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Highly efficient high temperature electrolysis†

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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 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 200 °C 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 200 °C) 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 € 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

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 NO_x. 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

reforming is not optimal because the fossil fuel feed is based on consuming non-renewable fuels and furthermore CO₂ is emitted. 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.

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.

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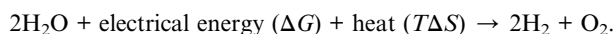
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When operated as an electrolysis cell the overall endothermic reaction is:



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 (ΔG), is considerably reduced. On the contrary, for low temperature electrolysis a larger quantity of electrical energy is necessary to overcome the endothermic heat of reaction. Furthermore, at high temperature the kinetics of the electrolysis reactions increase, resulting in a decrease in electrical losses in the cell because of the lower ohmic resistance in the electrolyte and lower polarisation losses from the electrode reactions.

It is natural to consider well known types of fuel cells as a starting point for electrolysis cells to gain from the substantial knowledge on fundamental material properties (conductivity, thermal expansion coefficient *etc.*) and optimised manufacturing techniques for these cells. However, the material demands change upon reversing the operation mode of the cells. Compared to fuel cells, the electrolysis cells are operated with a high water or steam content at the inlet to the H_2 electrode and a high H_2O fuel utilisation to minimise gas recycling, high temperature will be favourable and parameters such as potential and concentration gradients will be changed compared to fuel cell operation of the cells.

The different types of electrolysis cells will be discussed with emphasis on electrode materials and problems occurring when operating these cells at high temperature, which in this context is defined as above 200 °C. Potentially, alkaline cells could be developed to operate at high temperatures and this issue is dealt with in Section 2. However, the focus will be on the production of H_2 using solid oxide electrolysis cells (SOEC) as these cells are normally operated at temperatures between 800 and 1000 °C. 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 H_2 production. Even though promising electrolysis results have been obtained for SOECs it is evident that substantial development of electrode material is necessary to obtain highly performing and long-term stable electrolysis cells. Perspectives for future large scale H_2 production by electrolysis of steam using SOECs will be analysed together with economic estimates for the potential production price.

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 around 70–80 °C, have graphite electrodes with highly dispersed—and expensive—Pt catalysts and a proton conducting polymer membrane as the electrolyte. PEM electrolyser cells (PEMECs) for H_2 production are commercially available, but are even more expensive than PEMFC because the carbon

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 carrier.¹ As 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 150–200 °C, use orthophosphoric acid as the proton conducting electrolyte and Pt as catalyst on carbon support for both electrodes. Again, the carbon supported electrodes in PAFCs cannot withstand the oxidising conditions at high temperatures. Therefore, from a basic material point of view, PEM and phosphoric acid cells will hardly become the preferred types of electrolysis cells for large scale inexpensive H_2 production. However, PEM and phosphoric acid cells can be relevant for specific purposes where a low temperature is important and cost is not a key issue.

For the MCFCs a molten carbonate is used as a CO_3^{2-} -conducting electrolyte, porous Ni is used as the H_2 electrode and a mixture of NiO and Li_2O is used for the O_2 electrode. From an “electrolysis-thermodynamic” point of view molten carbonate cells are operated at more relevant temperatures around 650 °C. However, molten carbon electrolysis cells (MCEC) are not preferable as electrolysis cells for pure H_2 production because CO_2 is involved in the electrode reactions, which implies that for each mol of H_2 evolved; one mol of CO_2 must be transferred as carbonate through the electrolyte. This increases the complexity of the electrochemical reactions in the electrodes which in turn will lead to a lower overall efficiency.

Solid oxide cells (SOC) have been applied for electrolysis of steam, but most commonly used—and commercially available—are low temperature (~80 °C) alkaline cells for electrolysis. These cells have to be operated at rather high cell voltages. This causes heat production in spite of the electrolysis process being endothermic. These high cell voltages are necessary in order to achieve an acceptable H_2 production rate. Increasing the temperature to above 200 °C increases the electrode reaction rate to an acceptable extent with low enough cell voltages that the cell is self-cooled (thermoneutral potential). High temperature 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.

2. High temperature alkaline electrolysis cells

Water is a very poor ionic conductor, and ions must be added in 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 70–80 °C 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 electrical energy input is lowered. To the best of our knowledge only very limited experimental data for alkaline electrolysis at temperatures at 200 °C and above has been reported.^{2–4} Nevertheless it was shown that the efficiency of water electrolysis for production of H_2 over polished nickel electrodes increases significantly at

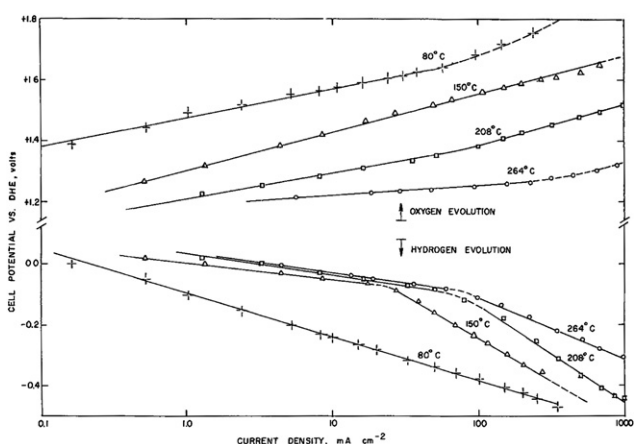


Fig. 1 Potential vs. current density for hydrogen and oxygen evolution on polished nickel electrodes in 50 wt% KOH solutions at temperatures from 80 °C to 264 °C.³ Reproduced by permission from The Electrochemical Society.

high temperature as shown in Fig. 1.³ Fig. 1 shows that an increase in temperature has a more pronounced effect on the oxygen evolution (OER) than the H₂ evolution (HER) reaction. Increasing the temperature significantly shifts the OER to lower potentials, which reflects a higher activation energy for OER compared to HER.³ Only small shifts in potential were observed for HER at temperatures above 200 °C at low current densities. Nevertheless, substantial polarisations are found for the H₂ evolution reaction on nickel electrodes in alkaline solutions at lower temperatures.³ The dual region of the Tafel slope was explained by a change in mechanism caused by the magnetic properties of nickel, although at present the exact mechanism is not fully understood. Regardless of the interpretation of the Tafel slopes, it is evident that an increase in temperature significantly improves the kinetics of both O₂ and H₂ evolution, and electrolysis at high temperatures would be beneficial.

The materials known to be applicable for alkaline electrolysis are very limited because of the highly corroding electrolyte solution 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 electrolyzers.^{5,6} To decrease the polarisation, several alloys (Ti–Ni⁷ and 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 alternatives to the nickel electrodes.^{9–11}

Most electrode materials have been tested at temperatures up to 160 °C with a slight increased thermal degradation at high temperature.^{5–7,12,13} Conventional nickel electrodes were shown to withstand temperatures of at least 200 °C, as they were used for the Apollo fuel cell system, normally operated at 204 °C and successfully tested at temperatures of 260 °C.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

become highly soluble in the electrolyte. For low temperature electrolyzers, the separator/diaphragm can be nickel oxide, asbestos or polymer. Both the polymers and asbestos become instable at temperatures above 120 °C.¹⁵ Consequently, new separator/diaphragm materials should be developed for HT-AEC. Oxide-ceramic diaphragms such as ceramics of titanates (BaTiO₃ and CaTiO₃) or even NiO^{15–17} can be suitable substitutes 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 circuit voltage (OCV) and recently Hickey *et al.*¹⁸ showed initial performance results and how such SOCs with noble metal electrodes can withstand fuel cell/electrolysis cycling for hundreds of hours. In spite of the fact that scientifically interesting results can be and have been obtained for SOECs using noble metal electrodes, they are too expensive to be relevant in the development of technologically and commercially relevant SOECs. The following review for SOECs will be focused on cost competitive choices for SOEC electrodes, *i.e.* electrodes based on ceramic materials and inexpensive catalysts.

For the choice of materials for SOECs it is natural to consider the well-known materials used for SOFCs, for which substantial R&D efforts have been used to investigate parameters such as conductivity, catalytic activity, matching thermal expansion coefficient, processing techniques *etc.*

Already in the early 1980s Dönitz, Isenberg and others reported on SOECs that basically used electrolyte and electrode materials that are still used for state-of-the-art SOECs.^{19–22} As for SOFCs the dense oxide ion conducting electrolyte consisting of 8 mol% Y₂O₃ stabilised ZrO₂ (YSZ) is typically used for SOEC, which is used together with Ni in the porous cermet H₂ 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 project¹⁹ and 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 supported^{23,24} and H₂ electrode supported cells have been applied.²⁵ SOECs have been tested at temperature ranging from 700 °C to 1000 °C and at ambient pressure and at steam-to-hydrogen ratios from 30 : 70 to 99 : 1.²⁶ Compared 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 combined 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 components, sealing *etc.* In the following the emphasis will be on

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

3.1. State-of-the-art H₂ electrodes for SOECs

The state-of-the-art Ni/YSZ cermet H₂ electrodes have been applied for three decades by now. Nevertheless, significantly different performance results have been reported for SOECs with Ni/YSZ electrodes²⁵ illustrating that manufacturing, and thereby the electrode microstructure, highly influence the electrode performance.

The Ni/YSZ network of catalytically active and electron conductive Ni and ionic conductive stabilised zirconia provides fast kinetics for the involved electrode reactions and the porous (~30% porosity) structure ensures fast diffusion in the H₂ electrode supported cells. However, it is well known that there is a fundamental material challenge regarding the non-optimal redox stability of Ni/YSZ cermet based H₂ electrodes which is a disadvantage that should be noticed as this possibly will make H₂ recycling a necessity. The redox stability issue may not be of importance for SOEC testing on a laboratory scale, but for future cost competitive SOEC systems it will be an issue to consider.

Initial performance. High initial performances have been reported on SOEC with Ni/YSZ H₂ electrode and Ni/YSZ support layer. Fig. 2 shows *iV* curves for high performing SOECs with Ni/YSZ H₂ electrodes. Using the chord of the electrolysis *iV* curve for the highest performing SOC an area specific resistance (ASR)[‡] as low as 0.27 Ω cm² was obtained at 850 °C, $p(\text{H}_2\text{O})/p(\text{H}_2) = 0.5/0.5$ for a full cell.²⁵ For similar cells tested as SOFCs it was found that at 850 °C approximately 25% of the resistance of the cell in this cell configuration is caused by processes in the H₂ electrode.²⁷ Slightly lower initial performance on single SOECs was obtained by O'Brien *et al.*^{24,28} on electrolyte supported button cells with Ni/YSZ electrodes *e.g.* an ASR of 0.35 Ω cm² at 850 °C and Marina *et al.*²⁹ obtained an ASR resistance of ~0.9 Ω cm² at 800 °C and $p(\text{H}_2\text{O})/p(\text{H}_2) = 0.5/0.5$ for a 500 μm Ni/YSZ electrode supported cell. Furthermore, Marina and co-workers²⁹

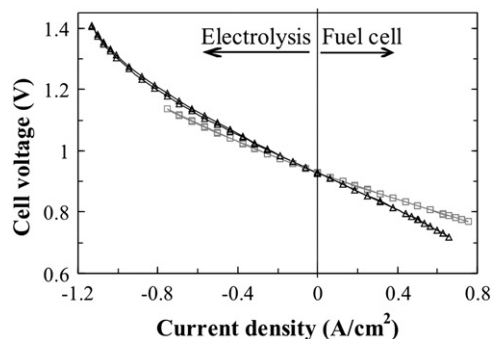


Fig. 2 Initial electrolysis (negative current densities) and fuel cell performance recorded by *iV* curves at 850 °C, $p(\text{H}_2\text{O})/p(\text{H}_2) = 0.5/0.5$ for a high and lower performing H₂ electrode supported SOC.²⁵ Reproduced by permission from The Electrochemical Society.

[‡] 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.

measured on Ni/YSZ-YSZ half-cells in both fuel cell and electrolysis mode, which has not often been reported.³⁰ At 800 °C, a polarisation of 50 mV and $p(\text{H}_2\text{O})/p(\text{H}_2) = 0.5/0.5$ they obtained an ASR_{half-cell} of 0.26 Ω cm² for fuel cell operation and 0.29 Ω cm² for electrolysis operation for the same cell. The same trend, that Ni/YSZ seems to have a higher activity towards oxidation of H₂ than reduction of H₂O, was recently reported for H₂ electrode supported cells²⁵ and YSZ electrolyte supported cells.^{31,23} For a durable high performing Ni/YSZ cermet electrode, long-term stability of the electrode microstructure is necessary to maintain a high number of active sites and optimal transport of gaseous reactants and products to and from these sites. Already in the 1980s a long-term stability of 1000 hours of a Ni/YSZ electrode in electrolyte supported tubular SOECs was reported by Dönitz and co-workers. Fig. 3 shows a 1000 h durability test for such an electrolyte supported single SOEC.¹⁹ No significant degradation was observed indicating a stable microstructure. The Ni/YSZ electrode microstructure was relatively coarse¹⁹ which resulted in a large area specific polarisation resistance of ~0.23 Ω cm² ¶ at 1000 °C¹⁹ whereas the ASR for today's state-of-the-art SOECs was reported to be around 0.17 Ω cm² at 950 °C for a full cell including the ohmic resistance.³² Unfortunately, satisfying electron microscopy evidence for the stability of the microstructure was not reported by Dönitz *et al.*

Ni/YSZ electrode microstructure. By applying an inexpensive production method such as tape casting, it is possible to produce planar SOECs with a microstructure as illustrated in Fig. 4A for a non-tested SOEC^{26,33} which have a mean Ni particle size of 1.00 ± 0.05 μm and a high porosity. Essentially no significant change

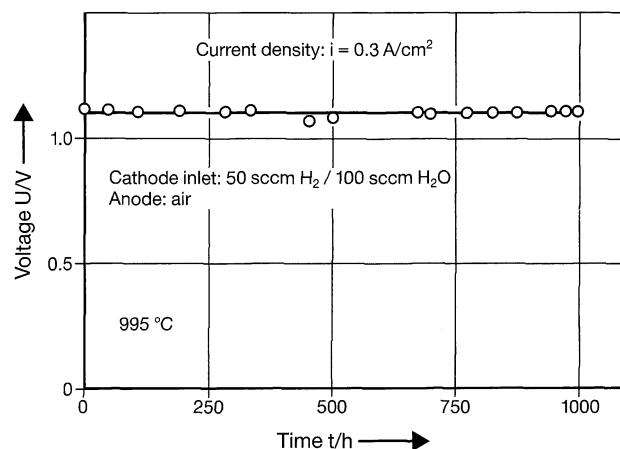


Fig. 3 Long-term electrolysis testing of a single electrolyte supported tubular SOEC with Ni/YSZ H₂ electrode reported by Dönitz *et al.*¹⁹ Test conditions were: 995 °C, -0.3 A cm^{-2} and $\text{H}_2/\text{H}_2\text{O} = 1/2$. The measured cell voltage of 1.07 V corresponds to a cell polarisation of 0.23 V *i.e.* a resistance of the cell of 0.78 Ω cm². Reproduced by permission from Elsevier.

§ In the text by O'Brien *et al.*²³ it 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 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 Dönitz *et al.*¹⁹

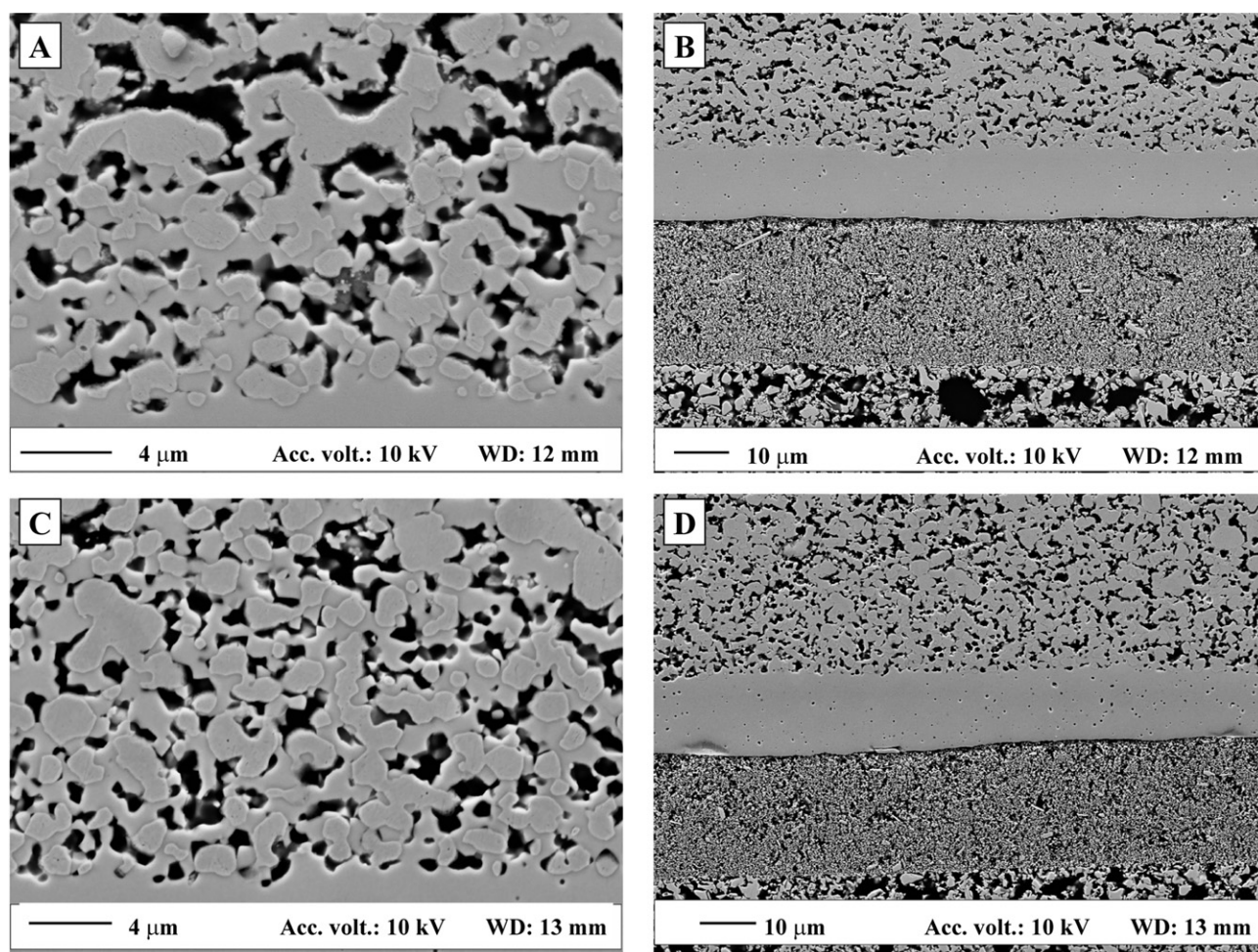


Fig. 4 Scanning electron micrographs. A) H_2 electrode of a reference cell. B) Overview of the H_2 electrode (top), YSZ electrolyte (middle) and the O_2 electrode of a reference cell. C) H_2 electrode of a SOEC tested for 1500 h at 850°C , -0.5 A cm^{-2} and $p(\text{H}_2\text{O})_{\text{inlet}} = 0.5\text{ atm}$ 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 850°C , -0.5 A cm^{-2} and $p(\text{H}_2\text{O})/p(\text{H}_2) = 0.5/0.5$ (comparison of Fig. 4A, reference cell, and Fig. 4C, electrolysis tested cell).²⁶ Also 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 $1.00 \pm 0.05\text{ }\mu\text{m}$ for a non-tested cell to $1.25 \pm 0.05\text{ }\mu\text{m}$ after electrolysis testing independent of whether the cell was tested for 150 hours or 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 mode.³⁴ Consequently, 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

closest to the electrolyte for SOECs tested at more harsh conditions *i.e.* at current densities higher than -1 A cm^{-2} .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 cm^{-2}), there are other material issues leading to degradation of the Ni/YSZ cermet electrode. Relatively limited numbers of long-term electrolysis tests of SOECs have been reported applying “up-to-date” Ni/YSZ electrode microstructure. Ceramtec and Idaho National Laboratory (INL) reported long-term electrolysis tests of SOECs applying state-of-the-art “up-to-date” Ni/YSZ electrodes.²⁴ Although 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 $0.5\text{ }\Omega\text{ cm}^2$ to $0.62\text{ }\Omega\text{ cm}^2$, corresponding to an increase in cell voltage of $\sim 20\%$ per 1000 hours at 800°C and -0.7 A cm^{-2} . Unfortunately Ceramtec and INL did not provide data (EIS or micro analysis and electron microscopy) that could identify at which electrode the degradation occur. Risø – DTU reported several electrolysis experiments

|| Negative current densities are used for electrolysis operation of the cell.

on single cells with Ni/YSZ H₂ electrodes.²⁶ The cells were found to degrade faster in electrolysis mode than fuel cell testing of similar SOCs.^{26,34} In electrolysis mode the cells were found to have a cell voltage degradation of 2% per 1000 h at -0.5 A cm^{-2} and 850 °C, 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.²⁶ Electron microscopy (SEM, transmission electron microscopy and scanning transmission electron microscopy) combined with energy dispersive spectroscopy (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. 5.³⁵ Accumulation of silica containing impurities at the grain boundaries and TPBs was previously reported for model systems³⁶ and half cells³⁷ and impurities in the raw materials greatly influences the performance the Ni/YSZ system.³⁸ Glassy phase impurities accumulated at the TPBs of the Ni/YSZ electrode upon electrolysis 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 concentration gradients and amount of H₂O incorporated in the glass phase.

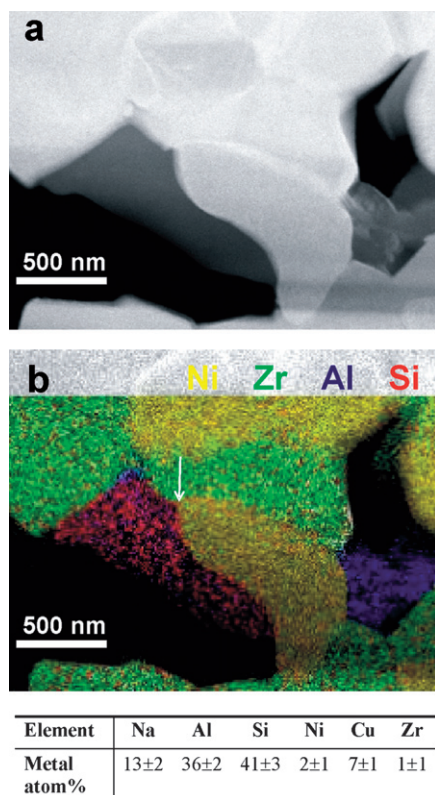


Fig. 5 a) An HAADF STEM micrograph and b) an EDS map of alumina-silicate impurity at a TPB a couple of microns from the electrolyte/electrode interface. The SOEC had been tested for 1316 h at and the main part of the degradation of the SOEC was attributed to the Ni/YSZ electrode based upon EIS results.²⁶ The arrow marks the TPB. The impurity 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.*³⁵ Reproduced by permission from The Electrochemical Society.

Beside impurities in the raw materials the build-up of impurities can originate from “external” sources such as glass sealing³³ which is usually not considered a Si-source during SOFC testing. A considerable $p(\text{Si}(\text{OH})_4)$ 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. Contamination 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 Brissé *et al.*³⁹ and previously by Westinghouse Electrical Corporation.⁴⁰ Westinghouse 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.^{22,41} EVD 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.^{47,48} It will be a demanding task to reach an optimal scavenger/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 parameters such as operating conditions, raw materials and production, 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 manufactured 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 one mono-layer of impurities at the reaction sites might be sufficient to significantly hamper the electrode reactions.

3.2. Alternative H₂ electrode materials for SOECs

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.^{49–51} They found that the optimal load of Ni was approximately 17 vol% at which the

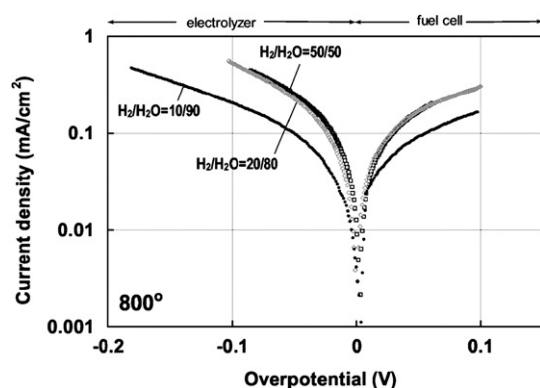


Fig. 6 iV curves for a H_2 electrode of $La_{0.35}Sr_{0.65}TiO_3/Ce_{0.5}La_{0.5}O_{1.75-\delta}$ at various $p(H_2O)/p(H_2)$ at 800 °C. From O. Marina *et al.*²⁹ Reproduced by permission from The Electrochemical Society.

mean Ni particle diameter was 82 nm compared to a lower performing electrode with a load of 26 vol% where the mean Ni particle diameter was 129 nm.⁴⁹ The polarisation resistance of the SDC based H_2 electrode with optimal load of nanosized Ni particles was 0.18 $\Omega\text{ cm}^2$ at 900 °C. This electrode is promising, however, the resistance it is still too high considering an internal resistance of 0.27 $\Omega\text{ cm}^2$ at 850 °C for a full cell including polarisation resistances of both electrodes and ohmic resistance of the electrolyte and auxiliary layers has been reported.²⁵ Long-term test of cells with a similar SDC H_2 electrode with highly dispersed nanosized Ni particle was reported to be stable over 1100 h of fuel cell testing in humidified H_2 at 800 °C and 0.6 $A\text{ cm}^{-2}$ but to the best of our knowledge results on long-term electrolysis testing *e.g.* at high $p(H_2O)$ and various temperatures and current densities for such SDC/Ni H_2 electrodes have not been reported.

Titanate based H_2 electrodes have also been developed for both SOFC and SOEC.^{29,52} Marina *et al.*²⁹ compared a standard Ni/YSZ electrode with a titanate/ceria based electrode ($La_{0.35}Sr_{0.65}TiO_3/Ce_{0.5}La_{0.5}O_{1.75-\delta}$) and found that from iV curves at 800 °C and $p(H_2O)/p(H_2) = 0.5/0.5$, the Ni/YSZ electrode was superior in fuel cell mode but the titanate/ceria based electrode showed a lower polarisation resistance (0.21 $\Omega\text{ cm}^2$) in electrolysis mode than the Ni/YSZ electrode (0.29 $\Omega\text{ cm}^2$). Increased performance in electrolysis mode compared to fuel cell mode was also reported for strontium titanates of similar compositions by Blennow.⁵² However, Marina *et al.* observed a significant reversible drop in initial performance of the titanate/ceria based electrode upon increasing the $p(H_2O)/p(H_2)$ 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 pO_2 .

3.3. State-of-the-art O_2 electrodes for SOECs

The state-of-the-art O_2 electrode is a composite of Sr doped $LaMnO_3$ and YSZ (LSM-YSZ),⁴³ and is widely applied.^{25,28,31,41,53–55} Problems with delamination of the O_2 electrode from the electrolyte were reported^{18,31,56} and might be caused by pressure differences occurring upon O_2 evolution in closed pores in the electrode/electrolyte interface.³¹ Such delamination can hardly be considered a purely material chemistry problem but is rather a question of optimising the preparation

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 O_2 electrodes with microstructures able to sustain thousands of hours as O_2 evolution electrode during electrolysis testing.

When tested in fuel cell mode degradation of O_2 electrodes based on stoichiometric LSM caused by formation of secondary phases that are poorly conductive such as $La_2Zr_2O_7$ or $SrZrO_3$ was reported.^{57–62} So far only a few reports on electrolysis tests with degradation of the LSM based O_2 electrode *e.g.* caused by such secondary phases have been published.⁶³ Nanoscale chemical analyses *e.g.* by EDS in a FEG-TEM/STEM for LSM electrodes of long-term tested SOECs are required to investigate a phenomenon such as formation of secondary phases.

3.4. Alternative O_2 electrode materials for SOECs

Even though the LSM based oxygen electrode appears to be applicable for long-term testing of SOECs alternative O_2 electrodes were reported.^{31,54,55,64} Wang *et al.* obtained higher performances when LSM was substituted with mixed ionic–electronic conductors (MIEC) such as Sr doped $LaFeO_3$ (LSF) or even better with Sr doped $LaCoO_3$ (LSCo) in both electrolysis and fuel cell mode.⁵⁵ The 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 μm) cells with Co– CeO_2 –YSZ H_2 electrodes at 700 °C. It should be noted that at higher temperature, *e.g.* above 800 °C which will be most relevant for electrolysis operation of the SOCs, a barrier layer will be required for O_2 electrodes such as LSF and LSCo to avoid formation of insulating secondary phases at the electrode/YSZ electrolyte. The stability of the LSF-YSZ electrode was only tested for 5 hours at 700 °C by Wang *et al.*⁵⁵ and this does not provide evidence for the long-term chemical and microstructural stability of their oxygen electrode for SOECs.

Also Momma *et al.*³¹ have reported on the use of $LaCoO_3$ based electrodes. They were unsuccessful using an electrode of

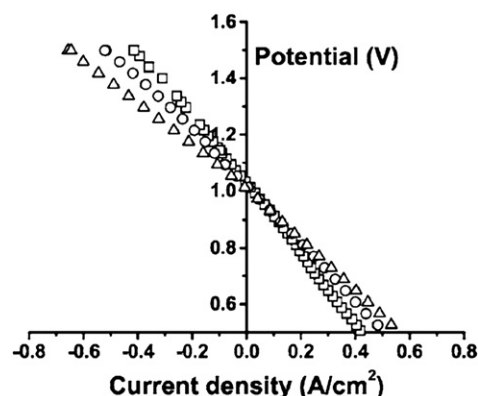


Fig. 7 Initial iV curves for electrolyte supported (100 μm) cells with composite O_2 electrodes of LSM-YSZ (\square), LSF-YSZ (\circ) and LSCo-YSZ (Δ) at 700 °C. 15% H_2O in H_2 was lead to the Co– CeO_2 –YSZ H_2 electrode and pure O_2 to the oxygen electrode.⁵⁵ Reproduced by permission from The Electrochemical Society.

LSM as the electrode delaminated from the YSZ electrolyte and therefore tested LaCoO₃ based electrodes with various Sr content. Momma *et al.*³¹ found 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 at -0.5 A cm^{-2} and 1000°C the cell with the non-doped LaCoO₃ reached the same degree of degradation as the cells with Sr-doped LaCoO₃ electrodes.

3.5. Alternative electrolyte materials for SOECs

Even though YSZ is by far the most commonly used electrolyte for SOECs some authors have reported on different alternative electrolyte materials^{28,49,54,65,66} and it was shown that the choice of electrolyte material can influence the electrode performance. Osada *et al.*⁴⁹ showed that the resistance of their Ni–SDC H₂ electrode was lowered significantly in the temperature interval from $700\text{--}900^\circ\text{C}$ 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 electrolyte⁵⁴ but Eguchi *et al.*⁵⁴ found 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⁺ (deterioration 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.* $700\text{--}800^\circ\text{C}$ 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 on the Ga site (LSGM) as reported by Elangovan *et al.*⁶⁵ 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 (typically $\sim 40\%$) cannot be lowered enough to avoid the thermodynamic driving force towards LaNiO₃ formation and still sustain its electrical continuity.

4. Perspectives for H₂ generation *via* electrolysis at high temperatures

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 $60\text{--}85\%$.⁷¹ The 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* biological processes (efficiency of around 10% ⁷²), thermo chemical cycles (*e.g.* zinc oxide–oxide and iodine–sulfur cycles, efficiency of $30\text{--}40\%$ ^{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

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 inexpensive commercial H₂ production on large scale it is important to estimate H₂ production prices using SOECs.

H₂ costs from high temperature electrolysis has been estimated to $1.1 \text{ € kg}^{-1}\text{--}1.8 \text{ € kg}^{-1}$ ^{156,77–79} (Using a current exchange rate of $1.46 \$ = 1 \text{ €}$.) One of the recurring conclusions was that the expense of the electricity dominates the H₂ cost and the electricity price therefore significantly influences the estimated H₂ production prices. The electricity cost in the estimations ranged from 0.014 € per kWh to 0.037 € per kWh .

The performance of a cell produced at Risø – DTU has been reported to be able to reach -3.6 A cm^{-2} at only 1.48 V at 950°C , *i.e.* an ASR of the cell of approximately $0.17 \Omega \text{ cm}^2$, 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

Table 1 Input for calculation of H₂ production cost.³² Reproduced by permission from Elsevier

Investment cost	6300 US\$/m ² cell area ^a
Purified water cost	2.3 US\$ m ⁻³
Depreciation time	10 years
Operation time	5 years
Interest rate	5%
Energy loss in heat exchanger	5%

^a A 5 kW plant based on SOFC technology is predicted to cost $350\text{--}550 \text{ € per kW}$.⁸¹ Assuming a power output of 1 W cm^{-2} this corresponds to an investment cost of $3500\text{--}5500 \text{ € per m}^2$ cell area.

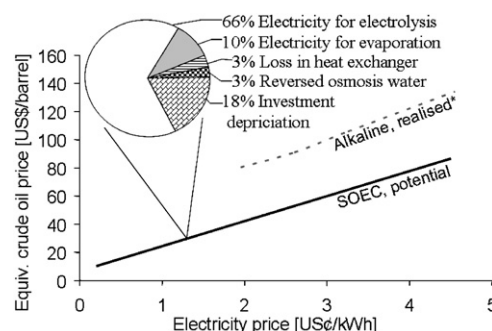


Fig. 8 H₂ production price vs. electricity price. For comparison the price of H₂ production from conventional low temperature alkaline electrolysis is shown as well.⁸⁰ The pie chart shows the production price parts given the assumptions in Table 1. Reproduced by permission from Elsevier.³²

and the estimated H₂ production prices therefore highly rely on electrode material development in order to produce long-term stable SOECs.

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

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 electricity) and electricity can be produced from the H₂ using SOFCs (when electricity is expensive and the demand is high).⁵⁶

5. Concluding remarks

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 200 °C significantly increases the electrolysis performance 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 necessary long term stability remains to be proven.

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 Ω cm² at 950 °C for a full SOC. Also for SOEC the lifetime is the main issue to be addressed before the technology 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 € per kWh H₂ production by high temperature steam electrolysis using SOECs is competitive 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 performing 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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