J. Hydrogen Energy*, **7**(4), 321(1982).
6. M. Ni, M. K. H.Leung, and D. Y. C. Leung, *Int. J. Hydrogen Energ*, **33**, 2337 (2008).
7. P. K. Lohssontorn, D. J. L. Brett, and N. Laosiripojana, *Int. J. Hydrogen Energ*, **35**, 3958 (2010).
8. J. S. Herring, J. E. O'Brien, C. M. Stoots, etc. *Int. J. Hydrogen Energ*, **32**, 440 (2007).
9. C. Y, A. Coffin and F. Chen, *Int. J. Hydrogen Energ*, **35**, 3221 (2010).
10. S. D. Ebbesen, J. Hogh, and K. A. Nielsen, *Int. J. Hydrogen Energ*, **36**, 7363 (2011).
11. W. B. Guan, H. J. Zhai, L. Jin, T. S. Li, etc. *Fuel Cells*, **3**, 445 (2011).
12. W. G.. Wang, W. Guan, H. Li, Z. Wang, etc. *ECS Trans.*, **25**(2), 85 (2009)
13. W. Guan, H. Zhai, F. Li, etc. *ECS Trans.*, **25**(2), 485 (2009)
14. C. Yang, C. Jin, A. Coffin, etc. *Int. J. Hydrogen Energ*, **35**, 5187 (2010).

15. J. S. Herring, J. E. O'Brien, C. M. Stoots, etc. *Int. J. Hydrogen Energ.* **32**, 440 (2007).