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Highly efficient high temperature electrolysis†

Anne Hauch,\*Sune Dalgaard Ebbesen, Søren Højgaard Jensen and Mogens Mogensen

Received 5th December 2007, Accepted 3rd January 2008   
First published as an Advance Article on the web 31st January 2008   
DOI: 10.1039/b718822f

High temperature electrolysis of water and steam may provide an efficient, cost effective and environmentally friendly production of H2 using electricity produced from sustainable, non-fossil

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| Published on 31 January 2008. Downloaded by DTU Library on 28/07/2015 12:29:53. | energy sources. To achieve cost competitive electrolysis cells that are both high performing i.e. minimum internal resistance of the cell, and long-term stable, it is critical to develop electrode materials that are optimal for steam electrolysis. In this article electrolysis cells for electrolysis of water or steam at temperatures above 200C for production of H2 are reviewed. High temperature electrolysis is favourable from a thermodynamic point of view, because a part of the required energy can be supplied as thermal heat, and the activation barrier is lowered increasing the H2 production rate. Only two types of cells operating at high temperature (above 200C) have been described in the literature, namely alkaline electrolysis cells (AEC) and solid oxide electrolysis cells (SOEC). In the present review emphasis is on state-of-the art electrode materials and development of new materials for SOECs. Based on the state-of-the-art performance for SOECs H2 production by high temperature steam electrolysis using SOECs is competitive to H2 production from fossil fuels at electricity prices below 0.02–0.03 V per kWh.  Though promising SOEC results on H2 production have been reported a substantial R&D is still required to obtain inexpensive, high performing and long-term stable electrolysis cells. | | |
| 1. | Introduction | reforming is not optimal because the fossil fuel feed is based |
| In recent years there has been an increased focus on H2 as an energy carrier due to parameters such as limited fossil fuel sources, increasing oil prices and environmental aspects such as emission of CO2 and NOx. Most of today’s H2 is produced via steam reforming and the main part is synthesised to chemicals (ammonia, methanol etc.) at the production facilities. However from an environmental point of view H2 production by steam | | on consuming non-renewable fuels and furthermore CO2 is emit-ted. Consequently it is necessary to develop cost competitive, efficient and environmental friendly means of H2 production, preferably using renewable energy sources such as solar energy and wind power. Electrolysis of steam can provide H2 at high efficiency and high purity. Furthermore electrolysis cells can be applied to optimise the efficiency of intermittent sources such as wind power and utilise waste heat and surplus energy from |

e.g. nuclear power facilities during off-peak hours.

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| Fuel Cells and Solid State Department, Risø – DTU, Technical University of Denmark, Frederiksborgvej 399, Roskilde, DK-4000, Denmark. E-mail: anne.hauch@risoe.dk; Fax: +4546775858; Tel: +4546775850 † This paper is part of a Journal of Materials Chemistry theme issue on hydrogen storage and generation. Guest editor: John Irvine. | | | | | | | | | | | | | In parallel with the increased interest in H2 production there has also been considerable—and successful—R&D work world wide to develop high performing and long-term stable fuel cells. Such cells can typically work both as fuel cells for electricity | | | | | | | | | | | | | | | | |
| production | | | and | | as | | electrolysis | | cells | | for | H2 | | production. | | |
| Anne Hauch is working as post | | | | | | Sune | Dalgaard | | | | Ebbesen | is | Søren | Højgaard | | | | | Jensen | | is | Mogens Mogensen is research | | | | | | | |
| doctoral | | researcher | in | | the | working as a post doctoral | | | | | | | working as a post doctoral | | | | | | | | | Professor at the Fuel Cells | | | | | | | |
| SOFC and SOEC group at | | | | | | researcher at Risø – DTU | | | | | | | researcher in the SOEC group | | | | | | | | | and | Solid | | State | | Chemistry | | |
| the Fuel Cells and Solid State | | | | | | and his research is focused on | | | | | | | in the Fuel Cells and Solid | | | | | | | | | Department, | | | | Risø | | – | DTU, |
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| – | DTU, | Denmark. | | She | | for high temperature electro- | | | | | | | Risø – DTU, Denmark. He | | | | | | | | | ing with electrochemistry for | | | | | | | |
| received her Masters degree | | | | | | lysis of both H2O and CO2. | | | | | | | studied physics and mathema- | | | | | | | | | 35 years. He has co-authored | | | | | | | |
| in inorganic physical chemistry | | | | | | He studied chemical engineer- | | | | | | | tics | at | Aarhus | | | | University | | | more | than | | 200 | | technical | | |
| from the Aarhus University, | | | | | | ing | at | Aalborg | | | University, | | and Copenhagen University, | | | | | | | | | papers, which in total have | | | | | | | |
| Denmark in 2003 and in 2007 | | | | | | Denmark, performed his PhD | | | | | | | Denmark | | | and | | received | | | his | been cited more than 2100 | | | | | | | |
| she completed her PhD work | | | | | | research | | in | | heterogeneous | | | Masters degree in physics in | | | | | | | | | times. | | | | | | | |
| dealing with the performance | | | | | | catalysis | | | at | University | | of | 2003. In 2006 he finished his | | | | | | | | | | | | | | | | |
| and durability of solid oxide | | | | | | Twente, The Netherlands and | | | | | | | PhD | work | | | on | solid | | oxide | | | | | | | | | |
| electrolysis cells (SOEC) at | | | | | | received his Doctor’s degree | | | | | | | electrolysis cells at Risø – DTU. | | | | | | | | | | | | | | | | |
| Risø – DTU. | | | | | | in 2007. | | | | | | |

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J. Mater. Chem., 2008, 18, 2331–2340 | 2331

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| When operated as an electrolysis cell the overall endothermic reaction is: | catalyst carrier used in the fuel cells oxidises fast under the highly oxidising conditions at the oxygen evolution electrode and other |

materials e.g. based on titanium alloys may be used as catalyst

2H2O + electrical energy (DG) + heat (TDS) / 2H2 + O2.

From basic thermodynamic considerations it is advantageous to operate the electrolysis cells at high temperatures where a substantial part of the required energy is provided as thermal energy and consequently the primary electric energy demand (DG), is considerably reduced. On the contrary, for low tempera-ture electrolysis a larger quantity of electrical energy is necessary

carrier.1As mentioned, it is thermodynamically advantageous to operate the electrolysis cells at high temperature; however this does not appear to be possible for PEM cells because the applied polymer membrane electrolyte cannot withstand long-term operation in strong oxidising conditions at the anodic polarised oxygen electrode at high temperature.

The PAFCs are operated at 150–200C, use orthophosphoric acid as the proton conducting electrolyte and Pt as catalyst on

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| Published on 31 January 2008. Downloaded by DTU Library on 28/07/2015 12:29:53. | to overcome the endothermic heat of reaction. Furthermore, at | carbon support for both electrodes. Again, the carbon supported | |
| high temperature the kinetics of the electrolysis reactions | electrodes in PAFCs cannot withstand the oxidising conditions | |
| at high temperatures. Therefore, from a basic material point of | |
| increase, resulting in a decrease in electrical losses in the cell |
| because of the lower ohmic resistance in the electrolyte and lower | view, PEM and phosphoric acid cells will hardly become the | |
| preferred types of electrolysis cells for large scale inexpensive | |
| polarisation losses from the electrode reactions. |
| It is natural to consider well known types of fuel cells as a | H2 production. However, PEM and phosphoric acid cells can | |
| starting point for electrolysis cells to gain from the substantial | be relevant for specific purposes where a low temperature is | |
| knowledge on fundamental material properties (conductivity, | important and cost is not a key issue. | |
| thermal expansion coefficient etc.) and optimised manufacturing | 2 For the MCFCs a molten carbonate is used as a CO3 | |
| techniques for these cells. However, the material demands | conducting electrolyte, porous Ni is used as the H2 electrode | |
| change upon reversing the operation mode of the cells. | and a mixture of NiO and Li2O is used for the O2 electrode. | |
| Compared to fuel cells, the electrolysis cells are operated with | From an ‘‘electrolysis-thermodynamic’’ point of view molten | |
| a high water or steam content at the inlet to the H2 electrode | carbonate cells are operated at more relevant temperatures | |
| and a high H2O fuel utilisation to minimise gas recycling, high | around 650 | C. However, molten carbon electrolysis cells |
| (MCEC) are not preferable as electrolysis cells for pure H2 | |
| temperature will be favourable and parameters such as potential |
| and concentration gradients will be changed compared to fuel | production because CO2 is involved in the electrode reactions, | |
| cell operation of the cells. | which implies that for each mol of H2 evolved; one mol of CO2 | |
| The different types of electrolysis cells will be discussed with | must be transferred as carbonate through the electrolyte. This | |
| emphasis on electrode materials and problems occurring when | increases the complexity of the electrochemical reactions in the | |
| operating these cells at high temperature, which in this context | electrodes which in turn will lead to a lower overall efficiency. | |
| is defined as above 200C. Potentially, alkaline cells could be | Solid oxide cells (SOC) have been applied for electrolysis of | |
| developed to operate at high temperatures and this issue is dealt | steam, but most commonly used—and commercially available— | |
| are low temperature (80C) alkaline cells for electrolysis. | |
| with in Section 2. However, the focus will be on the production |
| of H2 using solid oxide electrolysis cells (SOEC) as these cells are | These cells have to be operated at rather high cell voltages. | |
| normally operated at temperatures between 800 and 1000C. | This causes heat production in spite of the electrolysis process | |

The emphasis is on the electrode material issues for the SOECs because this plays a key role in the development of these cells to become cost competitive, high performing and long-term stable SOECs for efficient and environmentally friendly H2 production. Even though promising electrolysis results have been obtained for SOECs it is evident that substantial develop-ment of electrode material is necessary to obtain highly perform-ing and long-term stable electrolysis cells. Perspectives for future large scale H2 production by electrolysis of steam using SOECs

being endothermic. These high cell voltages are necessary in order to achieve an acceptable H2 production rate. Increasing the temperature to above 200C increases the electrode reaction rate to an acceptable extent with low enough cell voltages that the cell is self-cooled (thermoneutral potential). High tempera-ture alkaline electrolysis cells (HT-AEC) will be described in the next section. Electrode material aspects of solid oxide electrolysis cells (SOEC) are described in detail in Section 3.

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| will be analysed together with economic estimates for the | 2. | High temperature alkaline electrolysis cells |
| potential production price. |

Water is a very poor ionic conductor, and ions must be added in

Types of electrolysis cells

Well known fuel cells are polymer exchange membrane fuel cells (PEMFC), phosphoric acid fuel cells (PAFC), alkaline fuel cells (AFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC). The PEM cells typically operate at temperatures

order to form a conductive electrolyte (mainly potassium and sodium hydroxide solutions) so the reaction can proceed without too high resistance. Most commercial AEC are operated at 70–80C with a potassium hydroxide electrolyte (25–30 wt%) and nickel electrodes. As described in the previous section, increasing the operating temperature is favourable as the necessary electri-

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| around | 70–80 | C, | have | graphite | electrodes | with | highly | cal energy input is lowered. To the best of our knowledge only |

dispersed—and expensive—Pt catalysts and a proton conducting polymer membrane as the electrolyte. PEM electrolyser cells (PEMECs) for H2 production are commercially available, but are even more expensive than PEMFC because the carbon

very limited experimental data for alkaline electrolysis at temper-atures at 200C and above has been reported.2–4Nevertheless it was shown that the efficiency of water electrolysis for production of H2 over polished nickel electrodes increases significantly at

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| Published on 31 January 2008. Downloaded by DTU Library on 28/07/2015 12:29:53. |  | | become highly soluble in the electrolyte. For low temperature | | | | | | | |
| electrolysers, the separator/diaphragm can be nickel oxide, | | | | | | | |
| asbestos or polymer. Both the polymers and asbestos become | | | | | | | |
| instable at temperatures above 120C.15Consequently, new | | | | | | | |
| separator/diaphragm materials should be developed for HT- | | | | | | | |
| AEC. Oxide-ceramic diaphragms such as ceramics of titanates | | | | | | | |
| (BaTiO3 and CaTiO3) or even NiO15–17can be suitable substi- | | | | | | | |
| tutes for the polymeric or asbestos separators/diaphragms | | | | | | | |
| when operated at high temperatures. | | | | | | | |
| 3. | Solid oxide electrolysis cells | | | | | | |
| As for PEM cells and AECs, noble metals can be used for SOC | | | | | | | |
| electrodes for electrolysis cells that work reversibly across open | | | | | | | |
| Fig. 1 | Potential vs. current density for hydrogen and oxygen evolution | circuit voltage (OCV) and recently Hickey et al.18showed initial | | | | | | | |
| on polished nickel electrodes in 50 wt% KOH solutions at temperatures | | performance results and how such SOCs with noble metal | | | | | | | |
| from 80C to 264C.3Reproduced by permission from The Electro- | |
| electrodes | | can | withstand | fuel | cell/electrolysis | cycling | for |
| chemical Society. | |
| hundreds of hours. In spite of the fact that scientifically interest- | | | | | | | |
| high temperature as shown in Fig. 1.3Fig. 1 shows that an | | ing results can be and have been obtained for SOECs using noble | | | | | | | |
| metal electrodes, they are too expensive to be relevant in the | | | | | | | |
| increase in temperature has a more pronounced effect on the | | development of technologically and commercially relevant | | | | | | | |
| oxygen evolution (OER) than the H2 evolution (HER) reaction. | | SOECs. The following review for SOECs will be focused on | | | | | | | |
| Increasing the temperature significantly shifts the OER to lower | | cost competitive choices for SOEC electrodes, i.e. electrodes | | | | | | | |
| potentials, which reflects a higher activation energy for OER | | based on ceramic materials and inexpensive catalysts. | | | | | | | |
| compared to HER.3Only small shifts in potential were observed | | For the choice of materials for SOECs it is natural to consider | | | | | | | |
| for HER at temperatures above 200C at low current densities. | | the well-known materials used for SOFCs, for which substantial | | | | | | | |
| Nevertheless, substantial polarisations are found for the H2 | | R&D efforts have been used to investigate parameters such as | | | | | | | |
| evolution reaction on nickel electrodes in alkaline solutions at | | conductivity, catalytic activity, matching thermal expansion | | | | | | | |
| lower temperatures.3The dual region of the Tafel slope was | | coefficient, processing techniques etc. | | | | | | | |
| explained by a change in mechanism caused by the magnetic | | Already in the early 1980s Do¨nitz, Isenberg and others | | | | | | | |
| properties of nickel, although at present the exact mechanism | | reported on SOECs that basically used electrolyte and electrode | | | | | | | |
| is not fully understood. Regardless of the interpretation of the | | materials that are still used for state-of-the-art SOECs.19–22As | | | | | | | |
| Tafel slopes, it is evident that an increase in temperature signifi- | | for SOFCs the dense oxide ion conducting electrolyte consisting | | | | | | | |
| cantly improves the kinetics of both O2 and H2 evolution, and | | of 8 mol% Y2O3 stabilised ZrO2 (YSZ) is typically used for | | | | | | | |
| electrolysis at high temperatures would be beneficial. | | SOEC, which is used together with Ni in the porous cermet H2 | | | | | | | |

The materials known to be applicable for alkaline electrolysis are very limited because of the highly corroding electrolyte solu-tion and they become increasingly limited at high temperatures.

Both platinum and palladium show lower polarisation for oxygen evolution than nickel, but because of economical reasons, nickel is almost exclusively used in conventional electro-lysers.5,6To decrease the polarisation, several alloys (Ti–Ni7and Ni–Ir, Ni–Ru, Ni–Mo8) were tested and showed slightly lower polarisation. For pure nickel electrodes, mainly Raney-nickel, i.e. leached nickel–aluminium or nickel–zinc alloy is used, because of the high active surface area and porosity. Other highly porous materials such as Pt/C were suggested as alterna-tives to the nickel electrodes.9–11   
 Most electrode materials have been tested at temperatures up to 160C with a slight increased thermal degradation at high temperature.5–7,12,13Conventional nickel electrodes were shown to withstand temperatures of at least 200C, as they were used for the Apollo fuel cell system, normally operated at 204C and successfully tested at temperatures of 260C.14   
 The separators/diaphragms serve as an ionic conducting material as well as separating the product gasses. Separation of the product gasses becomes increasingly important at high pressure (necessary at high temperature operation) where oxygen

electrode. The most commonly used material for the porous O2 electrode is a composite of YSZ and strontium doped lanthanum manganite (LSM). SOEC tests reported in the 1980s were mainly performed on tubular formed SOECs (HotElly project19and Westinghouse Electrical Corporation22) with a porous oxygen electrode tube as cell support. In recent years planar cells have been preferable for SOECs where both electrolyte supported23,24 and H2 electrode supported cells have been applied.25SOECs have been tested at temperature ranging from 700C to 1000 C and at ambient pressure and at steam-to-hydrogen ratios from 30 : 70 to 99 : 1.26Compared to long-term tests of SOFC, only relatively few long-term electrolysis tests have been reported and unfortunately only a few include thorough analysis of the degradation mechanisms e.g. by electrochemical impedance spectroscopy (EIS) before, during and after electrolysis testing and by scanning and transmission electron microscopy com-bined with micro analysis of chemical compositions. Therefore many material aspects needs to be investigated in detail e.g. initial performance of electrodes including ‘‘new’’ materials, long-term stability, effect of cycling (temperature, operation mode etc.), effect of impurities in the raw materials, effect of manufacturing and also optimal materials for auxiliary compo-nents, sealing etc. In the following the emphasis will be on

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problems and perspectives for state-of-the-art SOEC electrodes and the development of improved and new electrodes.

measured on Ni/YSZ-YSZ half-cells in both fuel cell and electro-lysis mode, which has not often been reported.30At 800C, a polarisation of 50 mV and p(H2O)/p(H2) ¼ 0.5/0.5 they obtained

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| Published on 31 January 2008. Downloaded by DTU Library on 28/07/2015 12:29:53. | 3.1. | State-of-the-art H2 electrodes for SOECs | an ASRhalf-cell of 0.26 U cm2for fuel cell operation and 0.29 U cm2 | |
| The state-of-the-art Ni/YSZ cermet H2 electrodes have been | | for electrolysis operation for the same cell. The same trend, that | |
| Ni/YSZ seems to have a higher activity towards oxidation of | |
| applied for three decades by now. Nevertheless, significantly | |
| H2 than reduction of H2O, was recently reported for H2 electrode | |
| different performance results have been reported for SOECs | |
| supported cells25and YSZ electrolyte supported cells.31,23x For | |
| with Ni/YSZ electrodes25illustrating that manufacturing, and | |
| a durable high performing Ni/YSZ cermet electrode, long-term | |
| thereby the electrode microstructure, highly influence the | |
| stability of the electrode microstructure is necessary to maintain | |
| electrode performance. | | a high number of active sites and optimal transport of gaseous | |
| The Ni/YSZ network of catalytically active and electron | |
| reactants and products to and from these sites. Already in the | |
| conductive Ni and ionic conductive stabilised zirconia provides | |
| 1980s a long-term stability of 1000 hours of a Ni/YSZ electrode | |
| fast kinetics for the involved electrode reactions and the porous | |
| in electrolyte supported tubular SOECs was reported by Do¨nitz | |
| (30% porosity) structure ensures fast diffusion in the H2 | |
| and co-workers. Fig. 3 shows a 1000 h durability test for such | |
| electrode supported cells. However, it is well known that there | |
| an electrolyte supported single SOEC.19No significant degrada- | |
| is a fundamental material challenge regarding the non-optimal | |
| tion was observed indicating a stable microstructure. The | |
| redox stability of Ni/YSZ cermet based H2 electrodes which is | |
| Ni/YSZ electrode microstructure was relatively coarse19which | |
| a disadvantage that should be noticed as this possibly will make | |
| resulted in a large area specific polarisation resistance of0.23 | |
| H2 recycling a necessity. The redox stability issue may not be of | | U cm2{ at 1000C19whereas the ASR for today’s state-of-the | |
| importance for SOEC testing on a laboratory scale, but for future | |
| art SOECs was reported to be around 0.17 U cm2at 950C | |
| cost competitive SOEC systems it will be an issue to consider. | | for a full cell including the ohmic resistance.32Unfortunately, | |
| Initial performance. High initial performances have been | | satisfying electron microscopy evidence for the stability of the | |
| microstructure was not reported by Do¨nitz et al. | |
| reported on SOEC with Ni/YSZ H2 electrode and Ni/YSZ | |
| Ni/YSZ electrode microstructure. By applying an inexpensive | |
| support layer. Fig. 2 shows iV curves for high performing SOECs | |
| with Ni/YSZ H2 electrodes. Using the chord of the electrolysis iV | |
| production method such as tape casting, it is possible to produce | |
| curve for the highest performing SOC an area specific resistance | |
| planar SOECs with a microstructure as illustrated in Fig. 4A for | |
| (ASR)‡ as low as 0.27 U cm2was obtained at 850C, p(H2O)/ | |
| a non-tested SOEC26,33which have a mean Ni particle size of 1.00 | |
| p(H2) ¼ 0.5/0.5 for a full cell.25For similar cells tested as SOFCs | |
| 0.05 mm and a high porosity. Essentially no significant change | |
| it was found that at 850C approximately 25% of the resistance of | |
| the cell in this cell configuration is caused by processes in the H2 | |
|  | |
| electrode.27Slightly lower initial performance on single SOECs | |
| was obtained by O’Brien et al.24,28on electrolyte supported button | |
| cells with Ni/YSZ electrodes e.g. an ASR of 0.35 U cm2at 850C | |
| and Marina et al.29obtained an ASR resistance of0.9 U cm2at | |
| 800 | C and p(H2O)/p(H2) ¼ 0.5/0.5 for a 500 mm Ni/YSZ |
| electrode supported cell. Furthermore, Marina and co-workers29 | |
|  | |
| Fig. 3 | Long-term electrolysis testing of a single electrolyte supported |
| tubular SOEC with Ni/YSZ H2 electrode reported by Do¨nitz et al.19 | |
| Test conditions were: 995C,0.3 A cm2and H2/H2O ¼1⁄2 . The | |
| measured cell voltage of 1.07 V corresponds to a cell polarisation of | |

Fig. 2 Initial electrolysis (negative current densities) and fuel cell perfor-

mance recorded by iV curves at 850C, p(H2O)/p(H2) ¼ 0.5/0.5 for a high

and lower performing H2 electrode supported SOC.25Reproduced by

permission from The Electrochemical Society.

0.23 V i.e. a resistance of the cell of 0.78 U cm2. Reproduced by permis-sion from Elsevier.

x In the text by O’Brien et al.23it was only stated that ‘‘ASR values are similar for both fuel-cell and electrolysis modes of operation’’, however

from Fig. 5 and Fig. 10, especially sample E6 and ss14, it can be

‡ ASR values are those given in the text in the references or calculated from the chord of the iV curves in linear regions and are therefore not corrected for fuel or steam utilisation.

observed that ASR in electrolysis mode is slightly higher than ASR in fuel cell mode for the same cell.

{ Calculated from Fig. 16 in work by Do¨nitz et al.19

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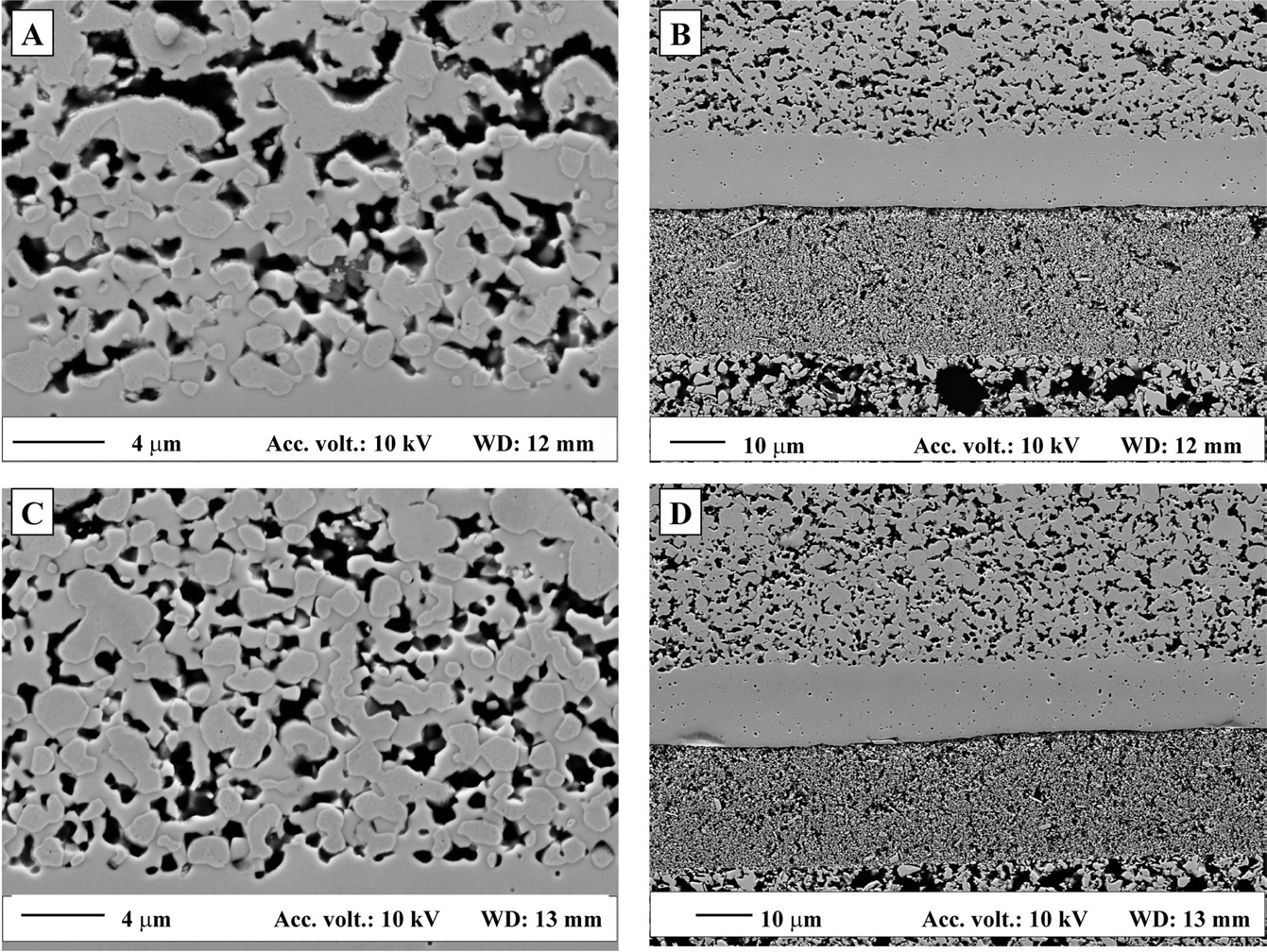


Fig. 4 Scanning electron micrographs. A) H2 electrode of a reference cell. B) Overview of the H2 electrode (top), YSZ electrolyte (middle) and the O2 electrode of a reference cell. C) H2 electrode of a SOEC tested for 1500 h at 850C,0.5 A cm2and p(H2O)inlet ¼ 0.5 atm and D) overview micrograph of the SOEC tested for 1500 h.26

in the microstructure of Ni/YSZ was observed during electrolysis for 1500 h at 850C,0.5 A cm2and p(H2O)/p(H2) ¼ 0.5/0.5 (comparison of Fig. 4A, reference cell, and Fig. 4C, electrolysis tested cell).k26Also no delamination of the Ni/YSZ electrode from the dense YSZ electrolyte was observed (comparison of Fig. 4B, reference cell, and Fig. 4D, electrolysis tested cell). A thorough analysis of the Ni particle size distributions revealed that the mean Ni particle size increased from 1.000.05 mm for a non-tested cell to 1.250.05 mm after electrolysis testing

closest to the electrolyte for SOECs tested at more harsh condi-tions i.e. at current densities higher than1 A cm2.26

Degradation of Ni/YSZ electrodes. Although Ni/YSZ cermet electrodes have microstructures that can sustain thousand of hours of electrolysis testing at moderate current densities (below 1 A cm2), there are other material issues leading to degrada-tion of the Ni/YSZ cermet electrode. Relatively limited numbers of long-term electrolysis tests of SOECs have been reported

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| --- | --- | --- | --- | --- | --- |
| independent of whether the cell was tested for 150 hours or | applying | ‘‘up-to-date’’ | Ni/YSZ | electrode | microstructure. |

1500 hours. However this change in the mean Ni particle size is not the main degradation mechanism for these SOECs.26 Similar change in the mean Ni particle size was observed for cells with the same initial Ni/YSZ microstructure when tested in fuel cell mode34Consequently, it is possible to produce cells with fine Ni/YSZ microstructures which are as stable over thousands of hours of electrolysis testing as over thousands of hours of fuel cell testing. However, significant microstructural changes were observed for the innermost few microns of the Ni/YSZ electrode

Ceramatec and Idaho National Laboratory (INL) reported long-term electrolysis tests of SOECs applying state-of-the-art‘‘up-to-date’’ Ni/YSZ electrodes.24Although they stated that a ‘‘stable performance was demonstrated’’ for their single cell test the corresponding cell voltage and development of cell resistance during electrolysis testing for 300 hours revealed an increase in cell resistance from 0.5 U cm2to 0.62 U cm2, corres-ponding to an increase in cell voltage of20% per 1000 hours at 800C and0.7 A cm2. Unfortunately Ceramatec and INL did not provide data (EIS or micro analysis and electron

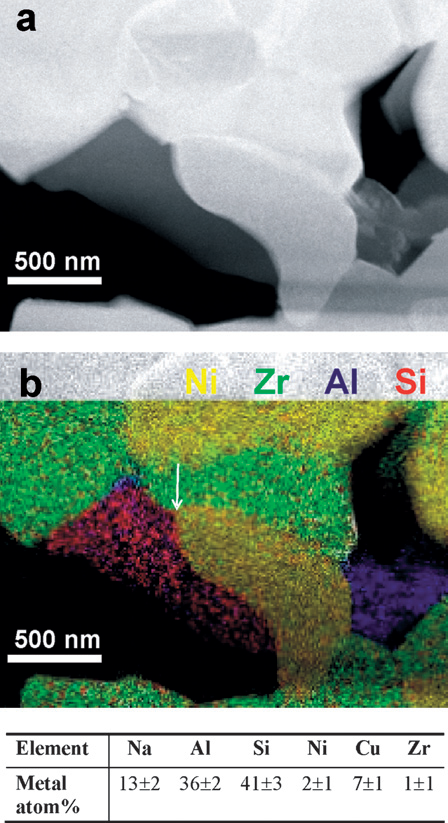
microscopy) that could identify at which electrode the degrada-

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| k Negative current densities are used for electrolysis operation of the cell. | tion occur. Risø – DTU reported several electrolysis experiments |

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on single cells with Ni/YSZ H2 electrodes.26The cells were found to degrade faster in electrolysis mode than fuel cell testing of similar SOCs.26,34In electrolysis mode the cells were found to have a cell voltage degradation of 2% per 1000 h at0.5 A cm2 and 850C, and by applying EIS it was found that the majority of the increased polarisation resistance was caused by a loss in performance of the Ni/YSZ electrode.26Electron microscopy (SEM, transmission electron microscopy and scanning transmis-sion electron microscopy) combined with energy dispersive spec-troscopy (EDS) revealed that a glassy phase containing silica impurities had built up at the triple-phase-boundaries (TPB) of the H2 electrode as illustrated by the EDS map in Fig. 5.35Accu-mulation of silica containing impurities at the grain boundaries and TPBs was previously reported for model systems36and half cells37and impurities in the raw materials greatly influences the performance the Ni/YSZ system.38Glassy phase impurities accumulated at the TPBs of the Ni/YSZ electrode upon electroly-sis operation can be expected to have different composition and physical properties compared to impurities observed for fuel cell tested cells due to the differences in e.g. potential and concentra-tion gradients and amount of H2O incorporated in the glass phase.



Beside impurities in the raw materials the build-up of impurities can originate from ‘‘external’’ sources such as glass sealing33which is usually not considered a Si-source during SOFC testing. A considerable p(Si(OH)4) exist over the glass sealing material at electrolysis operation conditions and form SiO2 upon reduction of steam in the Ni/YSZ electrode near the electrolyte. Contamina-tion of the Ni/YSZ electrode from an ‘‘external’’ source i.e. the glass sealing could be eliminated by coating of the glass seal or by applying a seal less test set-up for electrolysis testing as recently reported by Brisse´ et al.39and previously by Westinghouse Electri-cal Corporation.40Westinghouse presented SOEC test results on tubular cells where slurry coat electrochemical vapour deposition (EVD) was applied to manufacture the Ni/YSZ electrode and EVD was used to produce the YSZ electrolyte.22,41EVD has the advantages that the thickness of the layer can be controlled to within one micron and EVD provides electrolytes and electrodes with high purity, but the EVD process is incompatible with the demand for cost competitive production of SOCs.42,43

Main challenges for state-of-the-art H2 electrodes. As described in the previous section, inexpensive preparation methods that can easily be scaled up are available for production of Ni/YSZ cermet electrodes with a high performing microstructure that can withstand thousand of hours of electrolysis testing. The Ni/YSZ cermet electrode is absolutely promising for H2 electrodes for technologically relevant SOECs. Nevertheless, the degradation rates for state-of-the-art Ni/YSZ electrode in SOECs are too high. At present the main challenge appears to be to minimise and/or control glassy phase impurities that accumulate at the TPBs in the Ni/YSZ and thereby hamper the electrochemical reaction. A cell and test system completely free of impurities such as Si and Na is hardly an option especially not when costs are considered. As previously reported a possible solution could be to use a Si scavenger such as Al2O3 44–46 or to change the properties of the glassy phase impurities by the use of dopant glass modifiers such as potassium or vanadium oxides.47,48It will be a demanding task to reach an optimal scav-enger/dopant with several problems: 1) the knowledge regarding the composition and physical properties of the glass phase impurities in the electrode is limited and will depend on para-meters such as operating conditions, raw materials and produc-tion, 2) the optimal quantity and distribution of the scavenger in the Ni/YSZ electrode need to be determined and 3) Ni/YSZ electrodes with such scavengers/dopants should still be manufac-tured using inexpensive production methods.

Furthermore, there is a possibility that other impurities are present in quantities large enough to influence the performance of the Ni/YSZ electrode even though such impurity elements have not been detected in Ni/YSZ electrodes yet. Less than

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| Fig. 5 | a) An HAADF STEM micrograph and b) an EDS map of | one mono-layer of impurities at the reaction sites might be suffi- |

alumina–silicate impurity at a TPB a couple of microns from the electro-lyte/electrode interface. The SOEC had been tested for 1316 h at and the main part of the degradation of the SOEC was attributed to the Ni/YSZ

cient to significantly hamper the electrode reactions.

|  |  |  |
| --- | --- | --- |
| electrode based upon EIS results.26The arrow marks the TPB. The impu- | 3.2. | Alternative H2 electrode materials for SOECs |

rity phase is a Na containing alumina–silicate. Na is not visible in the map when both the Si and Al maps are overlaid, however Na is solely located within the alumina–silicate phase. Metal atom percentages for the alumina–silicate impurity phase are given below the EDS map. Dark regions are porosities. Figure from Hauch et al.35Reproduced by permission from The Electrochemical Society.

Alternative materials have been considered and tested as H2 electrodes for SOECs. Uchida and co-workers have reported on a H2 electrode of samaria doped ceria (SDC) with highly dispersed nanosized Ni particles.49–51They found that the optimal load of Ni was approximately 17 vol% at which the

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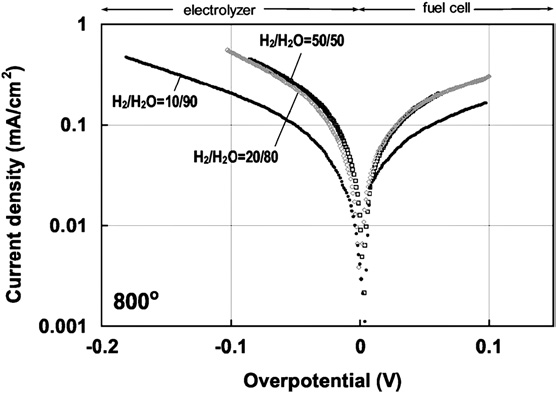


Fig. 6 iV curves for a H2 electrode of La0.35Sr0.65TiO3/Ce0.5La0.5O1.75d at various p(H2O)/p(H2) at 800C. From O. Marina et al.29Reproduced by permission from The Electrochemical Society.

steps to preserve the contact between the electrolyte and the LSM based electrode as observed even after 1500 hours of electrolysis testing (Fig. 4). Inexpensive production methods such as spraying and screen printing can be applied when producing LSM based O2 electrodes with microstructures able to sustain thousands of hours as O2 evolution electrode during electrolysis testing.

When tested in fuel cell mode degradation of O2 electrodes based on stoichiometric LSM caused by formation of secondary phases that are poorly conductive such as La2Zr2O7 or SrZrO3 was reported.57–62So far only a few reports on electrolysis tests with degradation of the LSM based O2 electrode e.g. caused by such secondary phases have been published.63Nanoscale chemical analyses e.g. by EDS in a FEG-TEM/STEM for LSM electrodes of long-term tested SOECs are required to inves-tigate a phenomenon such as formation of secondary phases.

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| mean Ni particle diameter was 82 nm compared to a lower | 3.4. | Alternative O2 electrode materials for SOECs |

performing electrode with a load of 26 vol% where the mean Ni particle diameter was 129 nm.49The polarisation resistance of the SDC based H2 electrode with optimal load of nanosized Ni particles was 0.18 U cm2at 900C. This electrode is promising, however, the resistance it is still too high considering an internal resistance of 0.27 U cm2at 850C for a full cell including polari-sation resistances of both electrodes and ohmic resistance of the electrolyte and auxiliary layers has been reported.25Long-term test of cells with a similar SDC H2 electrode with highly dispersed nanosized Ni particle was reported to be stable over 1100 h of fuel cell testing in humidified H2 at 800C and 0.6 A cm2but to the best of our knowledge results on long-term electrolysis testing e.g. at high p(H2O) and various temperatures and current densities for such SDC/Ni H2 electrodes have not been reported.

Titanate based H2 electrodes have also been developed for both SOFC and SOEC.29,52Marina et al.29compared a standard Ni/YSZ electrode with a titanate/ceria based electrode (La0.35Sr0.65TiO3/Ce0.5La0.5O1.75d) and found that from iV curves at 800C and p(H2O)/p(H2) ¼ 0.5/0.5, the Ni/YSZ elec-trode was superior in fuel cell mode but the titanate/ceria based electrode showed a lower polarisation resistance (0.21 U cm2) in electrolysis mode than the Ni/YSZ electrode (0.29 U cm2). Increased performance in electrolysis mode compared to fuel cell mode was also reported for strontium titanates of similar compositions by Blennow.52However, Marina et al. observed a significant reversible drop in initial performance of the titanate/ceria based electrode upon increasing the p(H2O)/p(H2) ratio from 0.8/0.2 to 0.9/0.1 as shown in Fig. 6. It was argued that this could be explained in terms of the decreased electrical conductivity of titanate/ceria composites at reduced pO2.

3.3. State-of-the-art O2 electrodes for SOECs

The state-of-the-art O2 electrode is a composite of Sr doped LaMnO3 and YSZ (LSM-YSZ),43 and is widely applied.25,28,31,41,53–55Problems with delamination of the O2 electrode from the electrolyte were reported18,31,56and might be caused by pressure differences occurring upon O2 evolution in closed pores in the electrode/electrolyte interface.31Such delami-nation can hardly be considered a purely material chemistry problem but is rather a question of optimising the preparation

Even though the LSM based oxygen electrode appears to be applicable for long-term testing of SOECs alternative O2 electrodes were reported.31,54,55,64Wang et al. obtained higher performances when LSM was substituted with mixed ionic–electronic conductors (MIEC) such as Sr doped LaFeO3 (LSF) or even better with Sr doped LaCoO3 (LSCo) in both electrolysis and fuel cell mode.55The improved initial performance for LSF and LSCo oxygen electrodes found by Wang et al. is evident from the electrolysis iV curves shown in Fig. 7 obtained on electrolyte supported (100 mm) cells with Co–CeO2–YSZ H2 elec-trodes at 700C. It should be noted that at higher temperature, e.g. above 800C which will be most relevant for electrolysis operation of the SOCs, a barrier layer will be required for O2 electrodes such as LSF and LSCo to avoid formation of insulat-ing secondary phases at the electrode/YSZ electrolyte. The stability of the LSF-YSZ electrode was only tested for 5 hours at 700C by Wang et al.55and this does not provide evidence for the long-term chemical and microstructural stability of their oxygen electrode for SOECs.

Also Momma et al.31have reported on the use of LaCoO3 based electrodes. They were unsuccessful using an electrode of

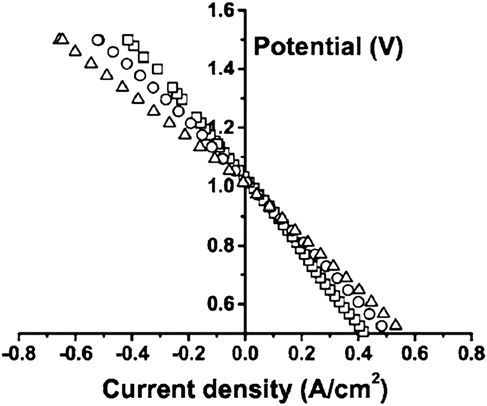


Fig. 7 Initial iV curves for electrolyte supported (100 mm) cells with composite O2 electrodes of LSM–YSZ (,), LSF–YSZ (B) and LSCo–YSZ (D) at 700C. 15% H2O in H2 was lead to the Co–CeO2–YSZ H2 electrode and pure O2 to the oxygen electrode.55Reproduced by permission from The Electrochemical Society.

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LSM as the electrode delaminated from the YSZ electrolyte and therefore tested LaCoO3 based electrodes with various Sr content. Momma et al.31found similar degradation rates for non-doped LaCoO3 electrode as LSM.

The non-doped LaCoO3 had the best initial performance but after only 80 hours of electrolysis testing at0.5 A cm2and 1000C the cell with the non-doped LaCoO3 reached the same degree of degradation as the cells with Sr-doped LaCoO3

massive research effort in the technologies of harvesting the renewable energy as well as in the conversion technologies is necessary in order to decrease the cost of ‘‘renewable’’ H2.76 Synthetic CO2 neutral hydrocarbons have the potential of being competitors to ‘‘renewable’’ H2, and therefore this option should also be carefully considered through serious research programs.

To justify that SOEC for H2 production is not only interesting from a scientific point of view but also have the potential for

electrodes. inexpensive commercial H2 production on large scale it is impor-

tant to estimate H2 production prices using SOECs.

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| 3.5. | Alternative electrolyte materials for SOECs | H2 costs from high temperature electrolysis has been estimated |
| to 1.1 V kg1–1.8 V kg156,77–79(Using a current exchange rate of |

Even though YSZ is by far the most commonly used electrolyte for SOECs some authors have reported on different alternative electrolyte materials28,49,54,65,66and it was shown that the choice of electrolyte material can influence the electrode performance. Osada et al.49showed that the resistance of their Ni–SDC H2 electrode was lowered significantly in the temperature interval from 700–900C upon changing the electrolyte material from YSZ to the more expensive, but more conductive scandia stabilised zirconia, ScSZ. A positive effect on the electrode performances in electrolysis mode has also been obtained upon substituting the YSZ electrolyte with a samaria-doped CeO2 electrolyte54but Eguchi et al.54found the H2 evolution rate for the cell with a SDC electrolyte was far too low at the applied current; most likely because of reduction of Ce4+to Ce3+(deterio-ration of ionic transference number) from the H2 electrode side. From an SOEC stack point of view it can be advantageous due to cost reduction to optimise SOECs for operating at a reduced temperature e.g. 700–800 C where YSZ is not an optimal electrolyte. An alternative electrolyte for such purpose could be doped lanthanum gallate e.g. with Sr on the La site and Mg

1.46 $ ¼ 1 V.) One of the recurring conclusions was that the expense of the electricity dominates the H2 cost and the electri-city price therefore significantly influences the estimated H2 production prices. The electricity cost in the estimations ranged from 0.014 V per kWh to 0.037 V per kWh.

The performance of a cell produced at Risø – DTU has been reported to be able to reach3.6 A cm2at only 1.48 V at 950C, i.e. an ASR of the cell of approximately 0.17 U cm2, and a 37% steam utilisation. Using this cell performance as an input for the H2 production cost estimation, together with values in Table 1, the calculated H2 production cost as function of the electricity price is shown in Fig. 8. Note that the H2 production cost does not include storage costs. Before the economic forecast in Fig. 8 can be achieved it is necessary to produce cells with sufficient performance stability. The initial performance is adequate, but the durability given in Table 1 is not yet met

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| Table 1 | Input for calculation of H2 production cost.32Reproduced by |
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| on the Ga site (LSGM) as reported by Elangovan et al.65 | Investment cost | 6300 US$/m2cell areaa |

However this will also require modifications of the Ni based H2 electrode to avoid the formation of LaNiO3 67–70 as the Ni volume percentage (typically40%) cannot be lowered enough to avoid the thermodynamic driving force towards LaNiO3

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| Purified water cost Depreciation time Operation time  Interest rate | 2.3 US$ m3  10 years  5 years  5% |

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| --- | --- | --- |
| formation and still sustain its electrical continuity. | Energy loss in heat | 5% |
| exchanger |

4. Perspectives for H2 generation via electrolysis at

high temperatures

a A 5 kW plant based on SOFC technology is predicted to cost 350–550 V per kW.81Assuming a power output of 1 W cm2this corresponds to an investment cost of 3500–5500 V per m2cell area.

When evaluating the commercial potential of steam electrolysis,   
it is important to be aware that hydrogen may be produced by

several other methods. Today production of H2 from fossil fuels is cheaper and more efficient than H2 from other sources. H2 can be produced from fossil fuels via reforming, partial oxidation or

coal gasification, all with a high efficiency in the order of 60–85%.71The disadvantages of H2 production from fossil fuels are the depleting resources as well as emission of CO2. Besides production of H2 from fossil fuels, H2 may be produced via bio-logical processes (efficiency of around 10%72), thermo chemical

cycles (e.g. zinc oxide–oxide and iodine–sulfur cycles, efficiency

of 30–40%73,74) photochemical processes (efficiency of around

10%75) and water/steam electrolysis (efficiency exceeds 95%19).

The primary means of production of synthesis gas and H2 is catalytic reforming of hydrocarbons, especially of natural gas.

At present H2 from fossil fuels in general and natural gas in particular is by far cheaper than H2 from other sources. A

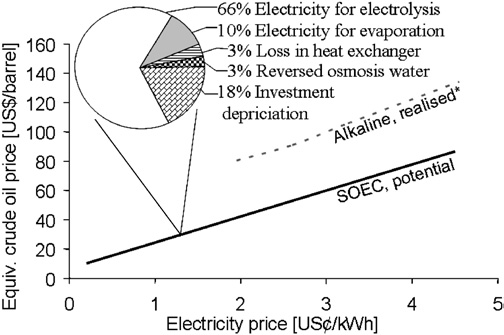


Fig. 8 H2 production price vs. electricity price. For comparison the price of H2 production from conventional low temperature alkaline electrolysis is shown as well.80The pie chart shows the production price parts given the assumptions in Table 1. Reproduced by permission from Elsevier.32

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| and the estimated H2 production prices therefore highly rely on | 6. | Acknowledgements |

electrode material development in order to produce long-term stable SOECs.

Comparing the higher heating values of H2 and oil, a price of 1 V kg1of H2 corresponds to an equivalent crude oil price of 30 V per barrel using figures from World Energy Council. The crude oil price of today is above 50 V per barrel corresponding to an equivalent of 1.7 V kg1of H2. Then it follows from Fig. 8 that for electricity prices below 0.02–0.03 V per kWh H2 production by high temperature steam electrolysis can be

This work was supported by the EC via the project ‘‘Hi2H2’’contract no. FP6-503765, Energinet.dk via the project no. PSO2007-1-7124, the Danish Programme Committee for Energy and Environment via SERC contract no 2104-06-0011 and the Danish National Advanced Technology Foundation via contract no 018-2006-2.

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| competitive with H2 production from fossil fuels. | 7. | References |
| As an increasing part of the electricity production is to come |

from renewable energy sources it will become necessary to‘‘store’’ the electricity to balance inequalities in the consumer’s electricity demands and the electricity produced by the renewable energy sources. The solid oxide cells can work reversibly. Hence, the SOEC is an obvious choice for ‘‘Peak Shaving’’, i.e. where inexpensive electricity is used to produce H2 (to store the electri-city) and electricity can be produced from the H2 using SOFCs (when electricity is expensive and the demand is high).56

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High temperature operation of water electrolysis significantly increases the performance of both alkaline electrolysis cells (AEC) and solid oxide electrolysis cells (SOEC). Increasing the operation temperature for AEC from the conventional 80–90 C to above 200C significantly increases the electrolysis perfor-mance and thereby the electricity to H2 efficiency. An obstacle for operating at high temperature is the lower stability of the materials. At present suitable cell and separator materials for HT-AEC, which are not more expensive than low temperature alkaline electrolyser materials, have been identified, but the

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For SOEC practical electricity to H2 efficiency of about 90% seems realistic and the initial performances reported for SOECs are promising with area specific resistances in electrolysis mode down to 0.17 U cm2at 950C for a full SOC. Also for SOEC the lifetime is the main issue to be addressed before the techno-logy is commercially viable. The main problem for state-of-the-art SOECs relates to the degradation of the Ni/YSZ based H2 electrode and it is necessary either to grossly improve the state-of-the-art Ni/YSZ electrode for electrolysis operation or develop highly performing and long-term stable H2 electrodes based on alternative materials.

At electricity prices below 0.02–0.03 V per kWh H2 production by high temperature steam electrolysis using SOECs is competi-tive to production from fossil fuels. Because the electrolysis cells can work reversibly, production of H2 via electrolysis in periods with low electricity prices, and reverse in periods with high electricity prices (as is often the case for electricity production from renewable energy sources) is an obvious choice for ‘‘Peak Shaving’’.

From a materials point of view a substantial fundamental R&D effort is necessary to develop inexpensive, highly perform-ing and long-term stable electrolysis cells. In the long-term more technologically related development is necessary to produce efficient and cost competitive SOEC systems for large scale H2 production e.g. in systems with renewable energy sources.

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