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Degradation in High-Temperature Co-Electrolysis Using Reversible Solid Oxide Fuel Cells: A Review

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Abstract

The need for cleaner and more efficient energy generation and storage is essential to cope with increasing energy demand and to reduce fossil fuel consumption. Solar, wind, hydroelectric, and other renewable energy sources are promising alternatives to fossil fuels, however, display considerable fluctuation in production due to their dependence on weather conditions. This is why supplementary alternative energy generation devices and storage are vital to progress towards a more feasible sustainable future, also including the options for more resilient energy systems, for instance with regards to grid reliability during natural disasters.

Reversible solid oxide fuel cells (rSOFC) have recently become a topic of interest in the energy industry due to their ability to produce fuel for storage in electrolysis mode and consume this fuel to produce electricity in fuel cell mode in one single unit when required. However, one of the primary issues hindering the widespread commercialisation of fuel cells is the lifetime on account of the effects of degradation on the cell. These effects, such as electrode poisoning, air electrode delamination, and fuel electrode redox stability, have been investigated extensively in the literature for solid oxide fuel cells (SOFC) and solid oxide electrolyzers (SOE) [1–4] separately, yet there are limited papers available on the degradation of reversible fuel cells and how cycling between the two modes affects the lifetime [5]. Co-electrolysis of H₂O and CO₂ using high-temperature SOEs is another pathway to reducing CO₂ emissions via energy storage and conversion devices with high-energy efficiencies and similarly, there is a gap in the understanding of degradation mechanisms with this mixed feed. This paper will present a review of the background, fundamental challenges and developments of SOFC, SOE and rSOFC, focusing on the different approaches to high-temperature co-electrolysis in terms of materials, fuel composition and how these influence the rate of degradation.

Introduction

Levels of atmospheric CO₂ have been rising drastically in the past decade due to deforestation and constant burning of fossil fuels. If this continues at the same rate, severe changes in the planet's climate are likely to be irreversible for thousands of years after emissions stop so it is essential that technologies are developed to reduce the human impact on the environment and build a more renewable system of energy supply.

SOFCs are well known in the energy industry as high efficiency electrochemical energy conversion devices capable of converting different fuels and oxygen directly into electrical power. High temperature SOFC consist of two electrodes, a fuel electrode and an air electrode, separated by a dense electrolyte. In a conventional SOFC, hydrogen, for example, is introduced to the fuel electrode of the cell where it is oxidised to form water and electricity whilst oxygen is reduced at the air electrode and the ions migrate across the electrolyte to the anode (as seen in Fig. 1). Advantageously, hydrocarbons such as methane or carbon dioxide can also be used as fuel in SOFC to produce electricity, hydrogen, and by-product carbon monoxide as an internal reforming reaction, which is further reacted with water to increase the hydrogen yield (water gas shift reaction, see Eqn 2). SOFCs benefit from high operating temperatures, which promotes internal reforming, increases fuel flexibility, eliminates the need for precious metal catalysts, and produces high quality by-product heat for combined heat and power systems. Efficiencies for this type of fuel cell can reach over 80% with heat recovery [6].

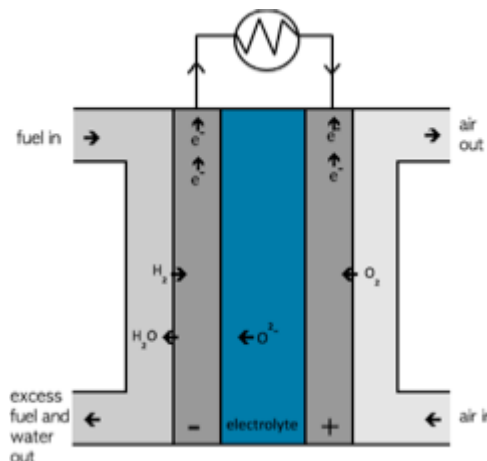


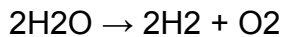
Figure 1: Schematic diagram of a SOFC.

The production of hydrogen today is predominantly by steam reforming of methane, as shown in eqn 1, or partial oxidation (eqn 2), followed by the water gas shift reaction (eqn 3). These methods have a high efficiency of 60 to 85% but still rely upon fossil fuels and produce large quantities of carbon monoxide and carbon dioxide [7].



A second, cleaner, way of producing hydrogen is from the electrolysis of water (eqn 4), which can be either low temperature electrolysis from a Polymer Electrolyte Membrane Electrolyser (PEM) or high temperature electrolysis in a SOE. Due to the elevated

temperatures of a SOE, it is a more efficient way of producing hydrogen than lower temperature PEM electrolysis in terms of thermodynamics and kinetics.



eqn 4

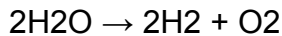
High temperature SOEs work in a similar way to SOFC, in fact, thermodynamically, they are described as SOFCs operating in reverse. They consist of a dense electrolyte in between two electrodes; the anode and cathode, however the SOFC cathode is now the SOE anode, and the SOFC anode is the SOE cathode. Because of this, and to minimise confusion, the SOE cathode is referred to as the fuel electrode and the SOE anode, the oxygen electrode. The electrolysis reaction occurs when an external voltage is applied across the two electrodes. The water is supplied to the fuel electrode where it is reduced to hydrogen and the oxide ions are conducted across the electrolyte to the oxygen electrode where oxygen is produced. Additionally, renewable energy sources, such as photovoltaic or wind power, can be integrated into the SOE system to supply the external voltage, hence reducing the electrical input and environmental impact [8]. Electrical efficiencies for SOEs can be close to 100% with respect to conversion of the input electricity when operating at thermoneutral voltage [9]. In practice it is often seen to be slightly less due to heat loss, polarisation losses or leakages. For a comprehensive understanding of the available literature on high-temperature co-electrolysis of CO₂/H₂O, readers are directed towards the 2017 review paper by Zheng et al. [10].

Hydrogen is abundant and easily produced from the aforementioned methods; however, society is not yet at a stage where a hydrogen economy can be implemented on a global or national scale. The main problems are the public's perception of the safety of its use, the current cost is high, and there is a lack of infrastructure to support a hydrogen infrastructure. Fortunately, natural gas is readily available within the current gas grid system so it is much easier to transport with no additional expenses. By using natural gas as a fuel in SOFC and SOE instead of hydrogen, we would be creating a more attainable intermediate step towards a carbon-free economy. Methane, the main component in natural gas, is more efficient at producing energy than hydrogen as it yields eight electrons per mole during reforming whereas hydrogen only yields two [6]. The co-electrolysis of CO₂/H₂O to produce high quality syngas has been researched for many years [11,12], with many academics focusing on the optimisation of cell materials and fuel composition to overcome difficulties with cell performance and stability. One consequence of using hydrocarbons is the higher rates of degradation, in particular carbon build-up and sulphur poisoning of the fuel electrode [13]. Using methane as a fuel for SOFCs is not a new concept, with research going into the effects of operating temperature, current densities, fuel composition and electrode materials and thickness [14–18]. It is clear to see how advancing in this field can assist in making a more sustainable and environmentally friendly future.

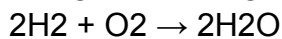
The main component affecting SOE efficiency is the electrical input required which promotes oxygen diffusion across the electrolyte; a higher voltage results in higher rate of diffusion, with oxygen partial pressure and chemical potential across the electrodes also influencing the diffusion rate. Thus, increasing the diffusion rate reduces the electrical input and increases the efficiency of the cell. In a conventional high temperature co-electrolysis cell, the fuel electrode is in a very reducing atmosphere, and the oxygen electrode is in an ambient air atmosphere. This creates a difference in oxygen partial pressure, causing aforementioned problems such as delamination and poor diffusion rates. To overcome this, fuel-assisted co-electrolysis cells expose the oxygen electrode to

reducing agents such as hydrogen, methane or carbon monoxide, which creates a reducing atmosphere similar to the fuel electrode, reducing the potential difference across the electrolyser and ultimately reducing electricity consumption [19–21]. When methane is used as the reducing gas, the overall efficiency of the SOE is nearly as good as the steam reforming reaction of methane, with the advantage of producing humidified hydrogen rather than a mix of hydrogen, carbon dioxide, water, carbon monoxide and methane.

The SOE reaction (Eqn. 4) and the SOFC reaction (Eqn. 5) are the reverse of each other, therefore the term rSOFC refers to a single cell or stack that can alternate between fuel cell mode to produce electricity, heat and water, and electrolyser mode to produce fuel; either hydrogen or syngas, from the electrolysis of water or carbon dioxide, respectively.



eqn 4



eqn 5

When coupled with solar, wind or other renewable energy sources, these systems have promising applications in power generation and storage, providing clean energy to the grid as and when required. The generated fuel can either be stored for subsequent use or directly consumed by the rSOFC to produce electricity.

Numerous papers describing high temperature rSOFC operation [22, 23] for hydrogen production are available in the literature, focusing on performance degradation of the oxygen electrode, material selection and cell performance in cyclic modes. Interest in this area is developing, with modelling [17, 24–26] and experimental investigations into degradation, overpotentials and lifetime analysis at the forefront of this research area. Compared to their SOE counterpart, SOFC technology and materials have been more widely researched, resulting in SOEs inheriting their advantages, and disadvantages. These issues are associated with the materials used in SOFC, which result in diminished electrochemical activity and thermomechanical stability when used in SOE mode. In rSOFCs, this becomes a problem when the higher degradation in electrolysis mode controls the performance of the cell as a whole [13].

Vibhu et al. [27] have demonstrated that oxygen electrodes operate differently in fuel cell and electrolysis mode, which is seen by a reduced performance due to delamination from a build-up of oxygen partial pressure on the electrolyte/electrode boundary [28]. For example, lanthanum strontium cobalt oxide (LSC), a common cathode material for SOFC, cannot be used in reversible operation due to the reducing atmosphere which decomposes the electrode [29]. Predominantly electronic-conducting oxygen electrodes (for example LSM) show significant performance degradation in electrolysis mode. To combat this, three mixed-conducting perovskite structures such as lanthanum strontium cobalt iron oxides (LSCF) to increase oxide ion transport and electronic conductivity is a method frequently applied to improve and stabilise performance [30].

The degrading of cells is one of the fundamental problems affecting both SOFC and SOE working under co-electrolysis. The principle issues that have been addressed in literature are delamination of the oxygen electrode, poisoning of the electrodes (carbon deposition, sulphur and chromium poisoning) and redox stability. Although co-electrolysis demonstrates the advantage of fuel flexibility, the higher quantities of carbon in the fuel supply compared to conventional hydrogen electrolysis is detrimental as it results in faster rates of carbon build-up or 'coking', decreasing the performance of the cell. Tao et al. [29] compare the use of a YSZ/LSCM cell in electrolysis mode, fuel cell mode, and fuel-

assisted electrolysis mode. The cell voltage drop was negligible in the first 2,500 hours and showed less than 1.5% per 1,000 hours degradation afterwards. Their tests resulted in a 4.5 cc/min-cm² hydrogen production rate with 1.58 V and 0.087 V required to electrolyse the steam in SOE mode and fuel-assisted mode, respectively, highlighting the significant amount of electricity saving by using a humidified methane.

1. Oxygen Electrode Degradation

It has been well established that the material choice for the oxygen electrode has a significant impact on delamination and performance stability. The term delamination describes the physical separation of the oxygen electrode from the electrolyte during operation. Materials such as lanthanum strontium manganites (LSM) [22,30,31], lanthanum strontium ferrites (LSF) [22,30], lanthanum strontium cobalt ferrites (LSCF) [22,32,33] and lanthanum strontium cobaltites (LSCo) [32] have been investigated for their resistance to delamination with the majority of researchers agreeing that LSCF is the highest performing oxygen electrode material under fuel cell and electrolysis mode [30].

One of the more widely accepted understanding of the degradation mechanism at the oxygen electrode is Virkar's [28], which explains how oxygen pressure can build up at the oxygen electrode/electrolyte boundary, causing microscopic cracks which link up to develop a much larger, delamination crack.

Long-term degradation tests were carried out during electrolysis mode by Ebbesen et al. [13] who found that the operating temperature of the cell was directly correlated to the degradation rate of the oxygen electrode and electrolyte in a Ni-YSZ/YSZ/LSM-YSZ cell. They discuss how only the oxygen electrode was affected, which indicates the degradation is caused by the overpotential at the Ni-YSZ fuel electrode triple phase boundary (TPB) from low oxygen partial pressure, a theory which is corroborated by others [23,34].

In 2007, work carried out by Guan et al. [22] for the U.S. Department of Energy showed a stack of 10 cells running under reversible operation for 1000 hours, reducing the initial degradation in electrolysis mode from 8000 to 200 mΩ cm²/1000 hrs by improving the microstructure of the oxygen electrode, which reduced the degradation via delamination.

2. Fuel Electrode Degradation

As previously mentioned, the main limitations with Ni-YSZ ceramic electrodes are the re-oxidation of the Ni and their susceptibility to poisoning by various contaminants; carbon, sulphur, and silicon, amongst others. Perovskite oxide materials are also used for fuel electrodes due to their relatively low cost and excellent thermal and mechanical stability. Whilst they have good resistance to both carbon and sulphur poisoning, they also offer mixed-valence for ionic and electronic conductance, and are catalytically more active than ceria for hydrocarbon oxidation [35]. For example, the electronic conductivity value for SFM is as high as 550 S cm⁻¹ in air and 310 S cm⁻¹ in hydrogen at 780°C for a symmetrical SOFC [36], and LSM is 240 S cm⁻¹ [37]. Papazisi et al. [33] carried out fundamental analysis of carbon tolerant fuel electrodes for rSOFCs, proving that LSCF has a more stable performance compared to the traditional Ni-YSZ electrodes in terms of carbon deposition, re-oxidation stability and reversibility under cycling between operational modes. They found that carbon deposition was in the form of nickel carbonyls and that Ni-YSZ electrode species were severely damaged by re-oxidation due to exposure to CO² as a fuel. Wang et al. [21] demonstrate the stability of SFM-SDC/LSGM/SFM-SDC cells for

methane assisted co-electrolysis, their results conclude that the fuel electrode does not show any obvious change in terms of grain growth or carbon deposition.

One other contaminant that effects fuel electrodes is Si, which can originate from glass sealants or as a contaminant in the fuel electrode material. Hauch et al. [38] have investigated how Si deposition onto the fuel electrode caused a degradation of 2%/100 hrs during long-term (1316 h) electrolysis testing. Addo [39] studied the stability, sulphur tolerance and electrochemical performance of Ni-YSZ and LMFCr fuel electrodes in rSOFC. He concluded that Ni-YSZ fuel electrodes performed better at lower temperatures and LMFCr electrodes at higher temperatures, in a sulphur environment. Additionally, the LMFCr performed better in SOE mode compared to SOFC mode.

3. Cycling

In attempts to reduce, or 'undo' degradation in rSOFC, thermal [40, 41] and current cycling [42] techniques have been employed with varying success. Thermal and current cycling is a process used in solid oxide cells to determine and understand degradation mechanisms. Current cycling has been used in the literature for durability testing for many years, Hughes et al. [43] demonstrated its significance in 2013 when they compared constant-current and reversing-current cells and concluded that periodically reversing the current slows the degradation process. Guan et al. [22] found that the rates of degradation during fuel cell, electrolysis, and cycling operation were very similar with only slightly enhanced degradation in electrolysis mode for an LSCF oxygen electrode. When using LSM and LSF as alternative oxygen electrode materials they found decreased performance, stability and area specific resistance (ASR). Earlier this year, Boeing and Sunfire GmbH demonstrated the largest commercial, fully autonomous hydrogen rSOFC system to date [44]. With a total of 1920 cells, the system operated for 1000 hours with 7 thermal cycles, as shown in Fig. 2.

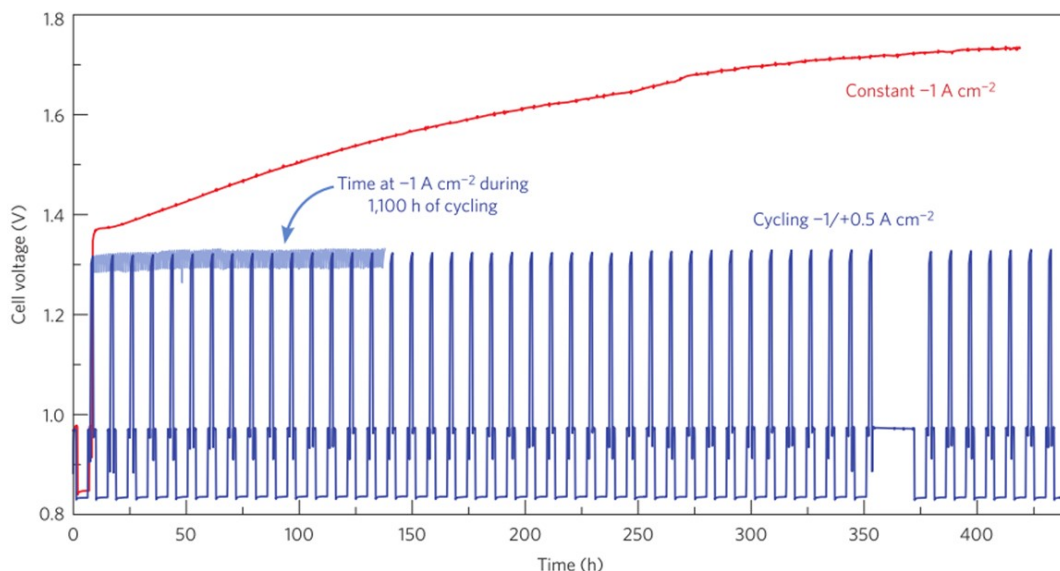


Fig. 2. Comparison of the SOC stability during a constant-current electrolysis test and a reversible cycling test. [44]

Tao et al. [29] developed a fuel-assisted SOE for hydrogen production, using perovskite-type materials and both wet syngas and wet methane as the fuel. The long-term stability tests revealed promising degradation results of less than 1.5%/kh in the 2500–4200 hours operation range using hydrogen, however the research did not extend to the effect the hydrocarbon fuels had on degradation rates. Nonetheless, these fuels; wet syngas and wet methane, reduced the amount of electricity consumed in electrolyser mode, were stable comparative to the conventional air/steam SOE and show reduced ASR compared to previous results. More recently, Graves et al. [45] demonstrated on Ni-YSZ/YSZ/LSM-YSZ cells how electrolysis induced degradation, which was previously thought to be irreversible, can be eliminated by reversing the current and operating the cell in fuel cell mode. They successfully observed no microstructural damage at the oxygen-electrode/electrolyte interface after cycling between electrolysis mode and fuel cell mode for 1 hour and 5 hours, respectively, for an overall time of 4000 hours. Similarly, Nguyen et al. [46] carried out long-term tests on a Ni-YSZ/YSZ/LSCF Jülich F-design planar short stack in reversible operation. They observed a voltage degradation of 0.6 %/kh at 0.5 A/cm² in fuel cell mode and nearly no degradation in electrolysis mode at -0.3 A/cm² at 750°C and 800 °C respectively. As previously mentioned, Hauch et al. [38] investigated fuel electrode degradation on Ni-YSZ/YSZ/LSM-YSZ cells and found that the degradation that occurred due to Si poisoning could be partly reversed by operating in fuel cell mode.

In 2016, Jung et al. carried out research on oxygen electrodes and concluded that composites of both electrode and electrolyte material (for example LSM-YSZ) are more durable under SOFC/SOE cycling compared to their non-combined counterparts (for example LSM) [47]. The performance of the LSM cell decreased after 10 cycles due to delamination whereas the LSM-YSZ electrode maintained stability during the same number of cycles.

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