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Durable SOC stacks for production of hydrogen and synthesis gas by high temperature electrolysis

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ABSTRACT

Electrolysis of steam and co-electrolysis of steam and carbon dioxide was studied in Solid Oxide Electrolysis Cell (SOEC) stacks composed of Ni/YSZ electrode supported SOECs. The results of this study show that long-term electrolysis is feasible without notable degradation in these SOEC stacks. The degradation of the electrolysis cells was found to be influenced by the adsorption of impurities from the applied inlet gases, whereas the application of chromium containing interconnect plates and glass sealings do not seem to influence the durability when operated at 850 °C. Cleaning the inlet gases to the Ni/YSZ electrode resulted in operation without long-term degradation, and may therefore be a solution for operating these Ni/YSZ based SOEC stacks without degradation.

1. Introduction

The widespread use of fossil fuels within the current energy infrastructure is considered as one of the largest sources of CO_2 emissions, which is argued to cause global warming and climate changes. Production of synthetic hydrocarbon fuels from renewable energy may be a solution to reduce oil consumption and carbon dioxide emissions without the need for modifications of existing infrastructure, e.g. in the case of production of methane (also called synthetic natural gas) or petrol/diesel, the infrastructure already exists in many countries. The usual raw material for synthetic hydrocarbon fuels is synthesis gas (a mixture of $H_2 + CO$). Hydrogen and CO can be produced via co-electrolysis of steam and carbon dioxide ($H_2O + CO_2 + \text{electricity} \rightarrow H_2 + CO + O_2$). Thus with electricity from renewable energy sources co-electrolysis may be an alternative route for production of hydrogen and synthesis gas without consuming fossil fuels or emitting green-house gases. Hydrogen may perhaps find a role in the future energy technology, although handling of hydrogen may be problematic. The production of synthetic hydrocarbon fuels seems more attractive because they can be applied without the need for modifications of existing infrastructure.

Steam electrolysis in Solid Oxide Cells (SOC) for hydrogen production was under development during the early 1980s [1–3] and has again become increasingly investigated during

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recent years as a green energy technology. On the other hand, the feasibility of co-electrolysis has only been shown in a few studies [4–7]. Mainly single cells have been tested for electrolysis performance and durability, and only a relatively limited number of studies focussing on the performance and durability of high temperature electrolysis stacks have been conducted [3,6,8–12]. When operating stacks, factors such as gas flow and thermal management, and chemical compatibility of cell components with interconnect materials become important. For example, it is well established that current state-of-the-art interconnect materials emits chromium vapour which has been shown to have a significant negative impact on oxygen electrode performance when operated in fuel cell mode [13–16]. This process, known as chromium poisoning, may theoretically also play an important role for the durability of electrolysis stacks [9]. Electrolysis cells (when tested as single cells) were found to degrade significantly when applying glass sealing [17–20]. For single cell tests, this glass sealing may be avoided [4,5], whereas for stack assembly, glass is the preferred sealing material because it can be modified to match the thermal expansion of other cell components, and glass sealings shows good hermeticity along with good thermal and chemical stability. Furthermore recent studies, when testing single cells without glass sealings have shown that minute concentrations of impurities in the inlet gases may cause similar significant degradation of the cells [4,5,21,22].

The aim of the present study is to examine the degradation of Ni/YSZ based Solid Oxide Electrolysis Cell Stacks (applying glass seals and chromium containing interconnects) during steam electrolysis and co-electrolysis of steam and carbon dioxide. Further, the effect of the gas-purity of the inlet gases is investigated.

2. Experimental method

The electrolysis cells used for the multi cells stacks were planar Ni/YSZ-supported SOCs (Ni/YSZ-YSZ-LSM/YSZ) of 12 × 12 cm (with an active electrode area of 9.6 × 9.6 cm). The cell details can be found elsewhere [23,24]. The nickel oxide in the Ni/YSZ electrode was reduced to nickel in hydrogen at start-up. Two stacks were tested for performance and durability, one for steam electrolysis (in 50% H_2O – 50% H_2) and one for co-electrolysis (in 45% H_2O – 45% CO_2 – 10% H_2). The stack testing was performed at testing was performed at Risø DTU National Laboratory for Sustainable Energy with a proprietary stack design by Topsøe Fuel Cells A/S (TOFC). The stack was sealed along the edges with a proprietary glass seal design by TOFC with a different composition than the albite glass seal ($NaAlSi_3O_8$) normally used for single cell teats in our laboratory. The stacks were composed of either six (in the case of steam electrolysis) or ten (in the case of co-electrolysis) repeating units (RU) containing cell and interconnects as indicated in Fig. 1. Several voltage probes were in contact with the interconnect plates and used to determine the voltage over each RU within the stack as well as for measuring impedance of the individual RU in the stacks. Because the probes are connected to the interconnects, and not directly to the cell, the measured voltage and impedance will include the contribution from both the cell and the interconnects as well as the contact between the cell and the interconnect. The measured voltage and impedance therefore represents the contribution from the entire repeating unit (cell, interconnect and contact between the cell and the interconnect). The interconnects were made of Crofer 22APU with a protecting LSM coating at the side of the oxygen electrode.

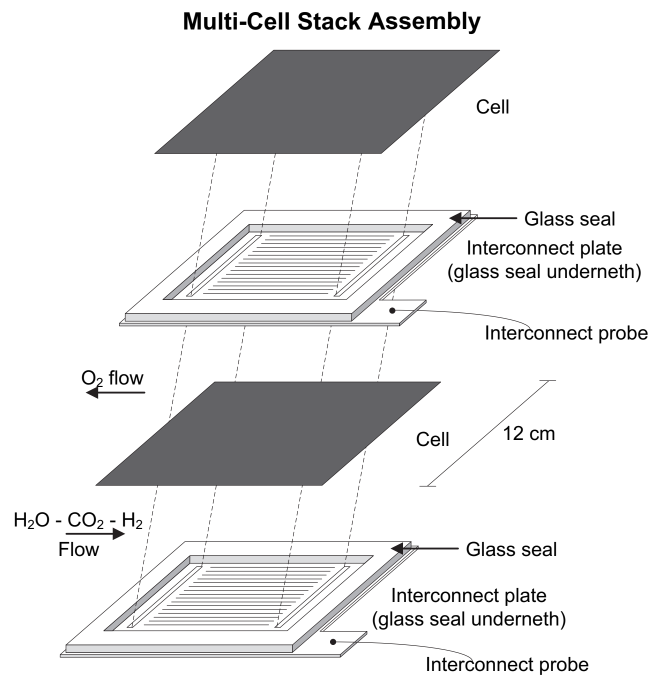

Fig. 1 – Schematic presentation of an assembly of two repeating units (RU) in a counter-flow pattern in stacks.

For the stack used for steam electrolysis, the gases were applied as received (the purity of the applied gases is stated in the following paragraph), whereas the gases supplied to the Ni/YSZ electrode for the stack applied for co-electrolysis were cleaned before entering the stack. The method for cleaning the inlet gases to the Ni/YSZ electrode is currently subject to a pending patent application [25].

2.1. *Initial characterisation*

After reduction, the performance of the individual repeating units (RU) were examined by performing DC and AC characterisation at varying gas mixtures at both the Ni/YSZ electrode (20% H_2O – 80% H_2; 50% H_2O – 50% H_2), and the LSM/YSZ electrode (pure oxygen or technical air from Air Liquide). Steam was produced by reacting oxygen (industrial grade, $O_2 \geq 99.5\%$, Air Liquide) with hydrogen (N30, $H_2 \geq 99.9\%$, Air Liquide) before entering the stack. When examining co-electrolysis in the 10-cell stack, additional DC and AC characterisation was performed with cleaned 45% H_2O – 45% CO2 – 10% H_2 at the Ni/YSZ electrode ($CO_2 \geq 99.7\%$, Air Liquide). A similar set of impedance spectra were recorded at OCV after electrolysis. The total flow rate to the Ni/YSZ electrodes during the initial characterisation was 666 L/h for the stack used for steam electrolysis, whereas only 360 L/h was supplied to the Ni/YSZ electrodes for the stack used for co-electrolysis.