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Review Article

Reversible solid-oxide cells for clean and sustainable energy

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Abstract

This review gives first a brief view of the potential availability of sustainable energy. It is clear that over 100 times more solar photovoltaic energy than necessary is readily accessible and that practically available wind alone may deliver sufficient energy supply to the world. Due to the intermittency of these sources, effective and inexpensive energy-conversion and storage technology is needed. Motivation for the possible electrolysis application of reversible solid-oxide cells (RSOCs), including a comparison of power-to-fuel/fuel-to-power to other energy-conversion and storage technologies is presented. RSOC electrochemistry and chemistry of H2O, CO2, H2, CO, CnHm (hydrocarbons) and NH3, including thermodynamics and cell performance, are described. The mechanical strength of popular cell supports is outlined, and newly found stronger materials are mentioned. Common cell-degradation mechanisms, including the effect of common impurities in gases and materials (such as S and Si), plus the deleterious effects of carbon deposition in the fuel electrode are described followed by explanations of how to avoid or ease the consequences. Visions of how RSOCs powered by sustainable energy may be applied on a large scale for the transportation sector via power-to-fuel technology and for integration with the electrical grid together with seasonal storage are presented. Finally, a brief comparison of RSOCs to other electrolysis cells and an outlook with examples of actions necessary to commercialize RSOC applications are sketched.

Keywords: electrolysis; fuel cells; solid-oxide cells; power-to-fuel; electrochemical syngas

Introduction

Global background

A strong demand for clean sustainable energy has appeared in most countries as a result of the fear of the greenhouse effect and the wish for cleaner air. Therefore, the natural question is: is there enough sustainable energy available?

The International Energy Agency (IEA)’s estimate of the World’s Total Primary Energy Supply was 13 761 Mtoe (million tons of oil equivalent), corresponding to 18.3 TWy (terawatt years) in 2016. Here, ‘supply’ means actual supply to customers [1].

The answer is no and yes. Right now, the answer is no, as only a small fraction of sustainable energy is available...
in forms that can cover the energy demand of the world, but, potentially, the answer is yes, because more than enough sustainable energy is available. In order to produce 18.3 TWy electrical energy from photovoltaic cells with conservative 10% efficiency, we need solar irradiation of 183 TW electrical power on average over the year. The average influx of energy from the Sun (corrected for scattering in the atmosphere and absorption by clouds) to the land area between the polar circles corresponds to 21 000 TW average electrical power calculated from data from Tsao et al. [2], i.e. 115 times more than we need. Actually, it takes only a small fraction of the world’s deserts to supply all the necessary energy to the world. Fig. 1 shows a global horizontal irradiation (GHI) solar-resource map on which we have shown how limited space it takes even when a photovoltaic (PV) efficiency of 10% is assumed. Table 1 lists the data with 10% efficiency for the six black spots in Fig. 1. It appears that only ~700 000 km² is enough, and it only constitutes a relatively small part of each of the six continents’ deserts. We note that no use of valuable farmland is necessary for this.

Apart from solar irradiation, energy from the Sun is also manifested in the form of wind and water streams. The potential of these two sources is significantly lower than that of solar radiation. Based on the data from Tsao et al. [2], the realistic technical potential of wind power is 23 TW and of hydropower 1.6 TW electric energy in average. Thus, it seems clear that we will have to rely on solar irradiation as our main sustainable-energy source of the future. Consequently, we need tremendous conversion and storage capacity in order to have a continuous reliable energy supply.

Furthermore, electric power from solar and wind may be generally competitive to fossil fuel within the near future as prices lower than electricity from coal have been reported and the cost seems to continue to drop fast. The global weighted average levelized cost of electricity of utility-scale solar PVs fell by 73% between 2010 and 2017, to USD 0.10/kWh, and large utility-scale PV electricity was down to USD 0.06/kWh in 2017 [4]; trends of further declining prices of PV electricity down to USD 0.03/kWh are claimed. So, solar power is becoming competitive to coal.

The necessity for energy conversion and storage

However, both solar and wind power are intermittent, and thus not always available when needed. Also, the availability of hydropower is not even over the year. Biomass is a sustainable-energy source that is steadily available, but it cannot provide enough energy for the whole world because most of the fertile land area is needed for food production.

Thus, to cover the world’s energy demand, it takes efficient and inexpensive energy-conversion and storage systems in order to fully utilize the intermittent solar and wind energy as well as varying hydropower. There are a number of such conversion and storage technologies available, i.e. pumping water into mountain water reservoirs, in compressed air and batteries. All of these are already in

Fig. 1 Global horizontal irradiation (GHI) solar-resource map. The area of PV solar installations necessary to cover today's world energy demand will be <700 000 km² in total, if established in e.g. the six areas marked with black spots in desert areas with high GHI over the year. The relatively small size of the total area (700 000 km²) is visualized as the red square, which is here arbitrarily placed on the map in the Indian Ocean by the equator. Efficiency of the solar installations is assumed to 10%. The map is from solar-resource data obtained from the Global Solar Atlas, owned by the World Bank Group and provided by Solargis [3].
use, but none of them is suitable for seasonal storage (over several months to years) and they are not suited for fueling heavy transport such as trucks, ships and aeroplanes. Thus, fuels like hydrogen, CO₂-neutral carbon-based fuels and/or ammonia produced from sustainable energy are necessary for chemical-energy storage and energy transportation. Conversion technologies that can produce such fuels from sustainable energy will for the time being need electrolysis to convert renewable electrical energy into hydrogen (H₂) from water and carbon monoxide (CO) from carbon dioxide (CO₂). From mixtures of H₂ and CO (syngas), it is possible to produce fuels like methane (CH₄), also called synthetic natural gas (SNG), methanol (CH₃OH), dimethyl ether (CH₃OCH₃, DME) and many other CO₂-neutral fuels based on electrolysis. To this comes ammonia (NH₃). These processes are called power-to-fuel (P2F), power-to-X (P2X) or similar expressions.

The technical advantages of fuels (chemical energy), i.e. P2F or P2X, over e.g. batteries and physical methods may be analysed based on (i) energy density and (ii) equivalent power density.

(i) **Table 2** gives approximate numbers for energy density and boiling points for the chemical-energy carriers. It is clear that, from boiling points and energy-density perspectives, CH₄, DME, CH₃OH and NH₃ are the easiest to handle. The very low boiling point of H₂ adds significant costs in the context of handling it, even though highly compressed H₂ (700 bar) may emerge as an applicable solution in many cases. Compressed air, storage of water at high altitude and batteries do not seem to be an option for storage over long periods in context with the transportation sector. The energy-density argument is in strong favour of conversion by electrolysis into chemical-energy storage.

(ii) The equivalent power density in the transportation of the fuel is also strongly in favour of storage in the form of fuels for aeroplanes, ships and trucks, and also to some extent for passenger cars. The following short example illustrates this. Assuming a filling rate of 20 L/

### Table 1: Potential solar PV installation area necessary to cover the world energy demand of 18 TWy, based on local horizontal irradiation data for six selected positions shown as black spots in Fig. 1.

<table>
<thead>
<tr>
<th>Position</th>
<th>GHI year average, kWh m⁻²</th>
<th>Number of km² needed to produce each 3 TWy per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sahara, Libya</td>
<td>2500</td>
<td>105 300</td>
</tr>
<tr>
<td>Nevada, USA</td>
<td>2150</td>
<td>122 400</td>
</tr>
<tr>
<td>Tibet, China</td>
<td>2150</td>
<td>122 400</td>
</tr>
<tr>
<td>Western Australia</td>
<td>2300</td>
<td>114 400</td>
</tr>
<tr>
<td>Antofagosta, Chile</td>
<td>2500</td>
<td>105 300</td>
</tr>
<tr>
<td>Ar Riyad, Saudi Arabia</td>
<td>2350</td>
<td>112 000</td>
</tr>
<tr>
<td>Sum of area of the 6 sites, km²</td>
<td>681 800</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2: Data for comparison of volumetric and gravimetric energy density for selected energy-storage technologies. Values are only approximate because of scatter in literature data. All handling technologies are well tested and seem safe.

<table>
<thead>
<tr>
<th>Storage type</th>
<th>MJ/L</th>
<th>MJ/kg</th>
<th>Boiling point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid methane</td>
<td>22</td>
<td>56</td>
<td>–162</td>
</tr>
<tr>
<td>Liquid dimethyl ether (DME)</td>
<td>22</td>
<td>30</td>
<td>–25</td>
</tr>
<tr>
<td>Methanol</td>
<td>16</td>
<td>20</td>
<td>+65</td>
</tr>
<tr>
<td>Liquid ammonia</td>
<td>12</td>
<td>19</td>
<td>–33</td>
</tr>
<tr>
<td>Liquid hydrogen</td>
<td>10</td>
<td>141</td>
<td>–253</td>
</tr>
<tr>
<td>Compressed air—20 MPa</td>
<td>0.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Water at 100 m elevation</td>
<td>10⁻³</td>
<td>10⁻³</td>
<td></td>
</tr>
<tr>
<td>Lead acid batteries</td>
<td>0.4</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Li-ion batteries</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

The reversible solid-oxide cell (RSOC) as a potent energy converter

The RSOC is very potent technology for these purposes, but it has to reach a more mature state (lower cost, longer lifetime, improved reliability) before it is ready for the general power and fuel market. Therefore, more RSOC research and development (R&D) has to be carried out. The present paper is a brief review and a guide to solid-oxide electrolysis cell (SOEC) and solid-oxide fuel cell (SOFC) literature, mainly about the cells based on: gaseous fuel|Ni–YSZ|YSZ|LSTr–YSZ|air or O₂; here, YSZ means yttria stabilized zirconia. Here, LSTr means (La₉, Sr₉)₀.₅, TrO₃, 0.₅ < x < 1 and 0.₉ < s < 1, Tr is one or more of the first row of transition metals of the periodic table. Below, in the ‘New types of RSOC’ section, is given a brief description of alternative RSOCs without high amounts of Ni, and of RSOC competitors in the form of cells with low-temperature proton-conducting electrolytes and alkaline electrolytes. This comparison shows that RSOCs hold the highest potential in terms of efficiency and potentially low-cost materials. Further, reversibility in order to convert sustainable electricity into chemical energy and back again into electricity is only possessed using RSOCs.

Naturally, it is not possible to cover all solid-oxide cell (SOC) literature, because a search using SciFinder on ‘solid oxide fuel cell’ and ‘solid oxide electrolysis cell’ returns...
over 37 000 and 15 000 references, respectively. Google Scholar searches give millions of hits for both. Thus, the references in the present paper are just selected books and articles that we know and have found essential. The present description on motivation for SOC R&D and on cell performance and durability is based on own experience and on SOFC books plus many SOC reviews such as references [5–10].

1 RSOC principle, materials and thermodynamics

An RSOC may be operated either as an SOFC or as an SOEC. This means that the very same cell can interchangeably be used in both modes. The overall principle is sketched in Fig. 2.

1.1 Cell design and materials

Fig. 3 shows an artificially coloured scanning electron microscope (SEM) micrograph of a cell of the same popular design as in Fig. 2—the so-called fuel-electrode-supported flat-plate design. The cell support and the fuel electrode are both made of nickel–yttria stabilized zirconia (Ni–YSZ cermet). The mechanical support is usually called ‘the fuel electrode support’, because it is made of approximately the same Ni–YSZ material as the fuel electrode. The support is typically made of a composite of 40 vol% Ni and 60 vol% Zr_{0.94}Y_{0.06}O_{1.96} with a relatively coarse structure with 30–35% porosity. The active fuel electrode is made of a Ni and Zr_{0.84}Y_{0.16}O_{1.92} composite with the same 40 vol%/60vol%, but with a significantly finer structure and a lower porosity than the cell support. Zr_{0.94}Y_{0.06}O_{1.96} is usually denoted as 3YSZ and Zr_{0.84}Y_{0.16}O_{1.92} as 8YSZ, because they contain approximately 3 and 8 mol% Y_2O_3, respectively. The full cell support is about 350 μm thick [11].

Both Ni–YSZ cermet layers are prepared and sintered as NiO–YSZ composites and then the NiO is reduced to metallic Ni when exposed to H₂ or polarized to e.g. –1 V versus an O_2 reference electrode (1 bar, 1000°C) for 1 h for (La_{0.75}Sr_{0.25})_{0.95}MnO₃ (LSM) and (La_{0.65}Sr_{0.35})_{0.95}Co_{0.95}Fe_{0.05}O_{3−δ} (LSCF) [11] and thereafter the temperature is reduced to the operation temperature. For LSC cells, the NiO reduction temperature is 850°C and the hold time is 2 h. The lower the NiO reduction temperature, the longer the necessary hold time [11].

The electrolyte consists of 8YSZ, as this composition has the highest oxide ion conductivity of yttria-doped zirconia. Ten mol% scandia (Sc_2O_3)-doped zirconia has even higher ion conductivity, but is more expensive [12]. The high conductivity is also the reason for using 8YSZ in the active fuel electrode. Several other SOC electrolyte materials exist, but all are less mechanically strong and less thermodynamically stable [12, 13]. The reason for using 3YSZ in the support is that this is one of the mechanically strongest ceramics due to its martensitic transformation ability (see more below).

For the time being, one of the most popular oxygen-electrode materials are the perovskite-structured (La_{0.6}Sr_{0.4})_{0.98}CoO₃ (LSC) and LSCF, of which both are excellent oxygen-reduction and oxide-ion-oxidation catalysts [14]. Furthermore, LSC is a mixed-oxide ion and electron conductor at 750°C and above. However, LSC reacts with YSZ at sintering temperature, and therefore a reaction barrier of Ce₀.₉Gd₀.₁O₁.₉₅ (CGO) is placed between the YSZ electrolyte and the perovskite, and the composite electrode is LSC mixed with CGO. Other Ruddlesden-Popper-structured oxides of the type Ln₂MtO₄, where Ln is a trivalent big lanthanide metal ion and Mt is a small divalent transition metal ion, have been reported as good O₂-electrode materials (see e.g. [15, 16]).

The area of a flat-plate single cell is typically in the range of 80–150 cm².

Many other designs and other cell materials and compositions have been reported. For some decades, oxygen electrodes of (La_{0.5}Sr_{0.5})MnO₃ (LSM) were preferred due the
high thermodynamic stability of LSM, and perhaps the stability issue may still convince some RSOC developers that this is the best oxygen-electrode material for RSOCs.

1.2 Cell stacks
In practice, single flat-plate cells are put into series in stacks or assemblies. A stack typically consists of 50–100 cells in order to obtain applicable voltages. Fig. 4 shows an expanded sketch of a bipolar flat-plate cell stack. A full stack must also contain gas seals and manifolds of some kind [7]. The dense electrolyte layer, the dense interconnector plate and the seals prevent the mixing of fuel gas and oxidant gas (oxygen or air).

Apart from this, a large number of other stack designs have been proposed and tested, such as round tubular, flat tubular and transverse stripe tubular cell arrangements, just to mention a few [17].

1.3 RSOC thermodynamics
Figs 5 and 6 show reversible thermodynamic diagrams for H₂O and CO₂ electrolysis at atmospheric pressure. If the reactions (½ O₂ + H₂ → H₂O and ½ O₂ + CO → CO₂) are reversed in the top of the figures, and ‘demand’ is exchanged for ‘content’, then exactly the same figures give the thermodynamics for the H₂ and CO fuel cells [9]. The relation between the two y-axes is simply the fact that energy measured in the unit of ‘volt (V)’ is equal to the energy measured in the unit of ‘kJ/mol’ divided by 2F (F is Faraday’s number). We may see the following in Figs 5 and 6.

At standard pressure (1 bar) and if partial pressures of pH₂/pH₂O = 1 and pO₂ = 1 bar, then Eᵣₑ₉ = ΔGᵣₑ₉/2F, where Eᵣₑ₉ is the equilibrium voltage of an electrolysis cell or fuel cell of any kind and ΔGᵣₑ₉ is Gibbs free energy of the formation of H₂O at the given temperature. The equivalent relations are valid for the CO₂–CO cell.

That ΔH/ΔG > 1, where ΔH is the enthalpy of formation, means that the electrolysis process is endothermic and the fuel-cell process is exothermic. Thus, in electrolysis mode, when the applied cell voltage E_cell is equal to Eᵣₑ₉ = ΔHᵣₑ₉/2F, then there is no heat production from the cell, i.e. the cell polarization, ΔE_pol = Eᵣₑ₉ – Eᵣₑ₉ = ΔHᵣₑ₉/2F – ΔGᵣₑ₉/2F. In other words, Eᵣₑ₉ is the thermoneutral voltage. The gap between the green and black curves in both Figs 5 and 6 means that the electrical-energy efficiency, ηᵣₑ₉ = 100% at E_cell = Eᵣₑ₉ (in the case of no heat loss to the surroundings).
and that, in the interval of \( E_{\text{eq}} < E_{\text{cell}} < E_{\text{tn}} \), it is necessary to supply heat in order to keep the cell temperature.

The electrical-energy efficiency is higher than 100% under such conditions but, naturally, the total energy will never reach 100%, as, in such cases, a heat supply is necessary to compensate for the endothermic heat demand plus the heat loss to the surroundings. Fig. 5 reveals that relatively low-grade heat having a temperature a little above 100°C is able to supply the necessary heat for evaporation of liquid \( \text{H}_2\text{O} \). This may be advantageous in cases where SOECs are integrated with other industrial processes that produce heat.

The current–voltage (iV) curve is approximately linear for RSOCs, i.e. \( i \propto E_{\text{cell}} - E_{\text{eq}} \), the cell polarization. Everything else being equal, the price of \( \text{H}_2 \) and \( \text{CO} \) produced by electrolysis will be inversely proportional to the current density, \( i \). In many cases, it is advantageous to operate in SOEC mode at a cell voltage just above \( E_{\text{in}} \) because then no cooling or heating system for stacks is necessary. (The slightly higher voltage than \( E_{\text{in}} \) is necessary in order to deliver the heat loss to the surroundings.) So, Figs 5 and 6 indicate that the cheapest gas will be produced at the highest possible temperature. The advantage of high temperature is further supported by the fact that polarization resistance is lower the higher the temperature is. However, everything is not equal with increasing temperature, as the stability of stack materials decreases rapidly with increasing temperature, and thus the optimal conditions have to be found as a compromise.

Anyway, the facts above about SOECs and the fact that most other electrolysis-cell types are not reversible mean that the RSOC is significantly more efficient and more flexible in operation than conversion, storage and re-conversion systems based on lower-temperature electrolysis and fuel cells.

2 Status of RSOC technology

This chapter reviews the status of RSOC technology with respect to performance, durability and mechanical strength, including area-specific resistance (ASR), power density, degradation types and rates for various types of RSOCs, all in relation to cell materials, design and operation conditions including sensitivity to impurities.

2.1 RSOC electrochemistry and performance

As mentioned above, it is important that an RSOC stack in SOEC mode be run as close to the thermoneutral condition as possible. \( E_{\text{in}} \) is in the range of 1.3–1.5 V for the co-electrolysis of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) in one gas mixture. The exact value depends on the operating conditions, including the composition of the \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) feed with a low concentration of \( \text{CO} \) or \( \text{H}_2 \), or a mix of all of them [18]. Figs 5 and 6 also reveal that there is no possibility of avoiding a lot of heat release in SOFC mode using \( \text{H}_2 \) and \( \text{CO} \) as fuel. Using e.g. \( \text{CH}_4 \) plus \( \text{H}_2\text{O} \) as fuel in SOFC mode (internal reforming) can limit the heat production significantly. The production of syngas with the right composition and high pressure (about 30 bar) using SOECs may produce \( \text{CH}_4 \) inside the fuel-electrode compartment [19] but, in order to make this version of the RSOC technology commercial, it is necessary to decrease the area-specific internal cell resistance to about 0.4 \( \Omega \text{cm}^{-2} \) at 450°C in order to be able to run the cell at \(-1\) A \( \text{cm}^{-2} \) at a cell polarization of 0.4 V, i.e. a cell voltage of 1.4 V. This is close to the thermoneutral potential of a 50%/50% mixture of \( \text{H}_2\text{O}/\text{CO}_2 \). However, it will require significant further development of the RSOC to lower the internal cell resistance sufficiently to make this possible, but there is no fundamental reason why it should not be possible. Until this has happened, we will have to

![Fig. 5](https://academic.oup.com/ce/article-abstract/3/3/175/5581681/3.317558981?download=1) Reverser thermodynamics for \( \text{H}_2\text{O} \) electrolysis at atmospheric pressure. If the reaction is reversed (\( ½ \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \)) in the top of the figure, and ‘demand’ is exchanged for ‘content’, then exactly the same figure gives the thermodynamics for the \( \text{H}_2 \) fuel cell. Reprinted from [9] with permission from American Chemical Society.
make our CH₄ by taking the syngas from the electrolyser to a catalytic methanation reactor at 30 bar and 400°C, or to other types of catalytic reactors that can produce synthetic fuels (synfuels) of almost any kind. Such reactors are already commercially available in the chemical industry.

Another chemistry that may be used in the future for chemical storage is based on ammonia (NH₃). The role of RSOC electrochemistry in this context is to produce H₂ in SOEC mode and then react some of the H₂ with all O₂ of the air to make pure nitrogen [N₂] using sustainable electricity [20]. Then, this N₂ is mixed with H₂ and reacted to NH₃ in a Haber-Bosch process [21]. When electricity again is needed, this can be produced using an RSOC in SOFC mode, which is fed with NH₃, as this is a fine fuel for SOFCs [22].

Furthermore, NH₃ is already the most produced chemical in the world, with a yearly tonnage above 10⁸ tons [23] based on fossil fuels. NH₃ is used as a fertilizer. The possibility of supplying H₂ produced by electrolysis to produce NH₃ can avoid the use of large quantities of natural gas and thus significantly lower the release of CO₂ into the atmosphere in the order of 1% of the total release of CO₂ to the atmosphere by humans [24].

Finally, there is the vast area of hydrocarbons and oxyhydrocarbons as synthetic CO₂-neutral fuels and as fuels for SOFCs. This is mainly chemistry rather than electrochemistry for the time being, as the RSOC temperature (>750°C) is too high for these carbon-based fuels, which are so brilliant for the storage of energy (see Table 2). Below, the hydrocarbon issues will be briefly described.

### 2.2 Reversibility and fuel chemistry

#### 2.2.1 H₂O/H₂ and CO₂/CO

The electrochemical reactions for the various electrode reactions in RSOC cells are given as follows.

The oxygen electrode is in all cases the positive electrode and the reaction is

\[
O^{2-} = \frac{1}{2} O_2 + 2e^- \tag{1}
\]

The reaction towards the right is oxygen evolution (electrolysis mode) and to towards the left is oxygen reduction (fuel-cell mode).

The fuel electrode is in all cases the negative electrode, and for H₂O/H₂, the reaction is

\[
H_2O + 2e^- = H_2 + O^{2-} \tag{2}
\]

Again, towards the right is hydrogen evolution (electrolysis mode) and towards the left is hydrogen oxidation (fuel-cell mode).

In analogy, the fuel-electrode reaction for CO₂/CO is

\[
CO_2 + 2e^- = CO + \frac{1}{2} O_2 \tag{3}
\]

The total reactions (H₂O ⇌ H₂ + ½O₂ and CO₂ ⇌ CO + ½O₂) change in both cases the number of gas molecules from 1 to 1½ and, as gas contains a lot of entropy, this is the reason for the strong endothermic electrolysis and exothermic fuel-cell reactions as visualized in Figs 5 and 6.

Fig. 7 shows three iV-curves for three SOCs with different compositions of oxygen electrodes, all produced and tested at the Department of Energy Conversion and Storage, DTU. At OCV, the Ni–YSZ|YSZ|LSM-YSZ SOC shows a low performance (0.27 Ω cm²) compared with Ni–YSZ|YSZ|CGO|LSCF-CGO (0.19 Ω cm²) and Ni–YSZ|YSZ|CGO|LSC-CGO (0.15 Ω cm²) [8]. All three cell types show good reversibility in the sense that the iV-curves pass back and forth over zero current density in a linear and symmetrical manner, i.e. the slopes (polarization resistances) are the same on both sides of the zero current.

Similar reversible behaviour has been reported for the electrolysis of CO₂ and for the co-electrolysis of mixtures of H₂O and CO₂ [9].
Initial performance and durability of RSOCs look fine in the reported literature. Figs 8–11 show the best reported data that we know of [25, 26]. These tests of cells from FuelCell Energy are indeed impressive. However, when comparing literature data, we have to be aware of the circumstances of the test. An example is that, if we compare the DTU cell test with the LSC electrode in Fig. 7 and the 800°C test of Fig. 8, there is a great difference even though they are both tested at 800°C. However, ASRs measured as the slope of the almost linear part of the curve from 0 to 0.5 A cm⁻² are both close to 0.15 Ω cm⁻². A main difference is that the DTU cell is tested with a 50/50 ratio of pH₂/pH₂O to the fuel electrode and pure O₂ to the oxygen electrode in order to simulate the average conditions of a practical SOEC, whereas the test at FuelCell Energy is tested with a 2/98 ratio of pH₂/pH₂O to the fuel electrode and air to the oxygen electrode, possibly with the purpose of obtaining the maximum hydrogen-production rate. A consequence of the differences in the gases supplied to the electrodes is that there is about 0.2 V difference in OCV between the tests. No details about the cell of Fig. 8 are presented in [25], but Dr Wood informed us at the conference that the cell was made of classic SOC materials. Thus, the two cells should be comparable and, in spite of the huge difference in their immediate appearance, they are in fact quite similar when the results are compared in comparable details.

It is also noticeable that the durability in SOFC mode looks as if it is considerably better than in SOEC mode. This is probably the case for most cells and cell tests done galvanostatically in SOEC mode seem to be degrading slightly faster (and earlier than a couple of years ago: much faster). One reason may be that the two operation modes have different sensitivities to common impurities (see below).

Fig. 12 illustrates a small laboratory demonstration that an existing Haldor Topsøe A/S (HTAS) RSOC stack is able to load-follow in a real energy system. It shows 16 days (384 h) of a test that ran for approximately 1600 h in total, of which about 1200 h were for the reversible wind-load-balancing profile. The stack was an eight-cell HTAS Delta-type stack. The profile was generated directly from time-series data of wind-power supply and electricity demand from the Danish island of Ærø. The stack managed to operate in these highly variable conditions of complete load-balancing that are needed in order to enable 100% renewable energy for the region. The stack performance was not harmed by these interruptions, demonstrating stable performance for several hundred hours [27].

2.2.2 CxHyOz
Hydrocarbon and oxyhydrocarbon (CxHyOz) cannot yet in general be used as direct fuels in Ni–YSZ-based SOFCs.
because they will crack, carbon will precipitate and the fuel electrode will become blocked and destroyed by the carbon (see the ‘Carbon deposition in Ni–YSZ SOEC electrodes’ section below). However, carbon-containing fuels can be used after catalytic treatment of the fuels [28–30]. Hydrocarbons may be reformed externally into H₂ and CO. Natural gas may also be reformed internally, as Ni is the reforming catalyst in all three cases below, and the Ni–YSZ cermet support and fuel electrodes of RSOCs are fine practical Ni-catalysts.

The most-used reforming method is steam reforming, which follows the chemical reaction

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2$$

and the water–gas shift reaction (Equation (5)) always run in parallel with Equation (4):

$$CO + H_2O \rightarrow CO_2 + H_2$$

Another important reaction is the methanation reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

and Equation (6) is reversible, but it is totally shifted to the left under the RSOC-operating conditions of today, i.e. temperatures of 700°C and above, and atmospheric pressure. It is necessary to decrease the temperature to <500°C and pressurize to about 30 bar in order to shift it sufficiently to the right.

Steam reforming is a strongly endothermic reaction that needs a lot of heat and will cool the inlet of the fuel
Thus, this puts serious demands on the mechanical strength of the cell and stack, but SOC technology has been developed to withstand this; however, when the stack can tolerate the cooling by internal-reforming cooling, it is advantageous, as it helps in cooling the very exothermic H₂ and CO oxidation processes in an SOFC. Thereby, the amount of surplus airflow can be decreased and less energy is lost to drive the high airflow that is usually used for cooling the SOFC stack [29]. Interestingly, this opens the possibility for an efficient way of using easily cracked fuels like ethanol or diesel, which cannot be used directly because of the mentioned carbon deposition in the Ni–YSZ electrode by the cracking process. Such fuel can be catalytically converted into a mixture of mainly CH₄ and H₂. Using this as the fuel will help in cooling the stack [29]. Control of the reforming reaction rate may be accomplished by having a tiny concentration of sulphur compounds in the gas feed, as this will impede the reforming rate [29].

2.2.3 NH₃ as an alternative carbon-free fuel

In the case of NH₃ as the fuel for an RSOC in fuel-cell mode, it works exactly as if the fuel was a mixture of H₂/N₂ = 3/1 [22] (see Fig. 13). Furthermore, fairly low degradation rates have been demonstrated on cells and stacks [30]. NH₃ cracking seems to be the first step in the conversion of the NH₃ in the fuel electrode, and it seems to take a lot of Ni surface to fully catalyse the cracking process at temperatures of 700°C and below [30].

The synthesis of NH₃ in an SOEC is not possible, as the equilibrium reaction

\[ 3 \text{H}_2 + \text{N}_2 = 3\text{NH}_3 \]  

is totally shifted to the left at temperatures above 600°C. This means that the synthesis of sustainable NH₃ has to be done by producing H₂ by H₂O electrolysis and by producing N₂ from air by the conversion of O₂ with H₂ followed by condensation of the formed H₂O.

2.3 Performance and durability considerations

A general rule of thumb seems to be that the better the initial performance, the more durable the cell or stack will be with respect to electrochemical degradation. This observation probably relies on the fact that the cell polarization is the driving force for the cell processes and, in most cases, also drives the degradation, while the tests are usually carried out in galvanostatic mode (constant current density), as this is the most easily seen from an instrumental point of view. However, it might be helpful for our understanding of degradation processes to do more tests in potentiostatic mode (constant potential), because galvanostatic mode will increase the overvoltage of the electrode process as the degradation processes proceed. Thus, galvanostatic testing may be a kind of uncontrolled accelerated testing. In spite of this, it is not guaranteed that the durability always will be better in potentiostatic than in galvanostatic tests, but it will probably be different [31].

Recent reviews on general degradation mechanisms and measures to prevent and repair degradation have been published by Graves [32] and Skafte [33]. These works are in particular relevant to bipolar flat-plate stacks with Ni–YSZ-supported cells (see Figs 4 and 14). The RSOC bipolar flat-plate stack must be able to convert the reactant gases, CO₂ and/or H₂O, and electrical energy into CO and/or H₂ in SOEC mode, and the reverse in SOFC mode. This takes a number of specific functions, which may be carried out by the following components in a stack repeating unit (SRU): (i) an electrochemical cell, (ii) a combined mechanical cell support and current distributor, (iii) an electric interconnector, which separates the reactant gases of two...
First of all, the thermodynamic and mechanical stability of all the components on the fuel side (YSZ, Ni–YSZ, glass seals) in contact with reactants (H₂, H₂O, CO, CO₂) and on the oxidant side (YSZ, YSZ-LSM, glass seals) in contact with O₂ and N₂ is important. In general, a solid material is not mechanically stable if it has a geometric flaw (e.g., a notch at the surface) and the stress state is high enough to overcome the necessary free energy of the formation of the surface(s) of the material(s). Further, the material will react if (∆G_{reaction} + electrical gain in energy) is negative and a reaction mechanism exists through which the reaction can take place. Actually, the electrical potential of the materials may influence also the mechanical stability, because the precise composition of materials is dependent on the potential and the mechanical properties are dependent on the composition of the material. ∆G_{formation} = –975 kJ/mol ZrO₂ at 800°C, which translates into a theoretical electrochemical potential stability range of ≈2.5 V, which is the maximum stability interval for a zirconia-based electrolyte, i.e., if the potential of the cathode (negative SOEC electrode) is lower than –2.5 V versus O₂ (1 bar), then the YSZ will split into Zr metal and O₂ gas. In practice, the stability interval may be significantly lower than 2.5 V, because YSZ will start changing composition at less negative potentials than –2.5 V versus O₂ (1 bar) if it can react with other cell components [35, 36].
2.3.1 Mechanical strength of the Ni–YSZ support

While strong and ductile metal-supported cells are being developed [37, 38], the majority of current cell designs rely on zirconia as the structural component, either as a Ni–YSZ support or as the electrolyte as a support. The three most commonly used materials are 8YSZ or 10Sc1CeSZ (or 10Sc1YSZ) for electrolytes with high ionic conductivity and in the Ni–YSZ support 3YSZ with superior strength, which stems from the martensitic phase transformation from tetragonal to monoclinic zirconia occurring at crack tips. It hinders the crack from growing and effectively enhances the strength [39]. While this is a well-proven mechanism at room temperature, the use of this material may have some drawbacks at higher temperatures [40], as we will cover in the following.

The strength has been shown to strongly depend on the temperature in the reduced condition when Ni–3YSZ is used as an electrode support [41]. This is primarily believed to be due to the strong temperature dependency of the energy dissipation of the plastically deforming nickel phase and not so much the 3YSZ. In the oxidized condition, i.e. as NiO–3YSZ, the strength is almost independent of temperature [41]. In NiO–3YSZ, the 3YSZ phase is the stronger and thus strength-determining. The strength increase from the phase transformation of 3YSZ is expected to vanish as the temperature gets beyond the metastable regime, where the phase transformation will occur [39]. Yet, 3YSZ is tougher than 8YSZ at high temperatures [40]. One hypothesis of the temperature independency is that the 3YSZ phase is shielded by compressive residual stresses in the microstructure (when cooled from sintering due to the higher thermal-expansion coefficient (TEC = 14⋅10–6 K–1) of NiO compared to 3YSZ (TEC = 11⋅10–6 K–1)). More recent research indicates that it is the slow grain growth in 3YSZ through sintering and resulting small grains as compared to 8YSZ that are partially the reason that 3YSZ maintains its strength [40].
A very important point is, however, that the chemical stability of 3YSZ is very poor in moist atmosphere and spontaneous phase transformation may occur within a few hours in the temperature interval of 100–200°C, with disintegration of the zirconia phase as a result [39]. This means that, during thermal cycling of 3YSZ, it must be protected by a dry atmosphere. Also, the high-temperature stability of the material was found to be limited.

Therefore, new material compositions for cell support were studied using CeO₂ as a co-dopant to Y₂O₃ in zirconia [40]. Various material compositions were analysed and optimized with respect to the structural stability for different sintering temperatures and new phase-stability diagrams developed. A new composition (NiO–1.5CeO₂:4.5YO₁.₅-SZ) was found to be a superior composition, providing 30% higher strength than NiO–3YSZ at room temperature and 10% higher strength at 800°C. The main gain is a better chemical stability against degradation by moisture using a CeO₂-doped compound, although it is still susceptible to degradation in moist conditions at 100–200°C [40].

Water is also influencing the long-term stability of the zirconia through so-called slow (subcritical) crack growth, where water can act as a corroding agent at the crack tip, breaking chemical bonds (also referred to as stress corrosion). The phenomenon basically provokes crack growth below the critical (very fast) crack growth measured in most fracture-toughness measurements. This phenomenon has gained more attention over the years [42, 43] and recent works have characterized this phenomenon in greater detail [40, 44]. The stress-intensity factor to provoke a slow-growing crack can thus be as much as 30–40% lower than the fracture toughness [40], and this must be carefully considered as a design criterion.

Another recent important finding is that the main structural component of the fuel-electrode-supported cells, NiO–YSZ, becomes considerably softer during the reduction period, allowing very fast creep in the structural parts of the composite [45]. The creep rate during reduction was measured to be between 7000 and 10 000 times faster than the creep rate during normal operation. This certainly is important for the stack assembly and reduction procedures, but it is also important for understanding the stress configuration inside the SOC stacks after reduction because the very fast creep is expected to reduce all residual stresses from TEC mismatches in the cell to zero at the point of reduction. Thus, to protect the electrolyte from compressive residual stresses, a reduction temperature above the operation temperature is preferred [45].

2.4 Cell degradation

The cell-degradation rate depends for a given cell and gas reactant mainly on the cell voltage/current density. Often, literature reports describe the degradation as being dependent mainly on current density, probably because most reported cell tests have been carried out in galvanostatic mode. Also, electrode overpotential is mentioned as important. Some inherent effects of current density and overpotential cannot totally be ruled out, but it seems that these claims are due to the fact that overpotential and current density are directly related to the electrode potential versus a reference electrode for each of the two electrodes. The electrode potential versus a well-defined reference is the main parameter that describes the thermodynamic state of a given electrode under given conditions. The Pt/O₂ (1 bar O₂, temperature) electrode is recommended as the common reference electrode for SOC electrodes, even though these electrode potentials are usually not directly available, but have to be calculated from electrochemical characterization of a cell (see e.g. [46] for a procedure). Recent tests have proven that the outcome of durability results is dependent on the test mode (galvanostatic or potentiostatic) [31]. This is a consequence of the importance of the electrode potential, as explained below. Furthermore, alternating the reversal of the current, i.e. changing the test mode from electrolysis to fuel cells forth and back, may almost stop the cell degradation (see below).

Figs 15 and 16 illustrate the most common electrical-potential-driven degradation mechanisms of the common SOC electrodes and electrolytes. In the case of the Ni–SZ (stabilized zirconia) cermet (Fig. 15), a very negative electrode potential reduces the zirconia into Zr metal, which dissolves in the Ni, and the tendency is that this will end up causing zirconia nanoparticles, which will block the Ni–SZ contact and thus the reduction of H₂O and CO₂, but, if the reduction of the cermet can be done gently enough, then the nanoparticles may for a while improve the electrode performance.

The nanoparticles are formed at relatively positive electrode potentials (up to approximately −1.4 V versus 1 bar O₂, 800°C) compared to the thermodynamically calculated potentials mentioned above. This will be discussed further below.

At very positive potential, the Ni is oxidized to NiO, which initially is formed as nanoparticles. In a kind of analogy to the SZ-reduction case above, a slow, short oxidation of Ni may temporarily activate the electrode. If the oxidation of Ni is continued, this will damage the electrode irreversibly, especially if the reduction–oxidation of Ni happens many times (redoxing); the cermet will be mechanically destroyed because of the large volume difference between Ni and NiO. After the re-reduction of NiO to Ni, the fast self-diffusion of Ni causes the Ni particles to coarsen. Some of the Ni particles will grow until their growths are stopped by the SZ. Then, during the next oxidation of Ni to NiO, further volume expansion takes place and so on.

A strong reduction will decompose perovskite and other possible oxide electrodes (Fig. 16). The initial stage of this breakdown is a formation of nanoparticles, which will reform the electrode-material composition, but keep the nanoparticle form for a while. Again, such nanoparticles...
will increase the electrode performance. At high positive potential, O\(_2\) bubble formation in grain boundaries with weakening of YSZ near LSM at ‘high’ oxygen-electrode overpotential occurs [48]. Here, ‘high’ anodic overvoltage may actually start at ~60 mV at 850°C (Ebbesen, unpublished work [49]).

2.4.1 Degradation of Ni–YSZ electrodes with high cathodic overpotential
In this section, the various kinds of degradation of the Ni–YSZ cermet electrode are summarized.

2.4.2 Electrode-potential-driven loss of contact
This kind of degradation is typically taking place within the first 1000 h of test at current densities above around 1 A cm\(^{-2}\) in good cells, i.e. Ni–YSZ electrodes at a potential in the range of approximately ~1.2 to ~1 V versus Pt/O\(_2\) (1 bar, 800°C). The phenomenon is summarized below. It is described in more detail in [50, 51]. However, the possible threshold value, above which this occurs, is not well determined and more work on this is definitely needed.

**Fig. 15** Commonly seen Ni–YSZ fuel-electrode-potential-driven activation and degradation phenomena that affect the Ni/YSZ/H\(_2\),H\(_2\)O or CO/CO\(_2\) three-phase-boundary (3PB). From ([47]) with permission from Springer.

**Fig. 17** shows the appearance in SEM pictures of the Ni–YSZ electrode part next to the electrolyte. It displays the structure of a non-tested electrode, of an electrode at gas inlet and outlet after tests during 678 h, and of one at inlet and outlet after 138 h at ~2.0 A cm\(^{-2}\) in co-electrolysis mode. Our hypothesis—illustrated in **Fig. 18**—is that the Ni migration starts due to loss of contact between Ni and YSZ particles.

The loss of contact was in a previous hypothesis assumed by some of the present authors to be caused by the positive free energy of the formation of Ni–YSZ interfaces in the strongest polarized part of the Ni–YSZ electrode [50], but this may not be the main reason. Furthermore, the previous hypothesis predicted only Ni migration in the case of steam electrolysis, but now similar Ni migration has been observed to occur also in steam-free CO\(_2\) electrolysis [52]. YSZ nanoparticle formation is proposed in our modified hypothesis to be due to thermomechanical breakdown of YSZ into nanoparticles at the Ni–YSZ 3PB [53], but, before describing this in slightly more detail, the observations of YSZ nanoparticles are presented.
2.4.3 Formation of zirconia nanoparticles around the Ni particles during SOEC operation

As indicated in Fig. 15, the Ni–YSZ electrode may be destroyed at highly negative Ni-electrode potentials. It was hypothesized that electrochemical reduction of ZrO$_2$ (from YSZ) occurred and was dissolved into a dilute (1 p.p.m.) Zr solid solution in Ni and formed Ni–Zr compounds at more negative potential. It was further hypothesized that, during a following re-oxidation of Zr to ZrO$_2$, when the contact between Ni and YSZ is lost, nanoparticles are precipitated around the Ni particles [35].

Fig. 19 gives the test history of the worst case observed at DTU and Fig. 20 shows SEM micrographs of the tested electrode.

A mechanism of this process is described in detail [35]. From thermodynamics of pure bulk materials, a potential of 1.52 ± 0.16 V versus O$_2$ (1 bar, 850°C) was calculated in order to dissolve 1 p.p.m. Zr solid solution in Ni and formed Ni–Zr compounds at more negative potential. It was further hypothesized that, during a following re-oxidation of Zr to ZrO$_2$, when the contact between Ni and YSZ is lost, nanoparticles are precipitated around the Ni particles [35].

Fig. 19 gives the test history of the worst case observed at DTU and Fig. 20 shows SEM micrographs of the tested electrode. The above hypotheses are valid for H$_2$O-containing atmosphere. However, a similar phenomenon has recently also been observed in dry CO$_2$/CO atmosphere during CO$_2$ electrolysis. This and the formation of zirconia nanoparticles far inside the stability range of YSZ require a different hypothesis.

2.4.4 New hypothesis for Ni–YSZ loss of contact and Ni migration

It appears that the loss of contact between Ni and YSZ is a prerequisite for Ni migration in Ni–YSZ composite electrodes and, when the Ni–YSZ contact is lost, then the Ni will start migrating, which will cause a loss of contact between Ni particles [50].

YSZ nanoparticles have been observed at the interface between Ni and YSZ particles and on the surface of Ni particles in Ni–YSZ electrodes tested with cell voltages below 1300 mV for more than 1000 h [35]. As mentioned, the formation of the nanoparticles occurs at an electrode potential well within the chemical-stability window and they occur primarily near the electrolyte/electrode interface [35]. For composite electrodes, a cathodic polarization of 160–300 mV is required to initiate the loss of Ni–YSZ interfacial contact at the 3PBs at 800°C and 90% steam as inlet
During the electrolysis of steam in a Ni–YSZ electrode, two types of heat are generated. One is Peltier heat ($-T \Delta S$) and the other is Joule heat. In a mixture of 98% H$_2$ and 2% H$_2$O, at 1000°C, the Peltier heat produced is 41 kJ/mol e$^-$ [57]. This corresponds to a cathodic polarization of 425 mV. The Peltier heat increases with decreasing H$_2$O concentration and, combined with the Joule heat, the heat evolution during electrolysis causes steep thermal gradients at the 3PB. The width of the 3PB is only a few nm and preliminary calculations indicate that temperature gradients of more than $10^4$°C cm$^{-1}$ are present at the gas|Ni|SZ 3PB. Similarly to any other ceramic material, YSZ expands with increasing temperature and, due to brittleness, it cracks once the thermomechanical stress caused by the steep thermal gradients exceed the differential fracture energy. This may explain why a certain cathodic polarization is required for the loss of Ni–YSZ contact at the 3PBs with the following initiation of Ni migration.

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Due to the gradient in the Galvani potential (also called electrostatic potential), which is a consequence of the relatively low O$^-$ conductivity compared to the high conductivity of Ni, the current density is largest near the electrode|electrolyte interface. Gas-diffusion limitations make the H$_2$O and CO$_2$ concentrations lowest near this interface, which means that the Peltier heat production is highest near the interface. This is hypothesized to cause YSZ fracturing and the formation of nanoparticles near the electrode|electrolyte interface is in agreement with the experimental findings [35]. If the current is reversed, then the Peltier heat decreases due to increasing H$_2$O concentration at the 3PB, and further the Peltier heat is negative and counterbalances the Joule heat. Therefore, nanoparticle formation is only observed in electrolysis mode.
Ni migration is reported to be of similar magnitude in H₂O/H₂ and CO₂/CO gases [52, 58, 59]. The concentrations of Ni-containing species in the Ni–O–H gas-phase system seem low if such species should explain the observed Ni-migration rate [60]. Further substantial differences in the activity of Ni-containing species in the Ni–O–H and Ni–O–C gas-phase systems and the chemical activity of these are all very low. All in all, this suggests that NiX compounds with activities above 10⁻⁷, X being impurities like P and As in sub-p.p.m. concentrations [61], may be involved in the Ni migration.

Once the Ni and YSZ contact has been broken, the electrochemical conversion of H₂O and/or CO₂ stops. Due to limited surface and gas diffusion, the partial pressure of H₂O and/or CO₂ in the gas phase increases near the broken 3PBs and the concentration of mobile (adsorbed and volatile) Ni (impurity) species increases. The concentration gradient of mobile Ni (impurity) species causes Ni to migrate towards the still active 3PBs, i.e. to migrate away from the electrolyte/electrode interface.

### 2.5 Prevention of cell degradation

A good point is that, in energy applications, it is in principle possible to counteract the cell degradation by alternating operation in SOECs and SOFCs, as the cells are reversible, and so are the initial stages of several of the degradation mechanisms as revealed in Fig. 21. This may soon become very important for the commercialization of SOCs.

### 2.6 Electrode poisoning

RSOCs are sensitive to a number of poisons like other electrolysis and fuel cells. Differently from the low-temperature fuel cells, RSOCs are sensitive to the poisoning effect of some trace impurities in the raw materials of the cell components, but also RSOCs in both modes are sensitive to a number of gaseous impurities such as compounds of B, S, P, As, Cl and Cr [14, 29, 63]. Some methods of mitigating the poisoning problems have been found (see e.g. [64]), but it is still an issue with respect to the extra cost of SOFC technology.

#### 2.6.1 Fuel electrodes

In particular, the 3PB in the Ni–YSZ electrode is sensitive to becoming blocked by the segregation of glassy SiO₂ together with Na₂O and many other trace (a few p.p.m. level) impurities in YSZ and Ni [65]. Here, it plays a role that the slightly volatile Si(OH)₄ forms even at high temperature and may migrate downhill on pH₂O gradients in the steam-containing gas phase. Thus, RSOCs are much more sensitive to this in SOEC mode than in SOFC mode, even though glassy silica certainly may block 3PBs in SOFC modes also [66–68].

No general measure against this has been demonstrated clearly apart from keeping the raw materials very clean. However, this may be very expensive. It seems that it is better to figure out how to handle the poisoning trace impurities rather than carry out ultra-cleaning of raw materials and processing, e.g. by using ‘scavengers’. In the case of silica, additives of temperature-stable alkaline oxides such as SrO, La₂O₃ and partially reduced CeO₂ (or Ce(IV)ₓCe(III)ₓO₂₋ₓ) may be good scavengers of the acidic SiO₂. The positive effect of infiltration with ceria into the Ni–YSZ electrode may at least partly be due to a scavenging effect of Ce³⁺ by reacting with the glassy silica and forming crystalline Ce₂Si₂O₇. The glassy stuff seems to be smeared out around the 3PB, while separate particles of crystalline material are not expected to block gas access to 3PB to any large extent.

The Ni–YSZ electrode is also sensitive to a number of gaseous compounds. Sulphur seems to be a very abundant impurity, as most H₂ today is derived from fossil fuels, and therefore the effect of S-compounds has been widely investigated.
According to Hansen and Rostrup-Nielsen [69, 70], S-containing impurities will usually dissociate at RSOC operation temperatures (>700°C) and atomic S will adsorb on active sites on the Ni surface, and thereby block the electrochemistry. The S adsorption on Ni has been found to follow a Temkin isotherm in H₂-containing gas, i.e. the enthalpy of the adsorption of sulphur varies linearly with coverage, and the performance degradation is proportional to the sulphur coverage. Further, they report that, in SOFC mode with a cell voltage of 0.7 V in the temperature range of 700–900°C, a coverage threshold of ~0.6, below which there is no effect on H₂ oxidation, is found. Based on the formula given in [69]:

\[
\theta_S = 1.45 - 9.53 \times 10^{-5}T + 4.17 \times 10^{-5}T \ln \left( \frac{p(H_2S)}{p(H_2)} \right) \tag{8}
\]

Plus, assuming pH₂ = 0.5 bar and 800°C, we find that this threshold in S coverage is equivalent to pH₂S = 3 × 10⁻⁸ bar or 0.03 p.p.m. Even though this is a very low, it also means that it is possible to clean a gas sufficiently by passing it over a Ni-containing filter like powdered Ni–YSZ cermet or a pre-reformer catalyst at 500°C or just slightly lower than the RSOC operation temperature. Further, they report that, in SOFC mode with a cell voltage of 0.7 V in the temperature range of 700–900°C, a coverage threshold of ~0.6, below which there is no effect on H₂ oxidation, is found. Based on the formula given in [69]:

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An interesting observation regarding the effect of exchanging YSZ with ScYSC in the Ni-cermet electrode is that apparent differences in S-poisoning resistance between cell types have shown up to be caused by differences in cell performance. Cells with Ni–YSZ electrodes were optimized by the improvement of the structure to the same electrochemical performance level as the Ni–ScYSZ electrodes, which had superior resistance to S poisoning apart from their better electrochemical performance. Then there was no measurable difference between the two cell types [72]. This indicates that RSOCs with good initial electrochemical performance degrade less than cells with bad initial performance at a given current density. This has probably to do with the overvoltage difference between good and bad electrode structures in galvanostatic testing.

Another way to avoid the S poisoning of Ni is naturally to use other materials than Ni and YSZ, or adding additives. Examples are to change to Ni–CGO or to add nanoceria to Ni–YSZ, or to change both Ni and YSZ to e.g. doped strontium titanates or La₁₋ₓSrₓMn₁₋₃ₓO₃ (LSCM). Not surprisingly, all other materials have their pros and cons and much more about this can be found in other reviews and textbooks [7, 10, 29, 63, 64].

### 2.6.2 Oxygen electrodes

Poisoning of the RSOC oxygen electrodes has been studied much less than the fuel-electrode poisoning, probably because oxygen-electrode poisoning has not been a big problem in laboratory tests. The poisoning by Cr(VI) oxides and oxyhydroxides is the most studied [14, 63, 73–75] because this problem appeared when stack building with interconnects of ferritic stainless steel such as Crofer became popular. Step one of the reaction that takes place on the top of the Cr₂O₃ passivating layer is an oxidation of the Cr(III) in the top of the solid Cr₂O₃ to Cr(VI) compounds in the gas phase. In dry air, CrO₃ is formed and, in moist air, a mixture of CrO₃ and CrO₃(OH)₂. Over a cathodically polarized O₂ electrode, the Cr(VI) compounds will be reduced to solid Cr(III) compounds on the active sites at the 3PBs.

---

**Fig. 21** Reversible operation. SOC stability during constant current-density (-1 A cm⁻²) electrolysis test compared to reversible-cycling test of 1 h electron conductor (FC) (-1 A cm⁻²) + 5 h fuel cell (FC) (+0.5 A cm⁻²). During open-circuit and FC mode, -25 L h⁻¹ of pH₂/pH₂O = 50/50 and FC mode -15 L h⁻¹ of pH₂/pH₂O = 10/90 gas was supplied. Pure O₂ at the O₂ electrode [62]. With permission from Springer.
which get blocked, and the electrode performance will decrease quickly with increasing current density. However, chromium poisoning may also take place at OCV and under anodic polarization in SOEC mode, but at a significantly lower rate. The reason is that the acidic Cr(VI) compounds will react with the SrO content of the perovskite electrode materials, forming chromates by reactions such as

\[
\text{SrO} \, (\text{solid}) + \text{CrO}_3 \, (\text{gas}) \rightarrow \text{SrCrO}_4 \, (\text{solid}) \quad (9)
\]

As this reaction is a purely chemical reaction, it is not directly affected by the electrode potential and it will not preferentially block the 3PBs at OCV and anodic polarization. Under these conditions, all of the surface of the Sr-containing perovskite will be attacked.

The main measure against chromium poisoning is to cover the surface of the chromium-containing steel with a suitable metal oxide. The spinel-structured Mn\(_{1.5}\)Co\(_{1.5}\)O\(_4\) seems to make a coating that is effective in preventing chromium evaporation from the steel surface [76] and has become a popular coating.

Other compounds that may affect perovskite-type oxygen electrodes negatively are SO\(_2\), H\(_2\)O and CO\(_2\). According to a review by Jiang [14], SO\(_2\) also reacts with the SrO content of LSCF electrodes, resulting mainly in SrSO\(_4\) above and SrS below \(-700^\circ\text{C}\), and LSCF electrodes are most susceptible at about 700°C. The oxygen surface exchange rate is reported to decrease by two orders of magnitude after exposure to 20 p.p.m. SO\(_2\) at 700–900°C for 2 days. As SO\(_2\) is a common pollutant in air (around 20 p.p.b. in cities), it may be necessary to clean the air feed to the O\(_2\) electrode in an SOFC.

The review by Jiang also deals with the effects of CO\(_2\) and H\(_2\)O and reports that, while an LSCF electrode seems resistant to CO\(_2\) and H\(_2\)O above 750°C, it showed severe degradation at 600°C in an atmosphere of 2.8% CO\(_2\) plus 2.6%H\(_2\)O in O\(_2\) with indications of formation of SrCO\(_3\).

### 2.7 Carbon deposition in Ni–YSZ SOEC electrodes

Ni is an excellent catalyst for carbon formation [77]. The deposition of carbon in the form of carbon nanotubes [78–81] (CNTs) (see Fig. 22) in the porous structure can fracture the electrode (see Fig. 23) leading to rapid failure of the device [82, 83]. To avoid this, it is highly important to understand when and how the electrode is at risk of carbon deposition.

One must distinguish between the operation with the two relevant carbonaceous gases, i.e. methane (CH\(_4\)) and carbon monoxide (CO), as well as for the two different operating modes, i.e. in fuel-cell mode as an SOFC and in electrolysis mode as an SOEC. Deposition of carbon can primarily occur by two different reactions:

\[
\text{CO} \, (\text{g}) \rightarrow \text{C} \, (\text{s}) + \text{CO}_2 \, (\text{g}) \quad (10)
\]

\[
\text{CO} \, (\text{g}) + \text{H}_2 \, (\text{g}) \rightarrow \text{C} \, (\text{s}) + \text{H}_2\text{O} \, (\text{g}) \quad (11)
\]

These are known as the Boudouard reaction and the reverse coal-gas reaction, respectively, both of which become favourable at lower temperatures. In addition to these reactions comes the decomposition of hydrocarbons, which, however, is less relevant for SOCs, since the hydrocarbons are typically reformed prior to carbon deposition taking place. Furthermore, there have been speculations that the electrochemical reduction of CO(g) and CO\(_2\)(g) directly to C(s) is possible [84].

Electrolysis of CO\(_2\) into CO or of H\(_2\)O/CO\(_2\) into H\(_2\)/CO (syngas) can result in carbon deposition at the interface between the electrode and the electrolyte [82–84]. Thermodynamics dictates the onset, as shown in the C–H–O ternary diagram in Fig. 24. Alternatively, one can also consider the voltage of the cell, as shown in Fig. 25, where it becomes apparent that carbon deposition can occur at a sufficiently high overpotential. Degradation

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**Fig. 22** Carbon nanotube initiated by a nickel particle being lifted out of position (tip-growth). Image is reproduced with permission from Elsevier [79].

**Fig. 23** Carbon fibres fracturing the porous electrode during co-electrolysis. Image is reproduced with permission from Electrochemical Society [82].
of the electrolysis cell by other means, e.g. impurity poisoning, may then eventually lead to carbon formation [85], which will cause a sudden failure. Furthermore, gradients of temperature, gas composition and the overpotential must be taken into account, since the local conditions at the reaction site govern whether carbon deposition will initiate [83, 86, 87].

Contrarily, operation in fuel-cell mode with CH₄ can result in carbon deposition at the electrode surface. This is typically less destructive, since carbon can grow into the gas channels, and since the nature of the operating mode is to oxidize the gas atmosphere. Operating just beyond the onset, carbon will deposit at OCV but, when drawing a current, the carbon is oxidized and steady operation can be expected [89]. This is, of course, a risky strategy, as, in the event of a power failure, carbon deposition at OCV may destroy the cell. CH₄ is typically reformed either externally or internally directly in the electrode via the reverse-methanation reaction:

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \] (12)

The product can then yield carbon deposition on account of either Equation (10) or Equation (11). Reports in the literature of carbon deposition during fuel-cell mode are plentiful and a complete review is beyond the scope of this paper, so the reader is referred to the review by Boldrin et al. [64].

The most popular pathway for mitigating the issue is substituting Ni (or doping the electrode) with ceria [84, 90–94]. The mechanism for the increased tolerance is linked to the presence of oxidized carbon intermediates, which energetically trap the carbon before forming destructive CNTs. It has been suggested that this enables a reversal of Equation (10) on the ceria surface [94]. Other interesting mitigation strategies are doping with more carbon-tolerant metals [88, 91, 95, 96], passivation with sulphur [83, 97], exsolution of the Ni particles [98], flowing excess oxidizing gas [99] or applying a positive bias [99], as mentioned earlier.

2.8 SOEC-operation strategies

2.8.1 Stack performance and durability criteria
RSOC stack and system manufacturers must have criteria for an SOE stack that can pass the criterion of acceptable operation. One is that the performance must be constant, i.e. a specified power (a given number of watts) put into the SOEC stack must give at least the production rate of CO and/or H₂ that was promised, and a given fuel input into an SOFC must give a minimum of the promised watts. This may in practice be done by starting the stack life at 700°C and then use increasing temperature to compensate for the degradation. The end-of-life criterion may then be set as reaching 825°C because, above this temperature, the commonly used interconnector plates of ferritic stainless steel will oxidize very quickly, and full oxidation of the interconnector plates means that the stack will be destroyed. Both the start and the end temperature may naturally be changed by the development of better cells and stacks.

2.8.2 Gas-product quality
Another criterion is the quality of the H₂ and/or the CO, which is paramount in chemical-industry application with on-site production of CO. This means that mechanical integrity is most important, i.e. almost no cracks or holes in the electrolyte, the interconnector plates or the seals can be allowed.
As air or N₂ may be used as a sweep gas on the oxygen side, it is possible to calculate the allowed leak rate of air and/or N₂ through the electrolyte, the interconnect and the seals, when the maximum accepted level of N₂ in the CO product gas has been decided.

3 New types of RSOCs

The conventional Ni–YSZ composite electrode (Fig. 26a) has been microstructurally optimized over many years to provide high reaction rates. However, it is also one of the most common sites of performance degradation, resulting from the high mobility of Ni, the susceptibility of Ni/YSZ/gas 3PBs to poisoning by impurities from the gas supply or from the cell raw materials, carbon deposition on Ni and other degradation mechanisms. Furthermore, state-of-the-art oxygen electrodes have electrode polarization resistance (RP) values of less than half the ~0.1 Ω cm² achieved with state-of-the-art Ni–YSZ at 700°C in H₂/H₂O [100–102].

For more than 25 years, research has sought to replace Ni–YSZ with alternative materials that avoid these degradation issues while providing similarly low RP. Most efforts have focused on discovering single-phase mixed ionic-electronic conductor (MIEC) oxide materials, which provide electrochemical reaction sites on the entire surface/gas two-phase boundary (2PB), making them less susceptible to blockage by impurities than 3PB-based electrodes (Fig. 26b). One of the earliest MIEC electrode materials is CeO₂ doped with Gd, Ca or Nb, first investigated in the early 1990s [104, 105] and still under development today [103]. Doped ceria has long been considered as an electrolyte material, where its substantial electronic conductivity is a problem and causes loss of cell-energy efficiency. However, its electronic conductivity is too low for a single-phase electrode. Nevertheless, this fluorite structured MIEC appears very promising as an electrocatalytic component of a composite electrode where another material provides sufficient electronic conductivity, as discussed further below. Most investigated single-phase MIEC electrodes are perovskites or double-perovskites with much higher electronic conductivity, such as La₀.₇₅Sr₀.₂₅Cr₀.₅Mn₀.₅O₃–δ [106], (La,Sr)(Cr,Fe)O₃–δ [107–109], SrₓMoO₄–δ (where X = Mg, Mn, Ni, Fe, etc.) [110–112], SrFeₓMoₓO₄–δ [113, 114] and PrBaMnₓO₄–δ [115, 116]. These materials show differing levels of compatibility with electrolyte materials like YSZ and varying performance, approaching that of Ni–YSZ, but still with RP >0.3 Ω cm² at 700°C in H₂/H₂O.

Unfortunately, although some of these oxides approach Ni–YSZ performance, all exhibit orders of magnitude lower electronic conductivity than Ni, often <10 S cm⁻¹ for the bulk material and an order of magnitude lower for a porous electrode made of the material, which adds ohmic resistance and makes electronic current collection challenging. Additionally, MIECs often present mechanical weakness due to their thermal- and chemical-expansion behaviour. Therefore, a wide variety of composites have been investigated, with similar separation of functions as in Ni–YSZ, in which Ni provides electronic conductivity and catalytic activity and YSZ provides ionic conductivity. Electron conductor (EC) alternatives to Ni include other metals such as Cu and Ag, some of the perovskites mentioned above and other perovskites that are almost pure ECs, not MIECs, such as SrTiO₃ doped with La, Y or Nb. Cu and other low-cost metals show comparably high electronic conductivity to Ni, but they have lower melting points and are unfortunately even more mobile than Ni. Classical composite structures like doped SrTiO₃ with doped CeO₂ have been tested but lack electrocatalytic activity, at least in part because around half of the electrochemically active doped CeO₂ surface area has been replaced with relatively inactive doped SrTiO₃ surfaces (Fig. 26c) [117].

An alternative, promising composite electrode architecture is based on porous ion-conducting backbones or scaffolds such as YSZ or La₀.₇₅Sr₀.₂₅Ga₀.₇₅Mg₀.₂₅O₄–δ or MIEC backbones such as doped CeO₂. After the high-temperature sintering stage to produce these porous substrates, ECs and electrocatalysts are added by the infiltration of metal precursor salt solutions that produce metal or metal-oxide coatings upon heat treatment at a lower temperature than the initial sintering temperature (Fig. 26d) [118]. This allows the use of materials that would react or decompose at the higher sintering temperatures and the ability to retain nanoparticles during the lower-temperature heat
treatment. This backbone architecture is also a nearly optimal structure, as can be seen via porous electrode modelling, with the backbones providing large highways for ion transport, extending the reaction zone far from the electrolyte into the electrode thickness. Indeed, ion-conducting backbones coated with dispersed doped CeO$_2$ nanoparticles and/or Ni or other EC show performance that matches or exceeds Ni–YSZ [37, 119–122], some of which have been successfully used in stainless-steel-supported cells. However, this performance is achieved using high-surface-area nanostructures, the long-term stability of which remains to be demonstrated.

Besides infiltration, another way to introduce nanoparticles is in situ by exsolving them from a host oxide. Reduction of certain oxides (such as La$_{0.8}$Sr$_{0.2}$Cr$_{0.82}$Ru$_{0.18}$O$_3$) by low oxygen partial pressure or cathodic polarization causes reduced metal nanoparticles (such as Ru in that example) to leave the crystal lattice and segregate at the surface [47, 123, 124]. Depending on the materials and exsolution procedure, the nanoparticles can exhibit unique properties—they can be pinned to the surface and thereby be very stable, and oxidation–reduction cycling can make them dissolve into and re-exsolve from the crystal lattice, regenerating their performance. The performance of infiltrated MIEC nanoparticles is also often activated by such oxidation–reduction cycles, the mechanism for which is not yet clear [32, 125, 126].

At present, the only commercially available cells with alternative fuel electrodes than Ni–YSZ use similar composites of Ni and doped ceria, which avoid only some of the issues that plague Ni–YSZ. With further development of advanced nanostructured electrodes with low or no Ni, next-generation cells may be able to integrate them and utilize their advantages.

4 Perspectives and visions for RSOC applications

This section deals briefly with perspectives and visions for RSOC applications with ideas of how to operate RSOC systems, such as systems for providing large sustainable electricity grids based on wind and photovoltaic power with short- and long-term (seasonal) storage of energy, and systems for the conversion of power-to-fuel for the transportation sector.

Fig. 27 illustrates how the RSOC potentially can become an essential part of a CO$_2$ plus H$_2$O to hydrocarbon recycling system. It is imagined to consist of a device for CO$_2$ capture from air and a P2F-production unit comprising an SOEC plus a catalytic hydrocarbon synthesis reactor. The latter has been a commercial product using the Fisher-Tropsch process since 1936. In fact, it is today possible to buy (with a long delivery time) all components for such a system. The Swiss company, Climeworks, has commercialized a process for the capture of CO$_2$ from air and the Danish company, Haldor Topsøe, has commercialized a process called eCOs for the on-site production of CO by electrolysis of CO$_2$ using SOEC stacks.

We envisage that such systems may be put up in deserts and coupled to photovoltaic or wind turbines (as shown in Fig. 27) in windy areas such as the Danish North Sea or Patagonia in Argentina. Then, products such as CH$_4$, or DME may be transported in pipelines or tankers to cities that need the fuel. This would have the large advantage that we, to a great extent can utilize our existing infrastructure.

Another vision is a large renewable electricity-conversion and storage system using RSOCs. Fig. 28 shows a schematic diagram of such a large-scale storage system using novel, not-yet-realized P2G technology combined with underground gas storage [128, 129].

The novel aspect in this is an RSOC with reversible CH$_4$ conversion. The already developed P2G technique via syngas described above can in principle be widely deployed but, unfortunately, for long-term, seasonal periods, this technology is expensive and provides a low round-trip efficiency. The high loss of entropy in the H$_2$O and CO$_2$ electrolysis (two molecules of H$_2$O or of CO$_2$ are converted into three molecules: two H$_2$ plus one O$_2$, or two CO plus one O$_2$). In the case of direct electrochemical synthesis of CH$_4$ inside the fuel-electrode compartment, the overall reaction is

$$2\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CH}_4 + 2\text{O}_2$$  (13)

There is no change in the number of gas molecules and therefore an almost negligible change in entropy. As mentioned previously, this will require a significant decrease in the RSOC operation temperature to below 500°C combined with an operation pressure of around 3 bar. We think that this may be within reach within a few years if the financial support of the efforts in this area would be just slightly increased. If this target is reached and combined with the sub-surface storage of CO$_2$ and with CH$_4$ delivered to or from the natural-gas pipeline network, then this will enable large-scale electricity conversion and storage with a real round-trip efficiency of up to 80% and an estimated storage cost of around 3 US$/kWh, i.e. comparable to pumped hydro and much better than previously proposed technologies.

5 Comparison of RSOCs to competing electrochemical-conversion technologies

A comparison of RSOCs to competitive low-temperature (<200°C) electrochemical-conversion technologies is presented in Fig. 29, which shows the ranges of polarization curves for SOECs, PEMECs (polymer electrolyte membrane electrolysis cells) and AECs (alkaline electrolysis cells). Fig. 29 clearly shows that the RSOC has by far the greatest potential to become the most efficient electrolyser. The R&D of RSOCs has improved the durability and reliability a lot since 2011, the year of publication of Fig. 29, so the RSOC is now in early commercialization. There is worldwide
increasing R&D activity in the area of all three electrolyser types, so they are all being improved continuously. However, as the low-temperature cells are not reversible, these cell types are competitors only in separate P2F and F2P systems, but not in reversible P2F–F2P systems, as envisaged in Fig. 28.

If a power utility today is going to build a large plant (several 100 MW), it will have to use systems with AECs, as this is the type with the lowest price, and with companies with large production capacity. A drawback of conventional AEC systems is that they are quite voluminous, and therefore the much more compact PEMEC systems, which also are being commercialized these days, are often preferred for demonstration projects. In order to get the RSOC into real commercialization, big investors who will build mass-production factories are needed. The RSOC state of R&D is ready for this and, if the R&D support is kept high, then the short-term prospects of great improvements are assessed to be significantly higher for RSOCs than for AECs and PEMECs. (The principal author of this review is also active in both advanced AECs and in PEMECs).

6 RSOC outlook

Now, we are ready to look at which main R&D undertakings should be carried out in order to promote RSOC commercialization. In the short term, we think that fabrication
methods that can assure a high uniform quality of cells and stacks are most important. As mentioned above, cells with high initial electrochemical performance are also the most durable due to lower electrode overpotential. Furthermore, it is very important to avoid gas leaks through the ~10-μm-thin electrolytes, because, even though leaks through pinholes may not affect the immediate initial cell performance, there will be an increased temperature around the pinhole due to local burning of fuel. This will cause local degradation of both electrodes and electrolyte due to grain and particle coarsening and due to the build-up of local mechanical stresses, which may cause crack formation, and the bad cell will go into an accelerating degradation process that eventually will spread to the adjacent cells.

These efforts may be done using the Ni–YSZ and perovskite-based cells, which are the cells with which we have the most experience. Naturally, all the recent improvements such as ceria additions to Ni–YSZ fuel electrodes, the use of impurity scavengers and the use of the new and stronger zirconia-based Ni cermets for cell support must be implemented. Development of less expensive methods for steam and CO₂-gas cleaning would in particular be helpful.

The next step in cell R&D should be the improvement of new electrodes that are less sensitive to impurities and carbon deposition, and with the more durable metal supports. Preferably, these cells should have operation temperatures below 500°C, as this would decrease the costs of RSOCs for P2F for aeroplanes and other heavy transportation vehicles (Fig. 27) as well as for the conversion and storage of electricity for the grid (Fig. 28).

In parallel to this, it is important to further develop CO₂-air-capture technology, as the cost of CO₂ from air needs to come significantly down in order to make RSOC-based P2F competitive with fossil fuels. In the early phase of commercialization, CO₂ from fossil fuel and biomass power plants and from cement and steel factories may be used.

7 Concluding remarks
The above review supports that the technical and economic problems have been solved to a level at which a next step clearly is large demonstration projects of energy systems. It is also clear that this should be accompanied by a focus on large R&D efforts in the area of energy conversion and storage in general, and that RSOC technology seems particularly attractive for further development, as there are obvious possibilities for significant improvements in an already very promising technology that fits very well into a sustainable-energy system based on solar and wind energy.

P2F is to be preferred over just storing hydrogen, because hydrogen is expensive to handle. Even though the efficiency will be lower for producing fuel, as there is a loss in converting syngas into fuel, it should be noted that we have more than enough inexpensive clean, sustainable energy in the near future and, in general, it is cost and not efficiency that is most important. The efficiency in our consumption of fossil fuel is probably not much above 25% today. The efficiency of the utilization of renewable electricity will most probably become significantly higher—maybe as high as 40%. Thus, all arguments including economics are now in favour of full transition to renewable energy.

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Conflict of interest
None declared.

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